THE STUDY OF RACEMISATION RATES IN BINAPHTHYLS AND RELATED COMPOUNDS.

A Thesis submitted to the University of London
for the degree of Doctor of Philosophy
by ANN SYLVIA MELLOR.

March 1961.

Bedford College,
Regent's Park,
N.W.1.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT.

This work is concerned mainly with the breakdown of the free energy of activation with the evaluation of quantities such as the energy of activation ΔE and entropy of activation $\Delta S^{\ddagger}$ of certain optically active compounds as a means of trying to understand the structural factors upon which their optical stabilities depend.

The compounds studied are members of a series of 1,1'-binaphthyl carboxylic acids and esters and a *peri* substituted naphthalene, N-benzenesulphonyl-8-nitro-1-naphthyl glycine. Their rate coefficients of racemisation at several temperatures have been determined - those for the 1,1'-binaphthyl compounds in two solvents, aqueous sodium hydroxide and N,N-dimethyl formamide - and the results used to determine ΔE, A and $\Delta S^{\ddagger}$, $\Delta F^{\ddagger}$, $\Delta G^{\ddagger}$ using the equations

$$k = Ae^{-\Delta E/RT}$$

$$\text{and} \quad k = \frac{eKkT}{h} e^{-\Delta E/RT} \; e^{-\Delta S^{\ddagger}/R}$$

In the experimental section the syntheses of the 1,1'-binaphthyl acids are described. The final part of this section is concerned with the preparation of optically active 1,1'-binaphthyl itself on which, as yet, no measurements of rate coefficients have been made. Also described is the preparation of 2,2'-carbomethoxy-3,3'-diphenic acid which was not obtained optically active.

The author is indebted to Dr. M. M. Harris for her constant help and encouragement, and wishes to thank Professor E. E. Turner, F.R.S., Professor P.B.D. de la Mare and all the Chemistry Department at Bedford College for their interest and advice.
She also wishes to thank the Department of Scientific and Industrial Research for a maintenance grant.

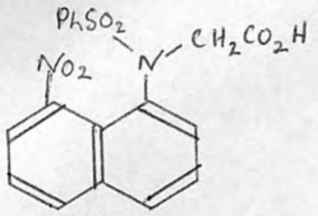
CONTENTS.

Synthetic Experimental

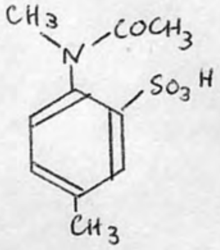
INTRODUCTION.

The study of optical activity dependent upon restricted rotation within the molecule about a single bond began with the biphenyls. Kenner (J., 1922, 614) resolved 2,2'-dinitro-6,6'-diphenic acid in an attempt to prove that, as they thought possible at the time, biphenyl was a folded molecule. When this theory collapsed the optical activity of suitably substituted biphenyls still had to be accounted for. Turner and Le Fevre, Bell and Kenyon and Mills all explained this activity as resulting from the blocking of substituent groups which prevented the two rings from achieving coplanarity; this meant there could exist enantiomorphous forms. Much of the fundamental work on substituted biphenyls has been done by Turner and his school in this country, and by Adams and his co-workers in America. (Gilman, Organic Chemistry, Vol.I, pp. 347-382. Adams and Yuan, Chemical Reviews, 1933, **12**, 261.)

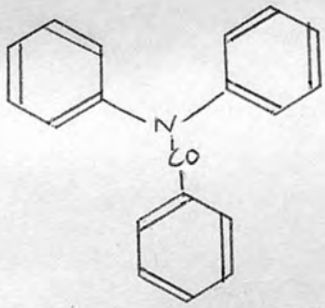
There were other examples of compounds which owed their optical activity to restricted rotation; for example Mills and Elliot (J., 1928, 1291) found optical activity in N-benzene sulphonyl-8-nitro-1-naphthylglycine (I), Mills and Kelham (J., 1937, 274) in a substituted benzene (II), Turner and Harris resolved a set of N-benzoyl-diphenylamine-2-carboxylic acids of the type represented by III, whilst Adams and his co-workers worked on a series of acids represented by IV. (J.A.C.S., 1941, 63, 1589)



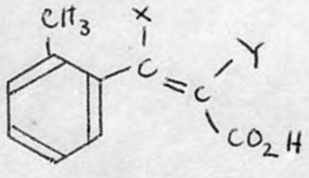
I



II



III



IV

As soon as the simple steric factors leading to asymmetric molecules of these various types were established an interest developed in the variations in the ease of racemisation which were found within structurally similar series. Attempts were made to assess optical stability in terms of the size of the interfering groups. Although steric factors are not alone in determining stability they provided a reasonable, qualitative, first approximation, if not a complete explanation.

Studies of the kinetics of racemisation of sterically hindered compounds have been made using the Arrhenius equation:

$$k = A\,e^{-\Delta E/RT}$$

and the Glasstone, Laidler and Eyring absolute reaction rate theory equation:

$$k = \frac{e k K T}{h}\, e^{-\Delta E/RT}\, e^{\Delta S^{\ddagger}/R}$$

k = transmission coefficient taken as 1

K = Boltzmann's constant

h = Planck's constant

R = Gas constant

(Glasstone, Laidler and Eyring, The Theory of Rate Processes, McGraw-Hill, 1941, p.197)

From the above expressions ΔE, the activation energy, or the energy barrier over which the molecule must go to invert its configuration, can be calculated. The Arrhenius probability factor A and the entropy of activation factor $\Delta S^{\ddagger}$ can also be fairly simply evaluated. The first people to use the Arrhenius equation for restricted-rotation racemisation were Kuhn and Albrecht (<u>Annalen</u>, 1927, <u>455</u>, 272) who worked on nitrodiphenic acids. They measured velocity coefficients for racemisation at 2 temperatures and calculated ΔE the energy of activation which is simply related to the enthalpy of activation by the expression: $\Delta H^{\ddagger} = \Delta E - RT$

These factors ΔE, A, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been used to describe the optical stability of any particular compound.

In general, the larger the value of ΔE the more optically stable the compound; but this is not always so as sometimes the entropy factor $\Delta S^{\ddagger}$, or the A-factor to which it is directly equatable, have some part to play in the optical stability. A quantity which is frequently used is ΔF , the free energy of activation and $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ $\Delta F^{\ddagger}$ reflects the measured quantity k ($k = \frac{KT}{h} e^{-\Delta F^{\ddagger}/RT}$) and this can be raised perhaps from unobservable to observable values by a large negative $\Delta S^{\ddagger}$ factor. For example Mills said that he thought the lower limiting value of ΔE, for observable activity, must be about 16kcal. mole^{-1} and yet the N-benzoyl-2'-fluoro-6-methyl-diphenylamine-2-carboxylic acid was obtained optically active in spite of having the extremely lower E value of 14.9 kcal.mole^{-1}. The fact that this molecule showed observable activity was ascribed to its unusually large negative entropy factor of -20.9 e.u.

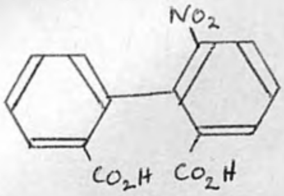
Cagle and Eyring (<u>J.A.C.S.</u>, 1951, <u>73</u>, 5628) drew together a great deal of data from the available sources and calculated $\Delta H^{\ddagger}$, A and $\Delta S^{\ddagger}$ values for racemisation for a number of compounds in an attempt to show what kind of structural factors influenced the entropy term of the absolute reaction rate equation.

Compound	Solvent	$\Delta H^{\ddagger}$ (cal/g mole)	$\Delta S^{\ddagger}$ e.u.	Reference
4,6,4'-Trinitro-2,2'-diphenic acid	2N NaOH solution	21,200	-18.5	1
6,4'-Dinitro-2,2'-diphenic acid	2N NaOH solution	25,700	- 4.2	2
2,2'-Diamino-6,6'-dimethyl diphenyl	Vapour phase diphenyl ether solution	45,600 44,100	-11.48 -11.54	3 3
2-Nitro-6-carboxy-6 methoxy diphenyl	Absolute ethanol	19,300	- 9.19	4
2-Nitro-6 carboxy-6' ethoxy diphenyl	Absolute ethanol	20,100	- 9.38	4
2-Nitro-6 carboxy-6' propoxy diphenyl	Absolute ethanol	20,000	-10.5	4
5,5'-Octamethylene-dioxy-2,2'-diphenic acid	Dioxane	22,100	- 9.24	5
5,5'-Decamethylene-dioxy-2,2'-diphenic acid	Dioxane	22,800	- 6.27	5
Sodium N-acetyl-N methyl-p-toluidine-3-sulphonate	Water	22,800	- 1.60	6
N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene	n-Butanol and methyl acetate	19,300	-26.9	7

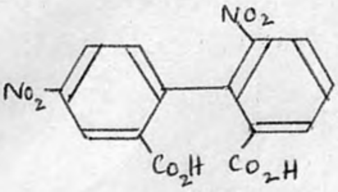
References.
1. Kuhn and Albrecht Annalen, 458, 221 (1927)
2. Kuhn and Albrecht Annalen, 455, 272 (1927)
3. Kistiakowsky and Smith, J.A.C.S., 58, 1043, (1936)
4. Li and Adams, J.A.C.S., 57, 1564, (1935)
5. Adam and Kornblum, J.A.C.S., 63, 188, (1941)
6. Mills and Kelham, J., 1937, 274.
7. Adams and Gordon, J.A.C.S., 72, 2454, (1950)

The idea was a stimulating one, but it was felt that the data available for calculation of the parameters quoted was inadequate. In some cases there were only two values of k at different temperatures to plot the graph to give $\Delta H^{\ddagger}$. The solvent used was often different for a pair of compounds, making it difficult to draw valid comparisons as solvent undoubtedly plays a significant part in some racemisations. De la Mare (Progress in Stereochemistry, Vol.I, Butterworths Scientific Publications, 1954, p.122) said he thought the authors should, "Await a considerable extension of the existing information." These criticisms were valid ones, but none the less this work, in which the authors made the best of the data they had gathered, was very valuable and an encouragement to further experiment.

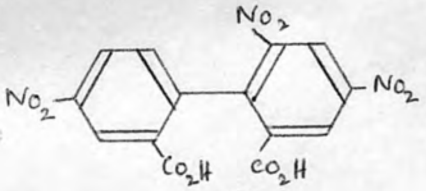
More detailed investigations along these lines were made by Brooks, Harris and Howlett (*loc.cit.*) into some N-benzoyldiphenylamine-2-carboxylic acids and into three nitro-diphenic acids (*J.*, 1957, 1954); both sets of experiments yielded some interesting results. For example with the nitro-diphenic acids:



V



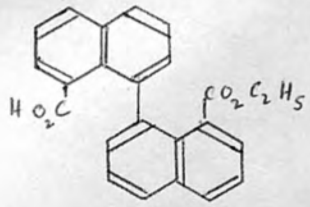
VI



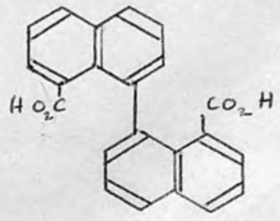
VII

The E-values for the racemisation of these acids in sodium carbonate solution were found to be the same, 22.6 kcal.mole^{-1}, within the limits of experimental error, though their optical stabilities as measured by first order velocity coefficients lay in the series VII > VI > V. This increase in stability on addition of a nitro-group, in a position in which it can have no steric effect at all, was shown to reside in the entropy factor which was -16.3 e.u. for VII the most stable acid, and -12 e.u. for V the least stable acid.

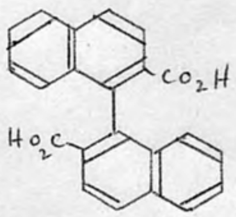
The 1,1'-binaphthyls are a set of compounds structurally similar to the 2,2'-disubstituted biphenyls but they are not exactly analogous. A number of substituted 1,1'-binaphthyls have been resolved, among them several of the 1,1'-binaphthyl carboxylic acids. There is an interesting series of these acids (including one half ester):



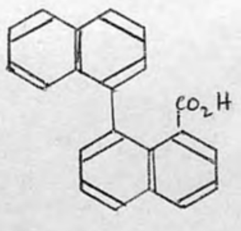
VIII



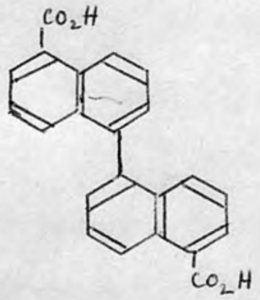
IX



X



XI

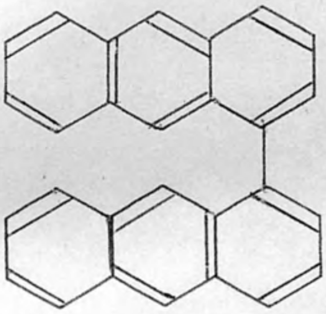


XII

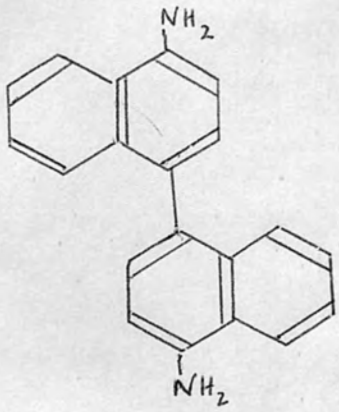
Judging by these drawings, or by classical models, and considering the obstacles to rotation about the 1,1'-bond, the expected order of stability on the grounds of bulk of interfering groups would be: VIII $>$ IX $\simeq$ X $>$ XI $>$ XII. However, it seemed from the work of Meisenheimer and Beisswenger (<u>Ber.</u>, 1932, <u>65</u>, 32) and of Hall, Ridgwell and

Turner (J., 1954, 2498) that XII was much more stable optically than IX as judged by rates of racemisation at one temperature in aqueous sodium hydroxide. [It has been found in the course of this work that even the monoethyl ester VIII is less stable than XII in sodium hydroxide solution.]

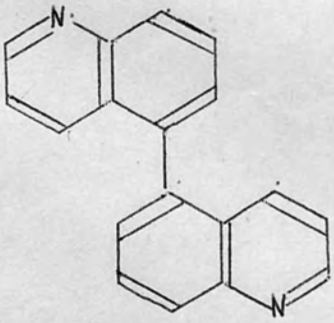
If the 1,1'-binaphthyl-5,5'-dicarboxylic acid is considered first, the only steric hindrance to rotation is that provided by the overlap of the hydrogen atoms in the 2- and 8-positions which, perhaps, might not seem a sufficient barrier. Bell, Morgan and Smythe (Chemistry and Industry, 1951, 634) say that scale diagrams show little or no overlap. In a paper by Bell and Waring (J., 1949, 1579) on 1,1'-bianthryl, the overlap of the 2' and 9 hydrogen atoms, which is the same as the 2' and 8 hydrogen atoms in 1,1'-binaphthyl, is said to be less than 0.2Å. Despite this, Bell and Waring resolved 1,1'-bianthryl (XIII) and, although they did not measure ΔE, they reported that it racemised after 7 hours in boiling chloroform. This demonstrates reasonably enough that the blocking provided by these hydrogen atoms is sufficient to cause observable optical activity. There are other examples of 1,1'-binaphthyls with only hydrogen in the blocking positions. Naphthidine (XIV) resolved by Theilacker and Hopp (Ber., 1959, 92, 2293) is a good example which has a half life period of three to four hours at room temperature in acetone and a ΔE of 21.4 kcal.mole^{-1}. Crawford and Smythe (*J.*, 1952, 4133) resolved 5,5'-diquinolyl (XV) and 4,4'-diquinolyl (XVI) whose half life periods at room temperature in N-hydrochloric acid were 2.5 hours and 1.3 hours respectively.



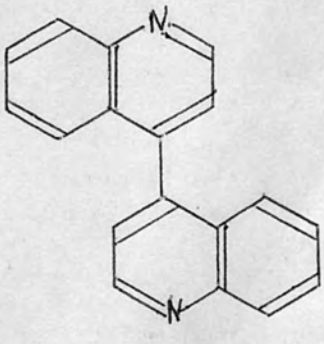
XIII



XIV



XV

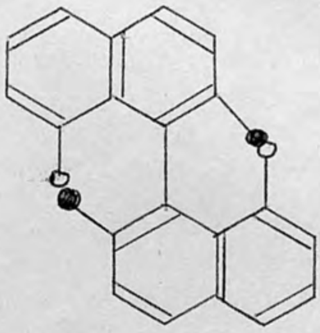


XVI

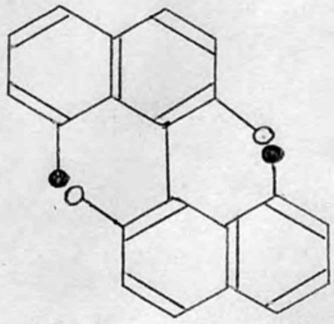
It would seem that binaphthyl itself, having an asymmetric molecular structure, could be expected to show optical activity at ordinary temperatures if a way could be found of obtaining it optically active. (J., 1950, 1963).

In view of all these things the stability of the 5,5'-acid is not so surprising as it appeared at first, but rather is in accordance with that of similarly constituted structures; it can be regarded as "normal". It then becomes "normal" for the 2,2'-acid (X) to be much more stable.

1,1'-Binaphthyl-8,8'-dicarboxylic acid (IX) and 1,1'-binaphthyl-2,2'-dicarboxylic acid (X) are geometrically very similar. In fact, if racemisation is pictured as taking place with the $-CO_2H$ group passing H-, the two transition states are nearly identical:



X

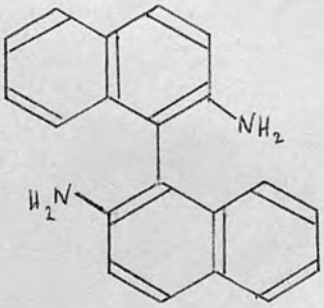


IX

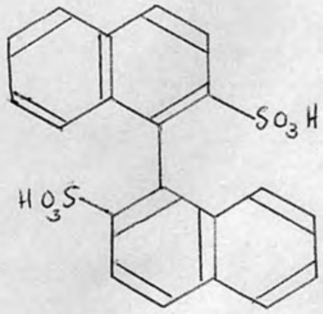
● = CO_2H

○ = H

Despite this apparent similarity their optical stabilities are very different indeed. The high optical stability of X has been shown by Kuhn and Albrecht (Annalen, 1928, 465, 282) and by Hall and Turner (J., 1955, 1242) who reported that its rotation was unchanged after boiling in N-methyl formamide for 8 hours. We have found from surveying the literature that extreme optical stability is a characteristic of all 2-substituted or 2,2'-disubstituted 1,1'-binaphthyls. Kuhn and Goldfinger (Annalen, 1929, 470, 183) prepared and resolved 2,2'-diamino-1,1'-binaphthyl XVII which was so optically stable it underwent reactions at 200° and yet the activity was retained. Another compound 1,1'-binaphthyl-2,2'-disulphonic acid (XVIII) was synthesised and resolved by Armarego and Turner (J., 1957, 13) and had unchanged rotation after 10 hours at 200° in aqueous sodium hydroxide in a sealed tube.

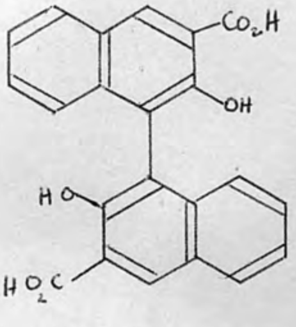


XVII

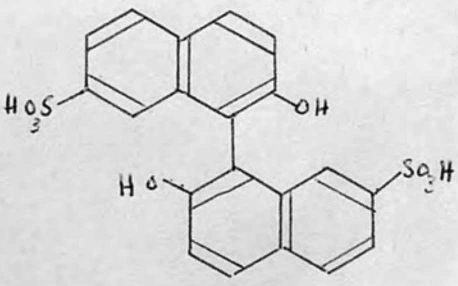


XVIII

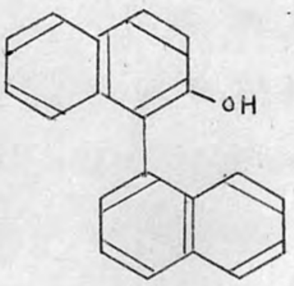
There are many other examples such as the compound made by Stanley and Adams (Rec.trav.Chem., 1929, 48, 1035) 2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxylic acid XIX and the substance prepared by the Russians Joffe and Grachev (J.Gen.Chem., U.S.S.R., 1935, 5, 950) 2,2'-dihydroxy-1,1'-binaphthyl-7,7' disulphonic acid (XX). Even single 2-substituted compounds show considerable stability, like 2-hydroxy-1,1'-binaphthyl (XXI) which was prepared by Berson and Greenbaum (J.A.C.S., 1958, 80, 653) and whose half life period in boiling benzene was two days.



XIX



XX



XXI

1,1'-Binaphthyl-8,8'-dicarboxylic acid (IX) was originally prepared and resolved by Stanley (J.A.C.S., 1931, 53, 3104), by Corbellini (Atti.accad.Lincei., 13, 702, 1931), by Meisenheimer and Beisswenger (Ber., 1932, 65, 32) and later by Hall, Ridgwell and Turner (*loc.cit.*) All these workers studied at least one racemisation and, although not all used the same solvent, they all agreed on the ease with which this acid racemised. There were attempts to explain the apparent anomaly by Ridgwell and his fellow workers using the electrical forces of the $-CO_2^-$ groups on one another when the acid was dissolved in sodium hydroxide. It was at one time suggested by Bell and Morgan (*J.*, 1954, 1716) that there might be dissociation into free naphthyl radicals but no free radicals were ever detected.

Stanley made an observation which now seems pertinent when he wrote, "The difference in stability may be due to the fact that the peri-substituted carboxyl groups in the 8,8'-dicarboxy-1,1'-binaphthyl render the molecule more labile and capable of distortion than when the carboxyl groups are in the 2,2'-positions."

It was thought at the outset of the present work that a careful investigation of this problem by finding ΔE, A and $\Delta S^{\ddagger}$ for each acid and its esters under strictly comparable conditions might shed some new light on the mystery.

Experimental

OPTICAL WORK AND RESULTS.

The acids used in the determination of racemisation rate constants were obtained in optically active form by resolution or by second order asymmetric transformation of their alkaloidal salts.

The acids were all fairly stable optically at room temperatures and therefore the decomposition of their salts was accomplished quite simply. The alkaloidal salt was dissolved in chloroform and this solution was then extracted with aqueous sodium hydroxide. The sodium hydroxide layer was washed with chloroform and then with ether. Air or nitrogen was blown through the solution to remove traces of organic solvents and then the solution could be used directly, if the racemisation rate was to be measured in sodium hydroxide; alternatively, the optically active acid could be precipitated with dilute hydrochloric acid.

Racemisation Procedure.

All polarimeter readings in this work were taken on the mercury green line 5461 A.

Polarimeter measurements were made using a 2-dm jacketed tube, except in the case of 1,1'-binaphthyl-8,8'-dicarboxylic acid when a 1-dm tube was used. The temperature was kept constant by a fast stream of water circulated round the polarimeter tube by a Brown circotherm pump from a large Dewar flask.

This worked very well for temperatures above room temperature, but for lower temperatures ice was added to the reservoir by hand at periodic intervals to maintain the temperature control. To maintain the temperature below that of the room for long periods of time a more complicated system was used. Full details of this are given in a paper by Harris and Mitchell (*J.*, 1960, 1905). Using this apparatus the temperature could be held accurately at - say - 15° for long periods of time - say - 20 hours. A standard thermometer was fitted into the stopper of the polarimeter tube so that the temperature of the solution could be read throughout each experiment. The thermometer was read to the nearest 0·1° with the aid of a magnifying glass. An accurate clock marked in minutes and 100 parts of a second was used and was always fully wound at the beginning of a rate.

The rotations of alkaloidal salts were usually taken in 'Solvent X', that is, chloroform which contains 2½% by volume of ethanol. Some rates of racemisation were taken in N-N-dimethyl formamide bought from B.D.H. Its refractive index was found to be 1·4280 at 20° (reported 1·4280 at 25°) which seemed to indicate a good degree of purity. Some rates of racemisation were taken in 0·1N sodium hydroxide, always taking care that there was enough sodium hydroxide present to make the full sodium salt of the acid.

The amount of active acid or ester or of alkaloid salt used in the racemisation varied according to the magnitude of the specific rotation of each particular one. (Accurate determination of the specific rotation of optically labile acids is not possible.) At t = 0 the solvent was added and the solution filtered into the polarimeter tube. The temperature of the solution was noted and readings were begun as soon as possible and were taken at suitable intervals throughout the run until the optical rotation became small. An observation was always made much later to confirm that the rotation had gone to zero, which meant there were no traces of alkaloid present.

The logarithm of the angle of rotation was plotted against the time and the slope of the straight line so obtained was used to calculate the rate constant, k, using the first order rate equation -

$$k = \frac{1}{t} \log_e \frac{(\alpha_0 - \alpha_t)}{(\alpha_t - \alpha_\infty)}$$

(Racemisations are usually first order rate processes.) The rate constants obtained were, in most cases, found to be easily reproducible (the exception being those for 1,1'-binaphthyl-8-carboxylic acid in 0·1N sodium hydroxide) but the fastest ones were usually repeated to ensure accuracy.

The rate constants of racemisation for each acid were taken over as wide a range of temperatures as could conveniently be obtained. The range was usually 40 to 50° and 8 to 10 rate constants at different temperatures were obtained. The exception here was 1,1'-binaphthyl-5,5'-dicarboxylic acid and its dimethyl ester in dimethyl formamide. Both had a tiny rotation on the mercury green line - within the error of the polarimeter - although if some alkali was added to the dimethyl formamide solution a reading of +0·5 was obtained. So in this case a different technique was employed which used more of the optically active material and only three rate constants at different temperatures were obtained. The technique is described under the section dealing with this acid.

The logarithm of the rate constant was plotted against the reciprocal of the absolute temperature and good straight lines were obtained. The slope of this line was found graphically and also using the method of least squares giving equal weight to the average result at each temperature. The slope was used to calculate the constants of the Arrheni~~o~~us equation -

$$k = A\,e^{-E/RT}$$

The activation energies obtained by the two methods were found to agree quite well.

The entropy of activation $\Delta S^{\ddagger}$ was calculated using the Gladstone Laidler and Eyring equation -

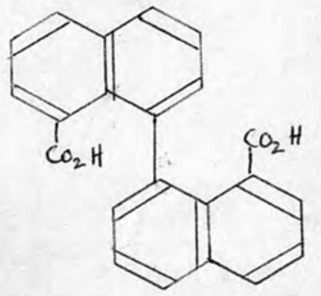
$$\text{rate constant} = e\frac{KT}{h}e^{\Delta S^{\ddagger}/RT}\;e^{-E/RT}$$

K = Boltzmann constant
h = Planck constant
R = Gas constant

taking the transmission coefficient as 1.

Throughout this work the energy of activation E will be referred to as the E-value, the entropy of activation as the S-value, the Arrheni~~o~~us A factor as the A-value, and so on.

1,1'-Binaphthyl-8,8'-dicarboxylic acid



Preparation of (+) and (-) salts with brucine.

The 1,1'-binaphthyl-8,8'-dicarboxylic acid (1g., 1M) was dissolved in a litre of boiling methyl alcohol and the solution filtered hot. Anhydrous brucine (1·4g., 1M) was dissolved in 40 cc methyl alcohol and added to the solution of the acid. Some methyl alcohol was distilled off, leaving about 200 c.c. of solution. Slow crystallisation occurred to give 1g. brucine (+)-acid as colourless, opaque prisms m.p. 260-275°, $[\alpha]^{21\cdot4}_{5461} = -481^{\circ}$. Meisenheimer and Beisswenger gave m.p. 255-262°, $[\alpha]_D = -395^{\circ}$.

The mother liquor was evaporated to dryness and the residue dissolved in 700 c.c. of boiling ethyl acetate. The solution was filtered and the volume reduced to about 200 c.c. 1g. of the brucine (-)-acid was obtained as colourless needles m.p. 220-250°, $[\alpha]^{21\cdot4}_{5461} = +483^{\circ}$. Meisenheimer and Beisswenger (<u>loc. cit.</u>) gave m.p. 228-234°, $[\alpha]_D = +377^{\circ}$.

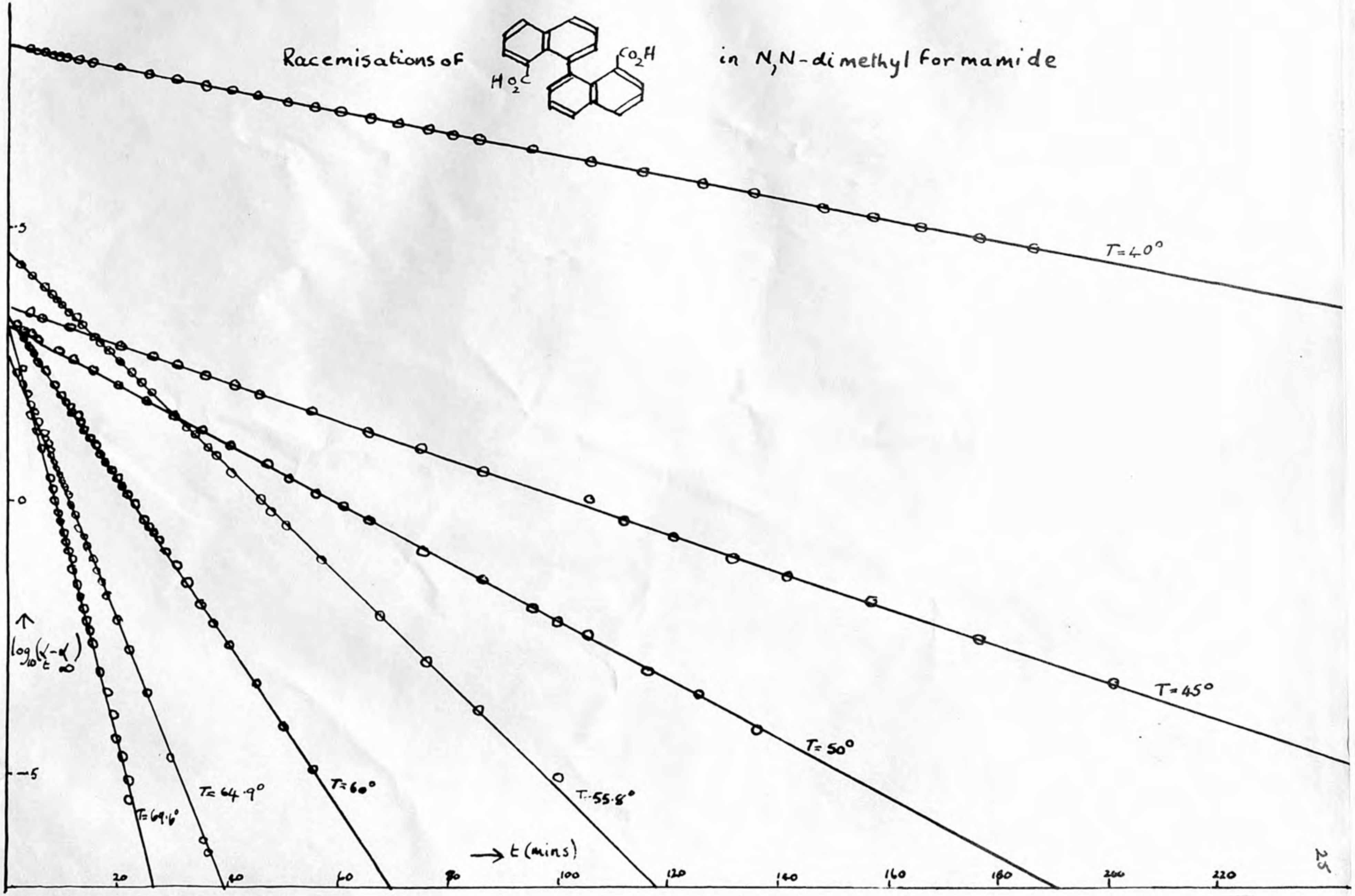
The method of obtaining optically active acid from the salt is given on p. 19 . The active acid melted at 320° (both forms) whilst the inactive acid melted at 304-6°. These high melting points were taken using an electrothermal apparatus. (Meisenheimer gave m.p. 304-6° for the inactive acid.)

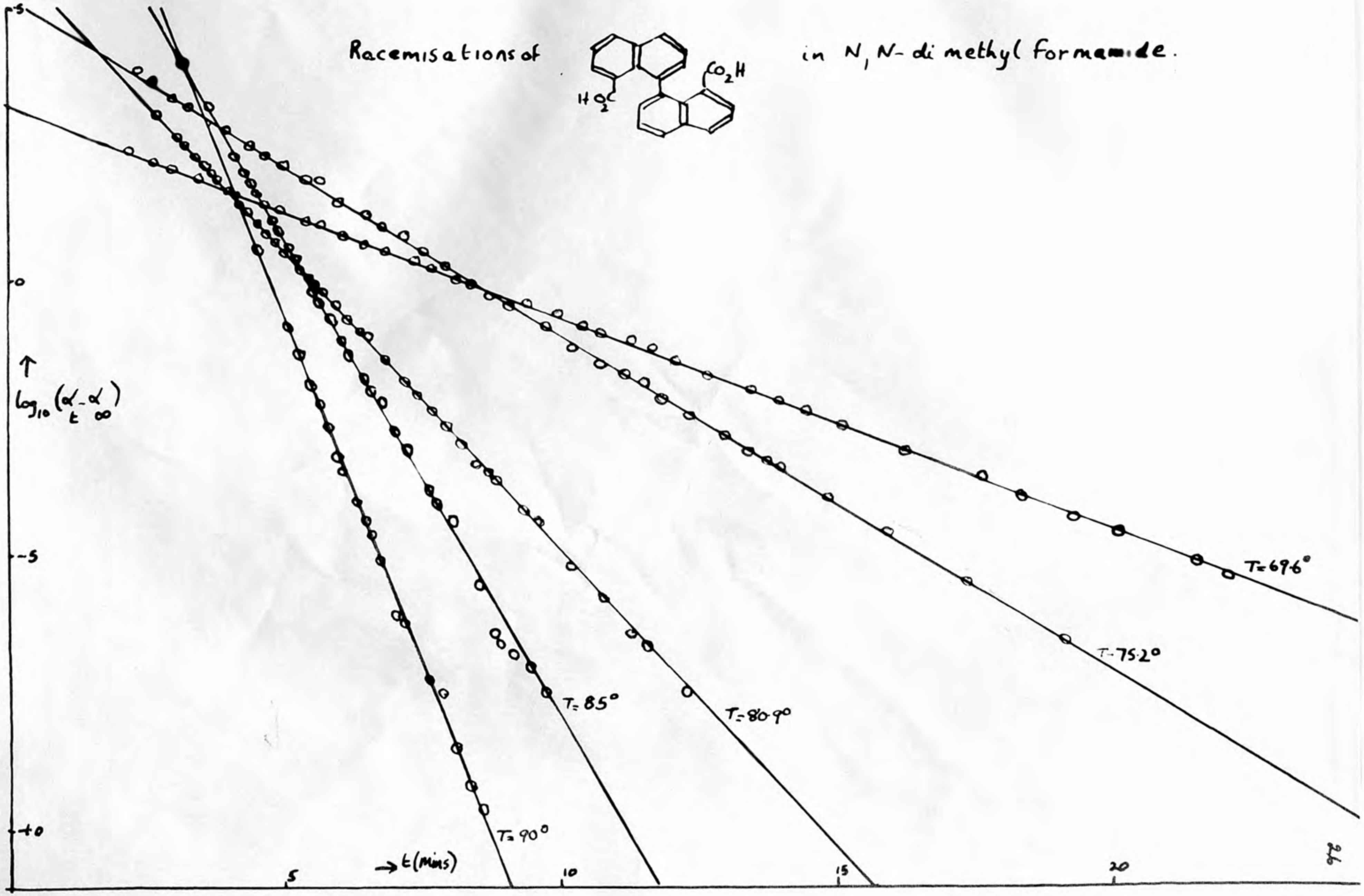
Determination of rate coefficients for racemisation of (+) and (−) 1,1'-binaphthyl-8,8'-dicarboxylic acid in N,N-dimethyl formamide.

Temperature in °C	Time of 1st reading after wetting	First reading	No. of readings	Time during which readings taken	$10^4k_{sec}^{-1}$
90	4.5 mins	(−)1.15°	19	4 mins	96
85.7	2.9 "	(−)2.09°	29	7 mins	73
85	3.5 "	(−)2.09°	30	8 mins	67
80.9	2.7 "	(+)2.02°	37	10 mins	42
75.2	2.3 "	(+)2.46°	35	17 mins	24
69.6	2.2 "	(+)1.75°	35	20 mins	15
64.9	2.8 "	(+)1.59°	31	32 mins	9.5
60	2.8 "	(+)2.11°	40	54 mins	5.7
55.8	2.0 "	(−)2.72°	31	98 mins	3.8
50	2.6 "	(+)2.06°	23	135 mins	2.1
45.1	3.4 "	(−)2.24°	22	200 mins	1.3
40	3.5 "	(+)6.69°	34	185 mins	0.78

(The acid from the brucine (+)-acid salt gave a (−)ve rotation in N,N-dimethyl formamide but a (+)-rotation in 0.1N aqueous sodium hydroxide and vice-versa for the acid from brucine (−)-acid).

Racemisations of [structure] in N,N-dimethyl formamide





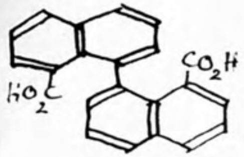
Racemisations of [structure] in N, N-dimethyl formamide.

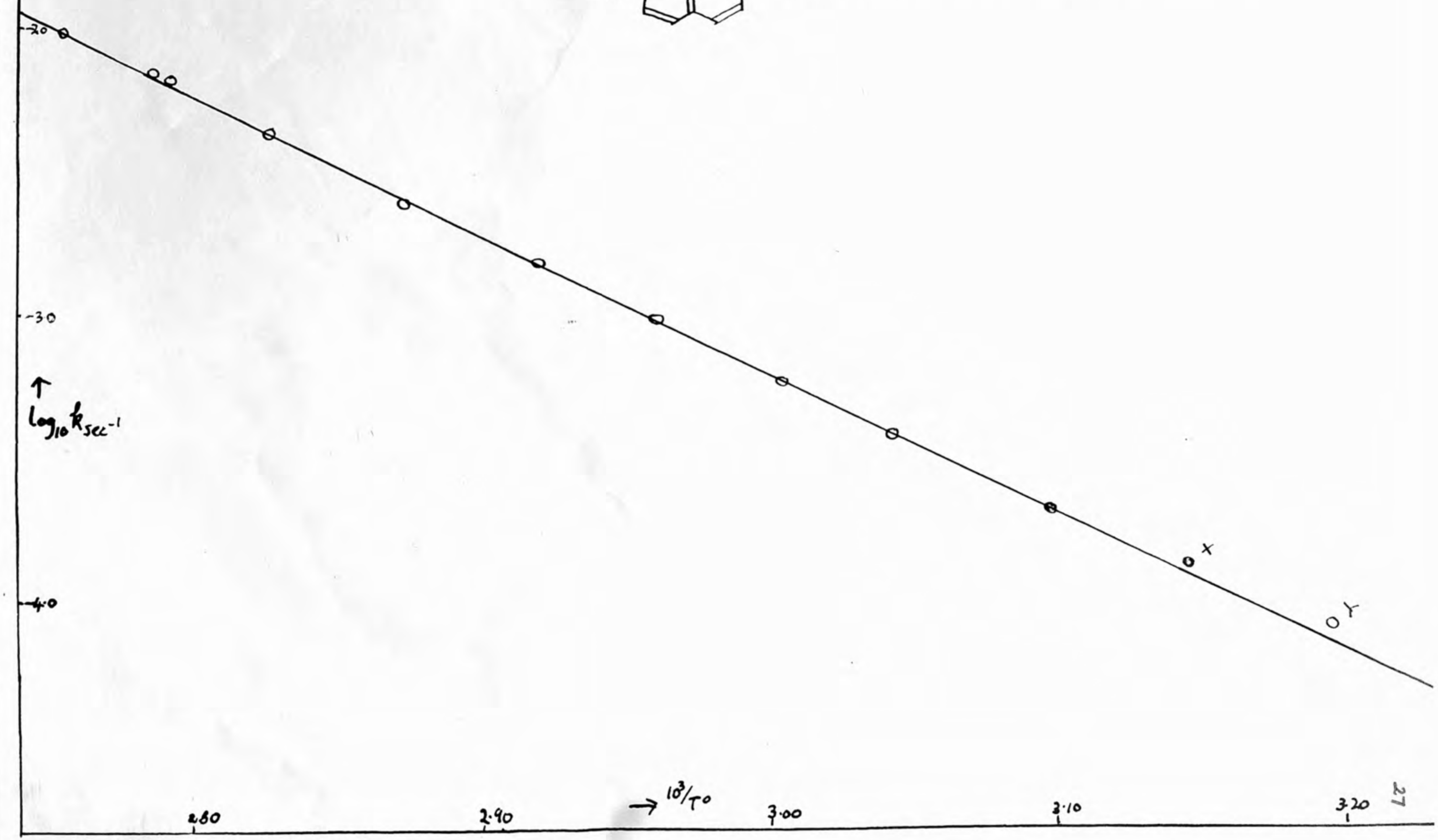
Determination of the Arrhenius parameters A and ΔE, and the entropy of activation $\Delta S^{\ddagger}$ and their parameters.

T°	$10^3/T$	$10^3 k_{\text{sec}^{-1}}$	$\log_{10} k_{\text{sec}^{-1}}$
313.0	3.195	0.0782	$\bar{5}.89326$
318.1	3.144	0.134	$\bar{4}.12775$
323	3.096	0.211	$\bar{4}.32346$
328.8	3.041	0.382	$\bar{4}.58218$
333	3.003	0.569	$\bar{4}.75534$
337.9	2.959	0.945	$\bar{4}.97676$
342.6	2.919	1.49	$\bar{3}.16202$
348.2	2.872	2.38	$\bar{3}.37803$
353.9	2.826	4.26	$\bar{3}.62890$
358.7	2.787	7.28	$\bar{3}.86213$
358	2.793	6.69	$\bar{3}.82558$
363	2.755	9.64	$\bar{3}.93399$

The best straight line taken graphically (see p. 27) gives:

$$\Delta E = 22.26 \text{ kcal.mole}^{-1}$$

Arrhenius plot for  in N,N-dimethyl formamide



Method of least squares. [Introduction to the Study of Physical Chemistry, Hammett, p.410]

$y = a + bx$

$x = \frac{a}{b} + \frac{y}{b}$

$k = Ae^{-\Delta E/RT}$

Let $x = 5 + \log_{10} k_{sec^{-1}}$ and $y = 10^3/T$

then $b = -k \times \frac{2.303}{E}$

$-\frac{a}{b} = \log_{10} A$

From statistical theory:-

$b = \frac{n\Sigma xy - \Sigma x \, \Sigma y}{n \, \Sigma x^2 - (\Sigma x)^2}$ n = number of points

In order to get an accurate result using this method it is necessary to use the value of the rate constant taken to 6 decimal places, though in reality this number of places has no significance.

T°	y	x	xy	x^2
313	3.19488	0.89326	2.853866	0.797913
318.1	3.143665	1.12775	3.545268	1.271820
323	3.095975	1.32346	4.097399	1.751546
328.8	3.041362	1.58218	4.811982	2.503294
333	3.003003	1.75534	5.271291	3.081218
337.9	2.959455	1.97676	5.850132	3.907580
342.6	2.918855	2.16202	6.310623	4.674330
348.2	2.871912	2.37803	6.829493	5.655027
353.9	2.825656	2.62890	7.428367	6.911115
358.7	2.787844	2.86213	7.979172	8.191788
363	2.754820	2.98399	8.220355	8.901212

$n = 11$

$b = \frac{-11.33511}{54.349800}$

$\therefore \Delta E = 21.94 \text{ kcal.mole}^{-1}$

The two methods of treatment of the experimentally determined figures give values of E which are very close. Their average value is 22.1 kcal.mole^{-1}.

The other quantities were calculated using the average value of E.

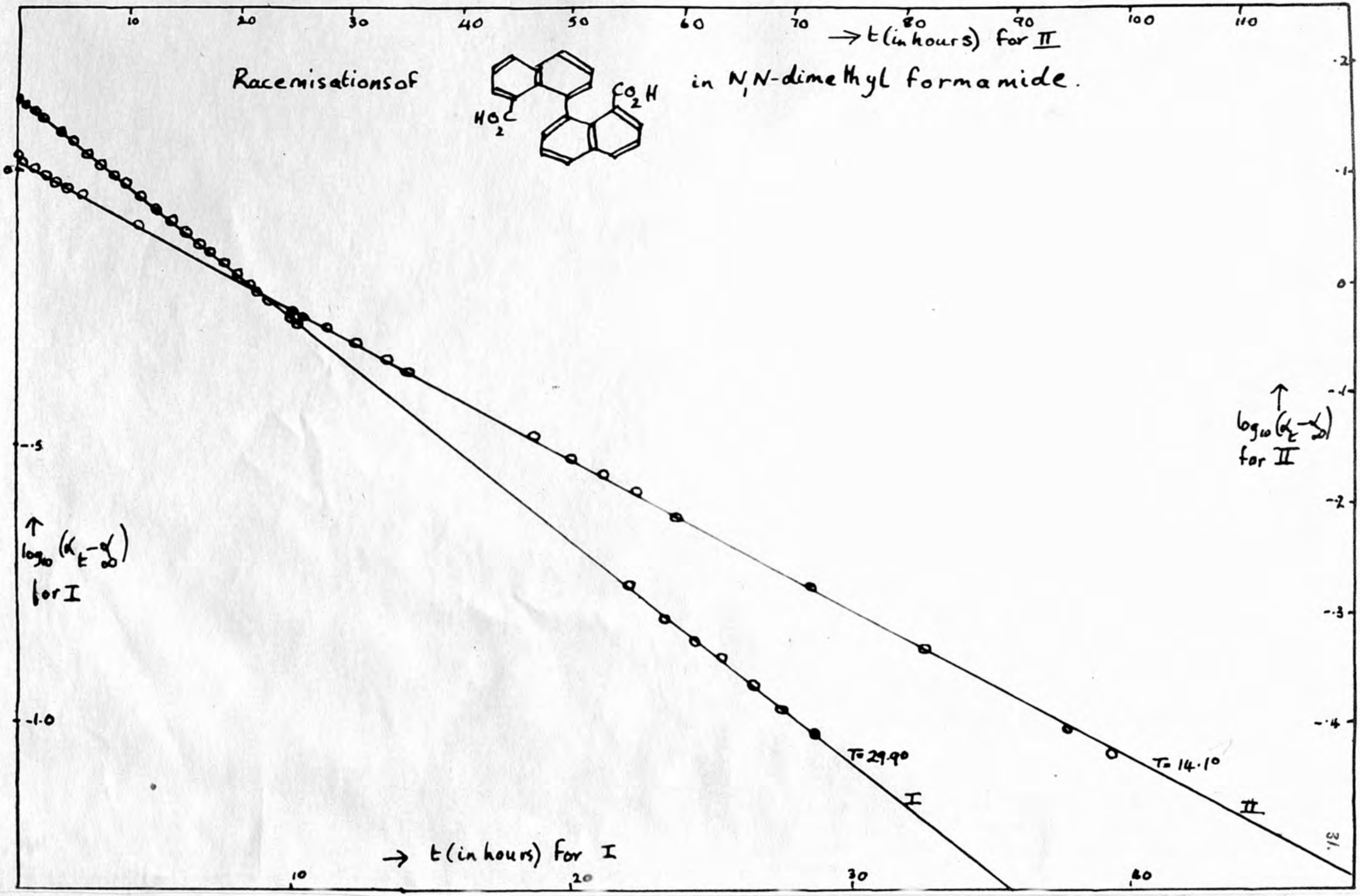
$$A = 10^{11.27} \ \text{sec}^{-1}$$

$$\Delta S^{\ddagger} = -9.1 \text{ e.u.}$$

$\Delta H^{\ddagger} = 21.4$ kcal.mole^{-1} $\Delta F^{\ddagger} = 24.5$ kcal.mole^{-1}

The half life period at 50° is 87 minutes.

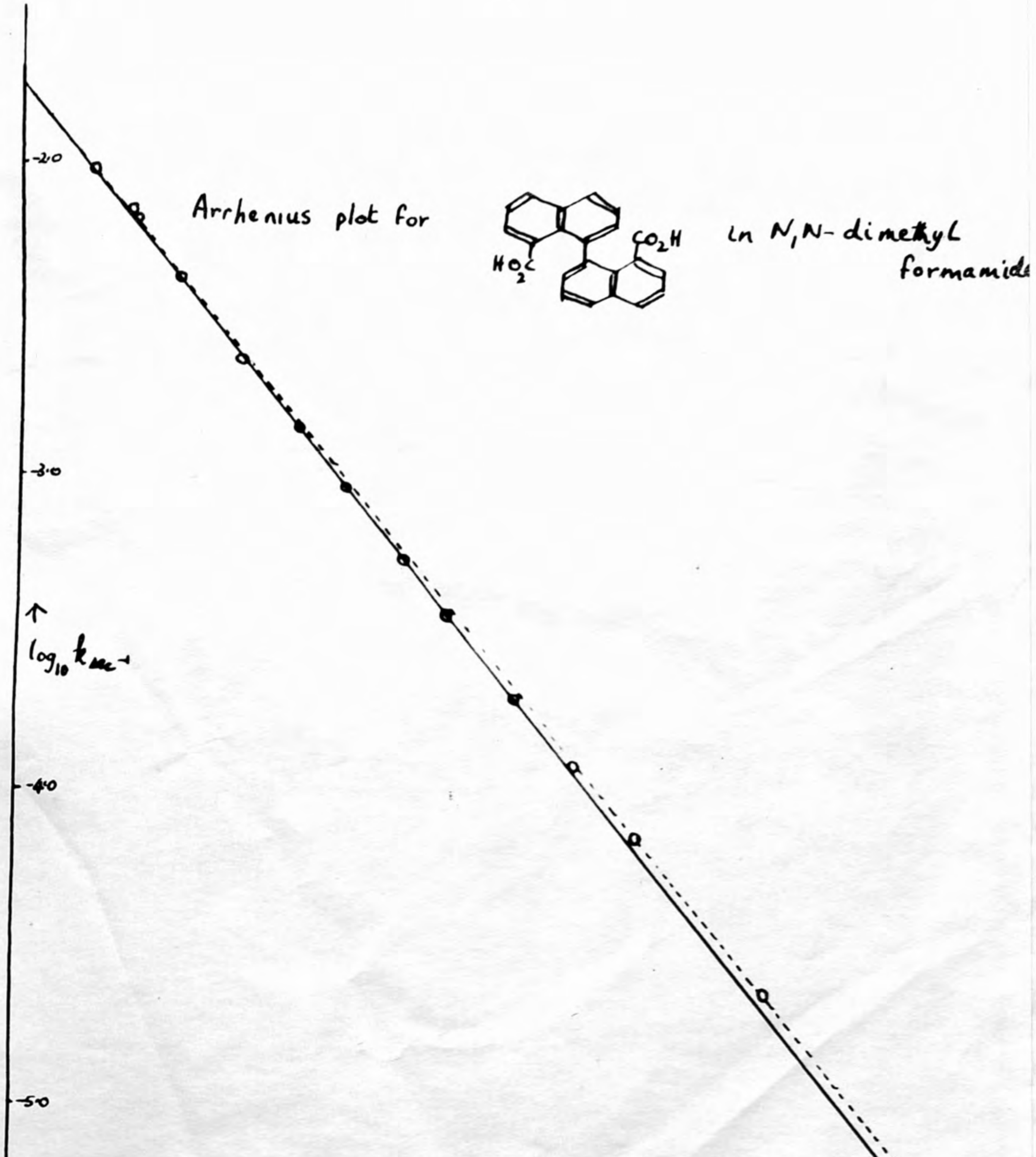
Some time after these measurements were made, when looking for possible indications of deviations from the simple first order process, it was noted that the lowest temperature points (marked X and Y on the graph on p. 27) were not exactly on the line. It was therefore decided to do some more determinations of rate coefficients at lower temperatures and so one was carried out at 29.9° and yet another at 14.1°. The one at 14.1° was very slow indeed and was kept running for six days. It could safely be left for 9 or 10 hours and would keep its temperature - this was using the apparatus designed by Mr. R. Mitchell (loc.cit.) The logarithm of the rate constants so obtained when plotted against the reciprocal of the absolute temperature showed a slight deviation from the straight line (see graph on p. 33). The value for E obtained by drawing a new line (shown by a dotted line on the graph) was 21.8 kcal.mole^{-1} which is hardly appreciably different from that already calculated. It may be, however, that over a wide range of temperatures, 15 - 90°, that E is slightly temperature dependent and it


Racemisations of
in N,N-dimethyl formamide.
HO2C
CO2H
→ t (in hours) for II
10
20
30
40
50
60
70
80
90
100
110
→ t (in hours) for I
10
20
30
40
↑ log10 (αt − α∞) for I
0
−.5
−1.0
↑ log10 (αt − α∞) for II
.2
.1
0
−.1
−.2
−.3
−.4
T = 29.9°
I
T = 14.1°
II

may not be justifiable to use this new line. It has been decided therefore to keep to the first determination of E saying it applies for the temperature range 40 - 90°.

Temperature. °C	Time of first reading	α at first reading	No. of readings	Time over which readings were taken	$10^3 k_{sec}{}^{-1}$
29.9	2	1.34°	31	28 hours	0.25
14.1	3	1.29°	26	120 hours	0.034

Temperature in degrees Absolute	$10^3/T$	$10^3 k_{sec}{}^{-1}$	$\log_{10} k_{sec}{}^{-1}$
302.9	3.301	0.25	$\bar{5}.4063$
289.1	3.483	0.034	6.5370



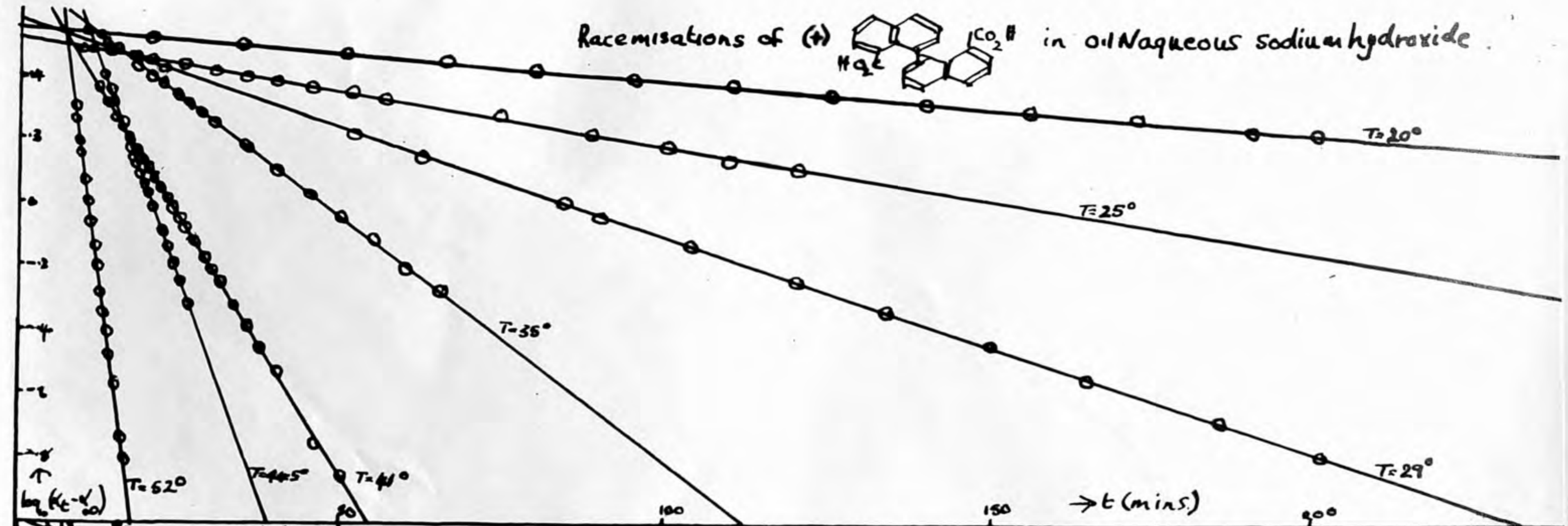
Arrhenius plot for in N,N-dimethyl formamide

Determination of rate coefficients of racemisation for the (+)-1,1'-binaphthyl-8,8'-dicarboxylic acid in 0.1N aqueous sodium hydroxide.

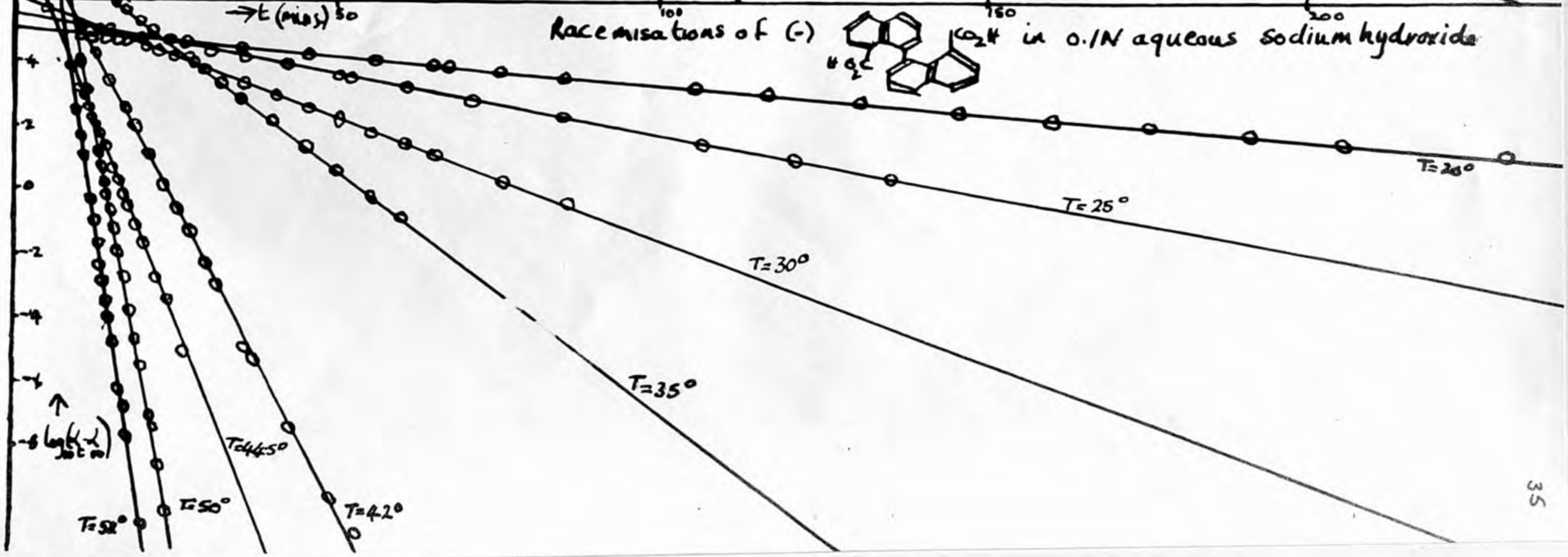
Temperature in °C	Time of 1st reading	First reading	No. readings	Time over which readings taken	10^4k
17	14 mins	(+)3.5°	15	350 mins	0.343
20	10 "	(+)3.45°	16	245 "	0.620
25	10 "	(+)3.10°	18	120 "	1.33
29	22 "	(+)2.59°	15	240 "	2.56
35	12 "	(+)3.33°	18	65 "	5.50
41	12 "	(+)2.26°	25	55 "	12.3
44.5	13 "	(+)2.49°	18	27 "	20.0
52	8 "	(+)1.82°	19	20 "	50.8

Determination of rate coefficients of racemisation for (-)-acid in 0.1N sodium hydroxide.

20	11 mins	(-)3.03°	20	230 mins	0.617
25	10 "	(-)3.22°	18	135 "	1.38
30	14 "	(-)3.2°	17	85 "	2.86
35	14 "	(-)4.10°	17	60 "	5.74
42	10 "	(-)3.17°	20	54 "	14.9
44.5	10 "	(-)2.42°	16	26 "	20.0
50	10 "	(-)2.54°	20	25 "	38.5
52	10 "	(-)1.99°	20	20 "	47.5



Racemisations of (+) in 0·1N aqueous sodium hydroxide



Racemisations of (-) in 0.1N aqueous sodium hydroxide

Determination of Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

(a) for (+) acid.

T^{o}	$10^{3}/T$	$10^{3}k\,sec^{-1}$	$\log_{10}k_{sec}^{-1}$
293	3.413	0.0619	$\bar{5}.7797$
298	3.356	0.133	$\bar{4}.1243$
302	3.311	0.256	$\bar{4}.4091$
308	3.247	0.549	$\bar{4}.74031$
314	3.185	1.23	$\bar{3}.0906$
317.5	3.150	2.00	$\bar{3}.3010$
325	3.077	5.08	$\bar{3}.7061$

(b) for (-) acid.

293	3.413	0.617	$\bar{5}.7903$
298	3.356	0.138	$\bar{4}.1418$
303	3.300	0.285	$\bar{4}.4558$
308	3.247	0.575	$\bar{4}.7596$
315	3.175	1.48	$\bar{3}.1728$
317.5	3.150	2.00	$\bar{3}.3010$
323	3.096	3.85	$\bar{3}.6770$
325	3.077	4.75	$\bar{3}.5849$

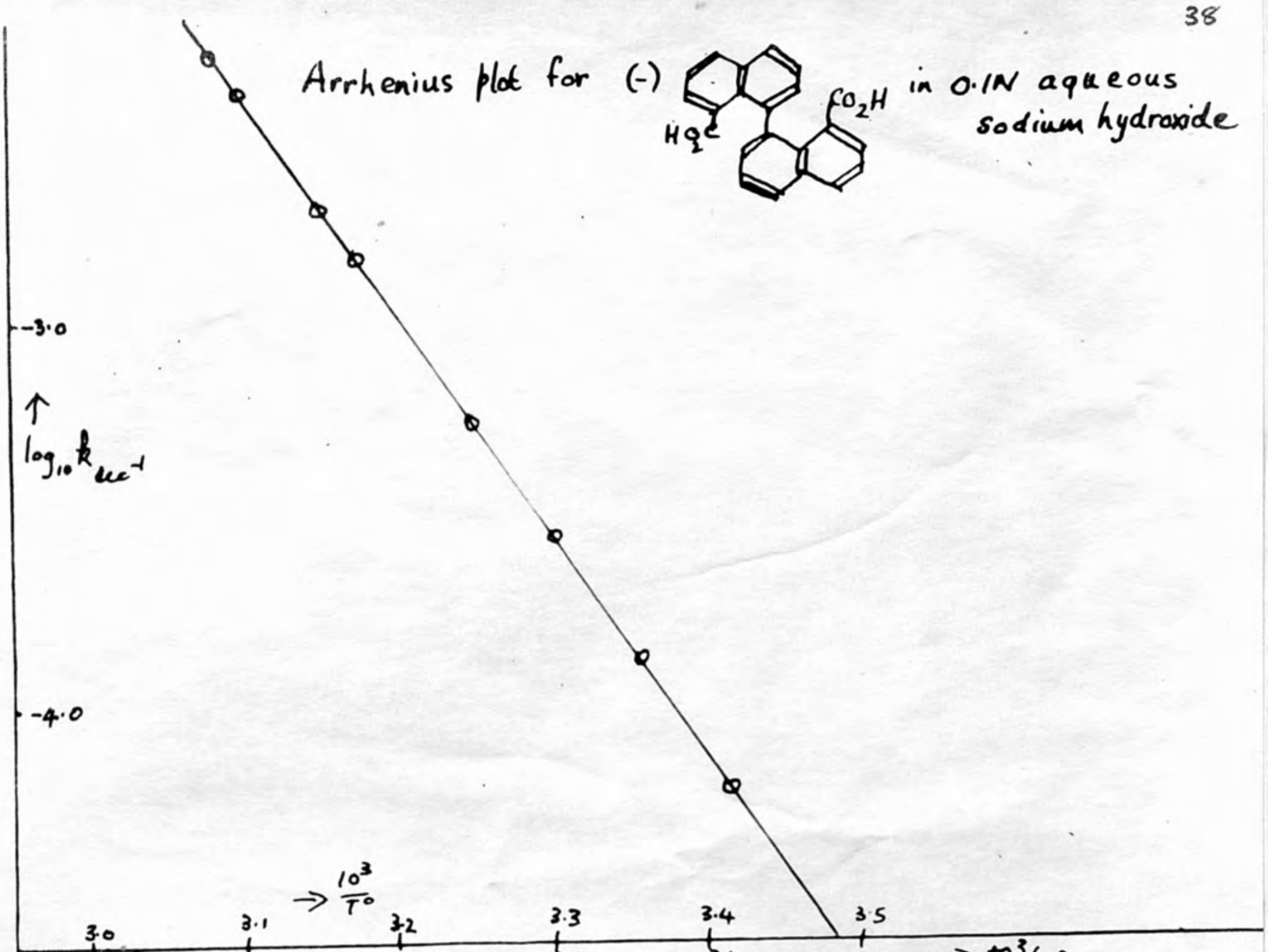
The best straight line taken graphically (see p. 38) gives: $\Delta E = 26.06$ kcal.mole^{-1} for the (−)acid and $\Delta E = 26.07$ kcal.mole^{-1} for the (+)acid.

Using this value for ΔE, and and $\Delta S^{\ddagger}$ were calculated.

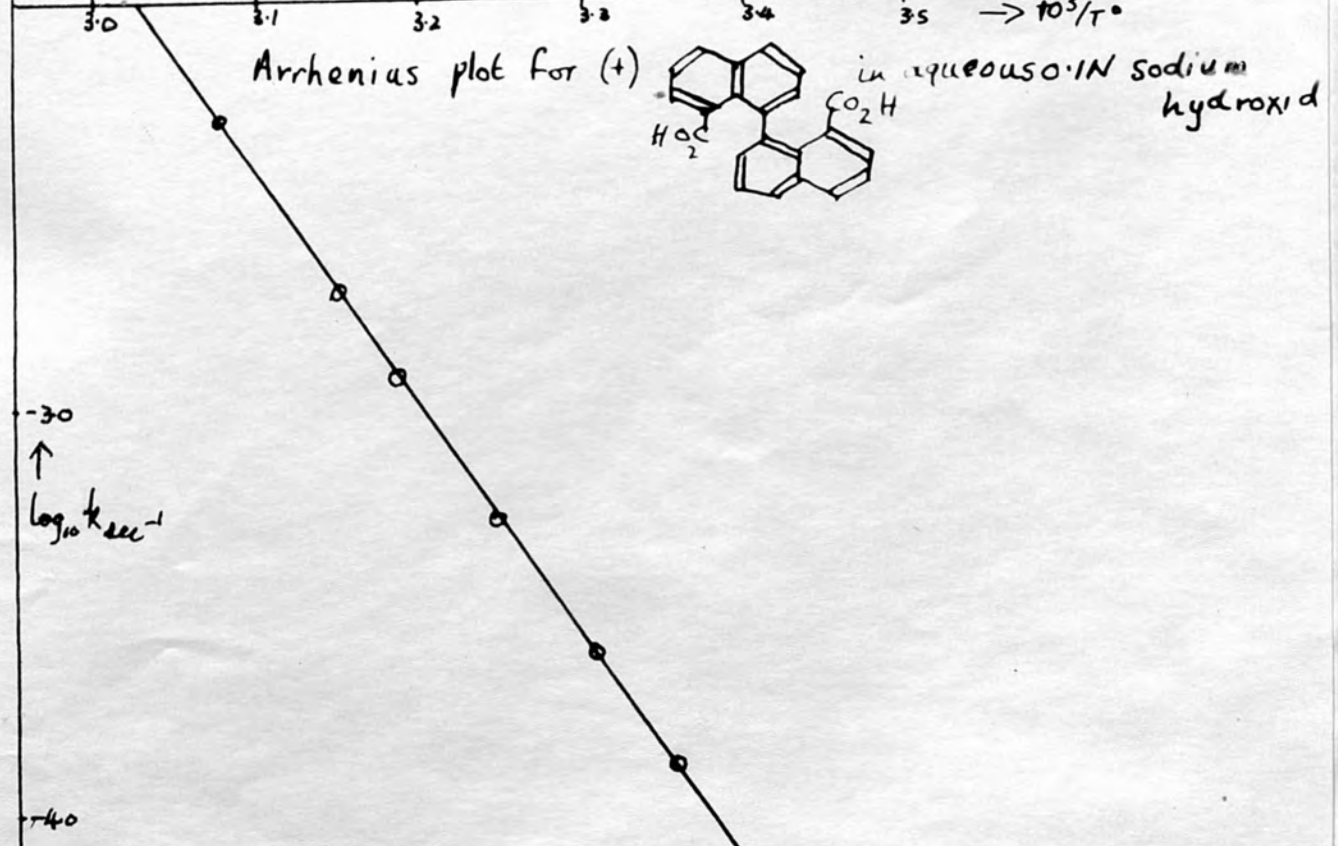
$A = 10^{15.2}$ sec^{-1} $\Delta S^{\dagger} = +9.2$ e.u.

The half life period was 2 minutes at 52°.

[These were the figures given in a Note to <u>Chemistry and Industry</u>, 1959, 949.]



Arrhenius plot for (-) in 0.1N aqueous sodium hydroxide



Arrhenius plot for (+) in aqueous 0.1N sodium hydroxid

Mean square calculation for both the (+) and the (-) acid.

T°	y	x	xy	x^2
290	3.4482758	0.5343118	1.942454	0.2854891
293	3.4129692	0.7902852	2.697219	0.6245507
293	3.4129692	0.7795965	2.6607388	0.6077707
298	3.3557046	1.1420765	3.8324714	1.3043387
298	3.3557046	1.1238516	3.7713139	1.2630421
303	3.3003300	1.4557582	4.7978818	2.1163204
302	3.3112582	1.4090874	4.6658522	1.9855273
308	3.2467532	1.7595923	5.7129619	3.0961650
308	3.2467532	1.7402837	5.6502717	3.0285873
315	3.1746031	2.1723110	6.8940529	4.7189348
314	3.1847133	2.0906190	6.6580221	4.3706878
317.5	3.1496062	2.3010300	7.2473383	5.2947390
323	3.0959752	2.5838963	7.9996788	6.6765201
325	3.0769230	2.7061201	8.3265232	7.3208599
325	3.0769230	2.6769678	8.2368238	7.1661566

$n = 16$ $\Sigma y = 51.9990680$ $\Sigma x = 27.5668154$

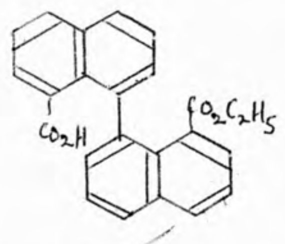
$\Sigma xy = 88.2389425$ $\Sigma x^2 = 55.1544285$

$$b = 0.17647$$

$$\therefore \Delta E = 25.93 \text{ kcal.mole}^{-1}$$

$$A = 10^{15.14} \text{ sec}^{-1} \qquad \Delta S^{\ddagger} = +8.6 \text{ e.u.}$$

Ethyl hydrogen 1.1'-binaphthyl-8.8'-dicarboxylate



Preparation of the brucine salt.
(Meisenheimer and Beisswenger (*loc.cit.*)
resolved this compound too, but by a different method.)

The ethyl hydrogen 1,1'-binaphthyl-8,8'-dicarboxylate (2.3g., 1M) was dissolved in 20 c.c. of boiling ethyl cellosolve and was added to anhydrous brucine (2.6 g., 1M) in 5 c.c. ethyl cellosolve. The solution was filtered hot and then 15 c.c. of hot water was added to the filtrate. After standing for some time, crystallisation occurred. 3.9 g. of colourless prisms m.p. 193° were obtained. This was a second order asymmetric transformation as 80% of the product came out as one diasteroisomer, $[\alpha]^{21.4^\circ}_{5461} = -419^\circ$ in Solvent X.

The active acid, m.p. 199° (inactive 193-5°) had $[\alpha]^{17}_{5461} = -336.1$ in N,N-dimethyl formamide.

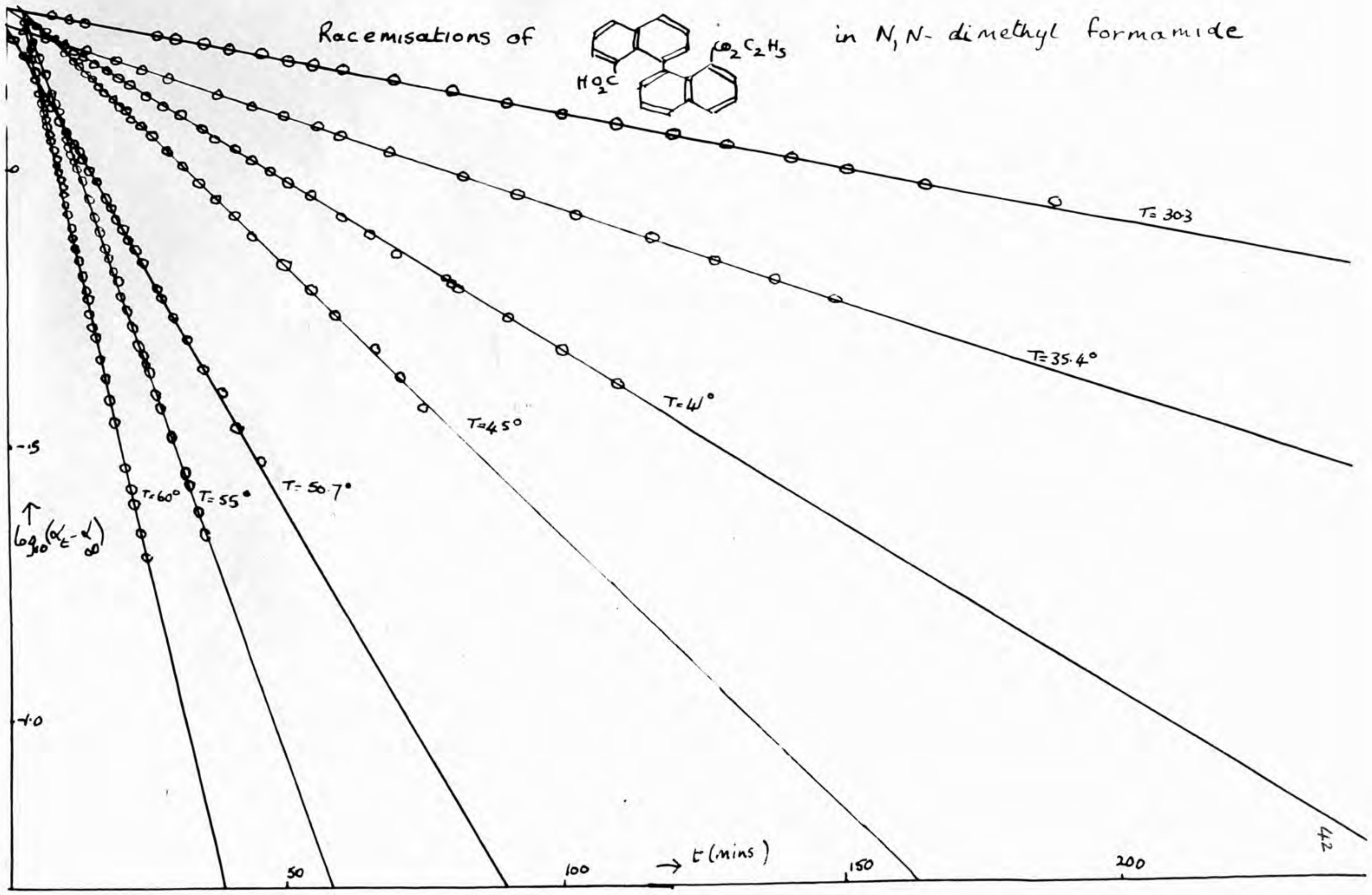
Meisenheimer and Beisswenger (*loc.cit.*) said the salt sintered at 130°, bubbled at 140° and finally melted at 210°, $[\alpha]^{20}_{D} = +352^\circ$. They gave $[\alpha]_D = +405^\circ$ for the free acid in sodium hydroxide.

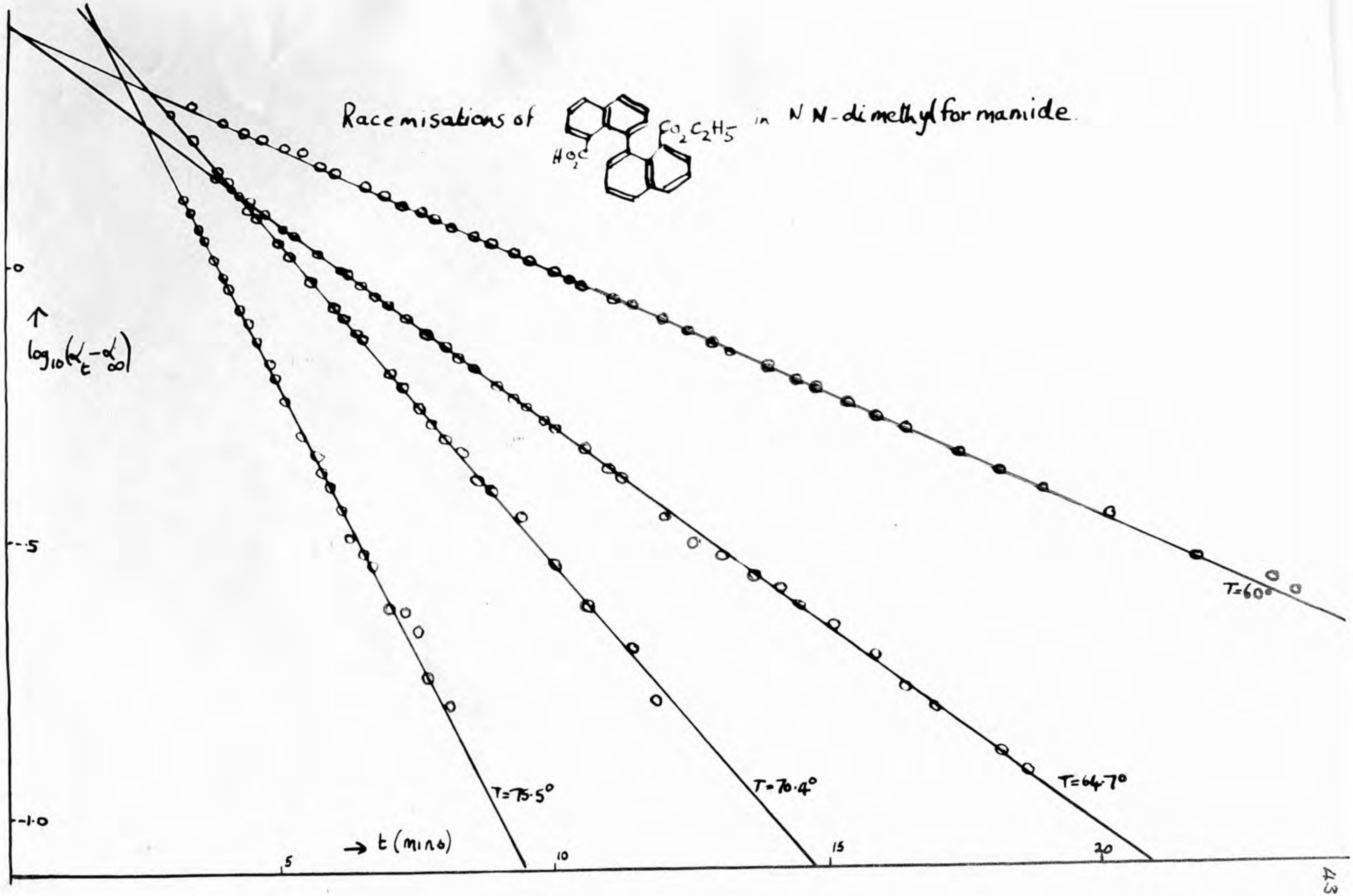
This acid gives a (+)ve rotation in sodium hydroxide and a (-)ve one in N.N-dimethyl formamide.

Determination of rate coefficients for racemisation of ethyl hydrogen-1,1'-binaphthyl-8,8'-dicarboxylate in N,N-dimethyl formamide.

Temperature in °C	Time of 1st reading in minutes	First reading	No. of readings	Time over which readings taken	$10^4 k\ \mathrm{sec}^{-1}$
30.3	4	(-)1.99°	25	186 mins	0.785
35.4	3	(-)1.81°	24	145 mins	1.31
41	3	(-)1.92°	35	106 mins	2.46
45	4	(-)1.96°	36	71 mins	3.79
50.7	2	(-)1.76°	45	44 mins	6.70
55	4	(-)1.91°	47	32 mins	11.1
60	4	(-)1.98°	42	22 mins	18.6
64.7	4	(-)1.46°	37	16 mins	29.0
70.3	4	(-)1.77°	26	8 mins	47.1
75.5	3	(-)1.32°	27	5 mins	75.3

Racemisations of in N, N- dimethyl formamide





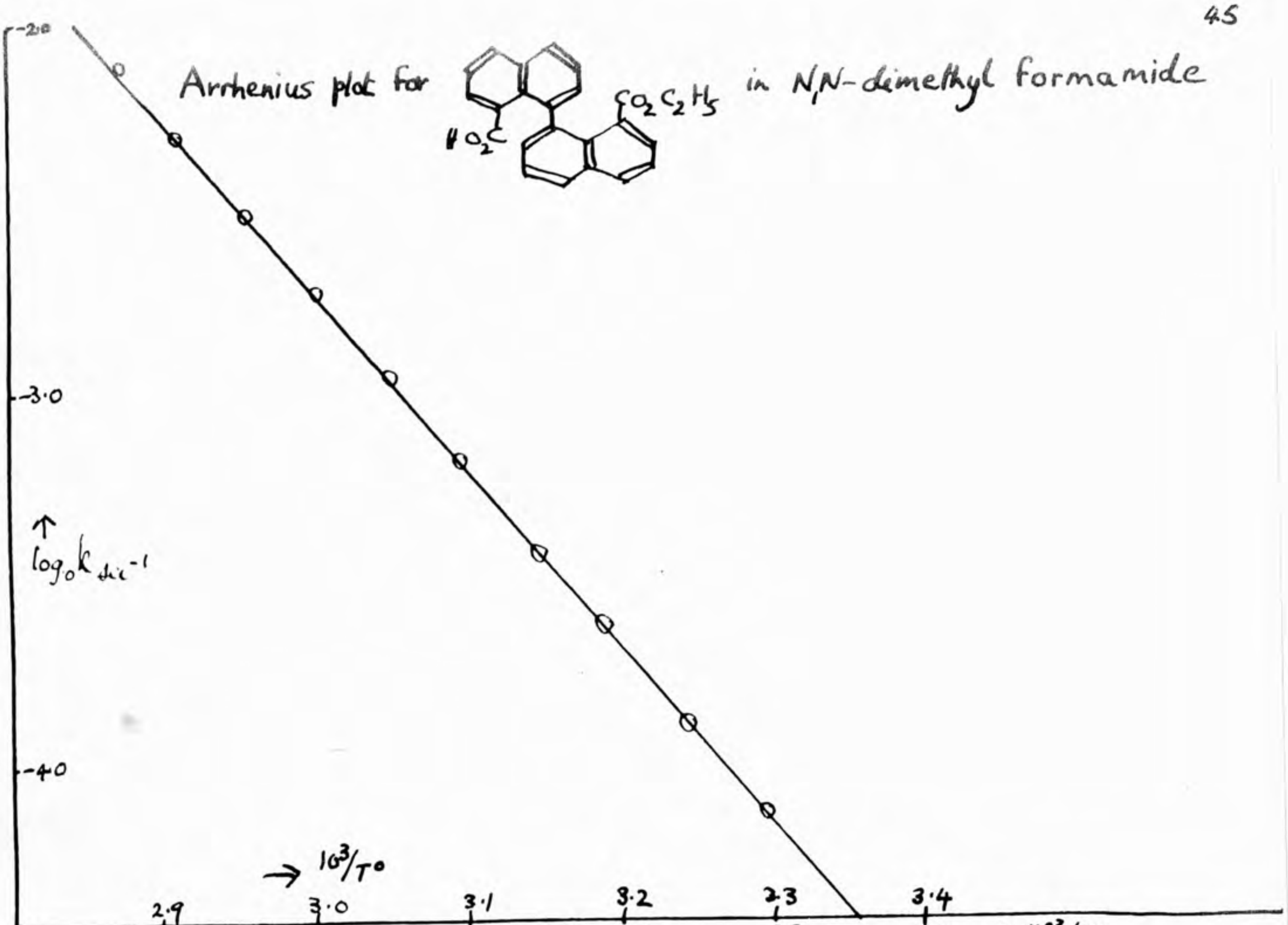
Racemisations of HO$_2$C … CO$_2$C$_2$H$_5$ in NN-dimethylformamide.

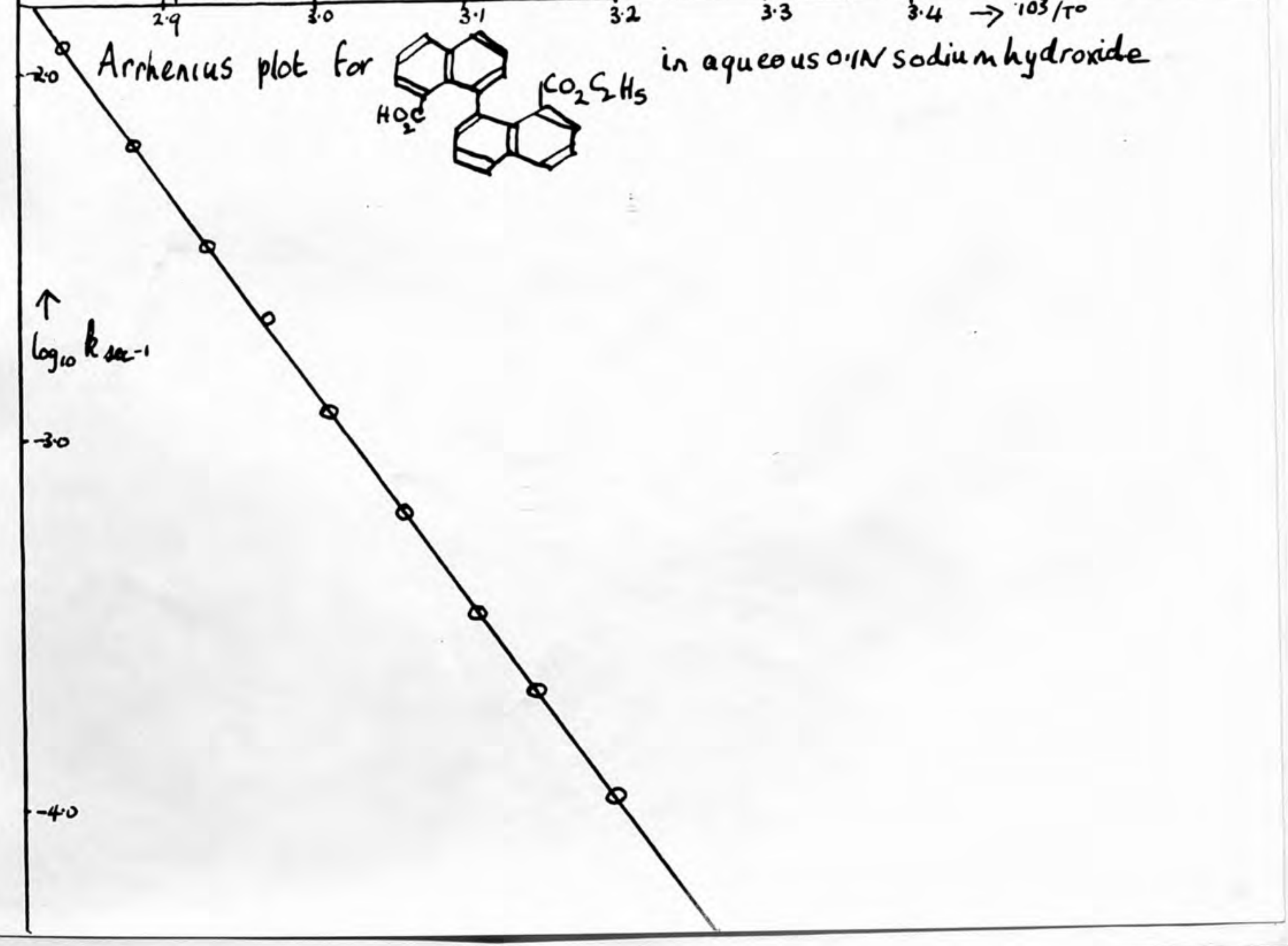
Determination of the Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

T^o	$10^3/T$	$10^3k_{sec}{}^{-1}$	$\log_{10}k_{sec}{}^{-1}$
303.3	3.297	0.0785	$\bar{5}.8951$
308.4	3.243	0.1312	$\bar{4}.1179$
314	3.185	0.246	$\bar{4}.3913$
318	3.145	0.379	$\bar{4}.5784$
323.7	3.089	0.670	$\bar{4}.8263$
328	3.049	1.11	$\bar{3}.0461$
333	3.003	1.86	$\bar{3}.2702$
337.7	2.961	2.90	$\bar{3}.4624$
343.3	2.2912	4.71	$\bar{3}.6727$
348.5	2.870	7.53	$\bar{3}.8768$

The best straight line taken graphically gives:

$\Delta E = 21.68$ kcal.mole^{-1} (see p. 45)


Arrhenius plot for
HO_2C
$CO_2C_2H_5$
in N,N-dimethyl formamide
-2.0
-3.0
↑ $\log_{10} k$ sec⁻¹
-4.0
→ $10^3/T°$
2.9
3.0
3.1
3.2
2.3
3.4


2.9
3.0
3.1
3.2
3.3
3.4
→ $10^3/T°$
Arrhenius plot for
HO_2C
$CO_2C_2H_5$
in aqueous 0.1N sodium hydroxide
-2.0
↑ $\log_{10} k$ sec⁻¹
-3.0
-4.0

Mean square calculation.

T°	y	x	xy	x^2
303.3	3.297065	0.89508	2.951137	0.801168
308.4	3.242542	1.11809	3.625451	1.250125
314	3.184713	1.39124	4.430700	1.935549
318	3.144654	1.57857	4.964056	2.491883
323.7	3.0892800	1.82629	5.641921	3.335335
328	3.049780	2.04626	6.238596	4.187180
333	3.003003	2.27035	6.817868	4.187180
337.7	2.967359	2.46237	7.306736	6.063266
343.3	2.912904	2.67275	7.782791	7.143593
348.5	2.869440	2.87680	8.254805	8.275978

$n = 10 \qquad \Sigma y = 30.759740 \qquad \Sigma x = 19.13780$

$\Sigma xy = 58.014064 \qquad \Sigma x^2 = 40.638566$

$$b = \frac{-8.53688}{40.13177}$$

$$\therefore \quad \Delta E = 21.51 \text{ kcal.mole}^{-1}$$

The average value of ΔE from these two methods is 21.597 kcal. mole^{-1}

$$A = 10^{11.43} \text{ sec}^{-1}$$

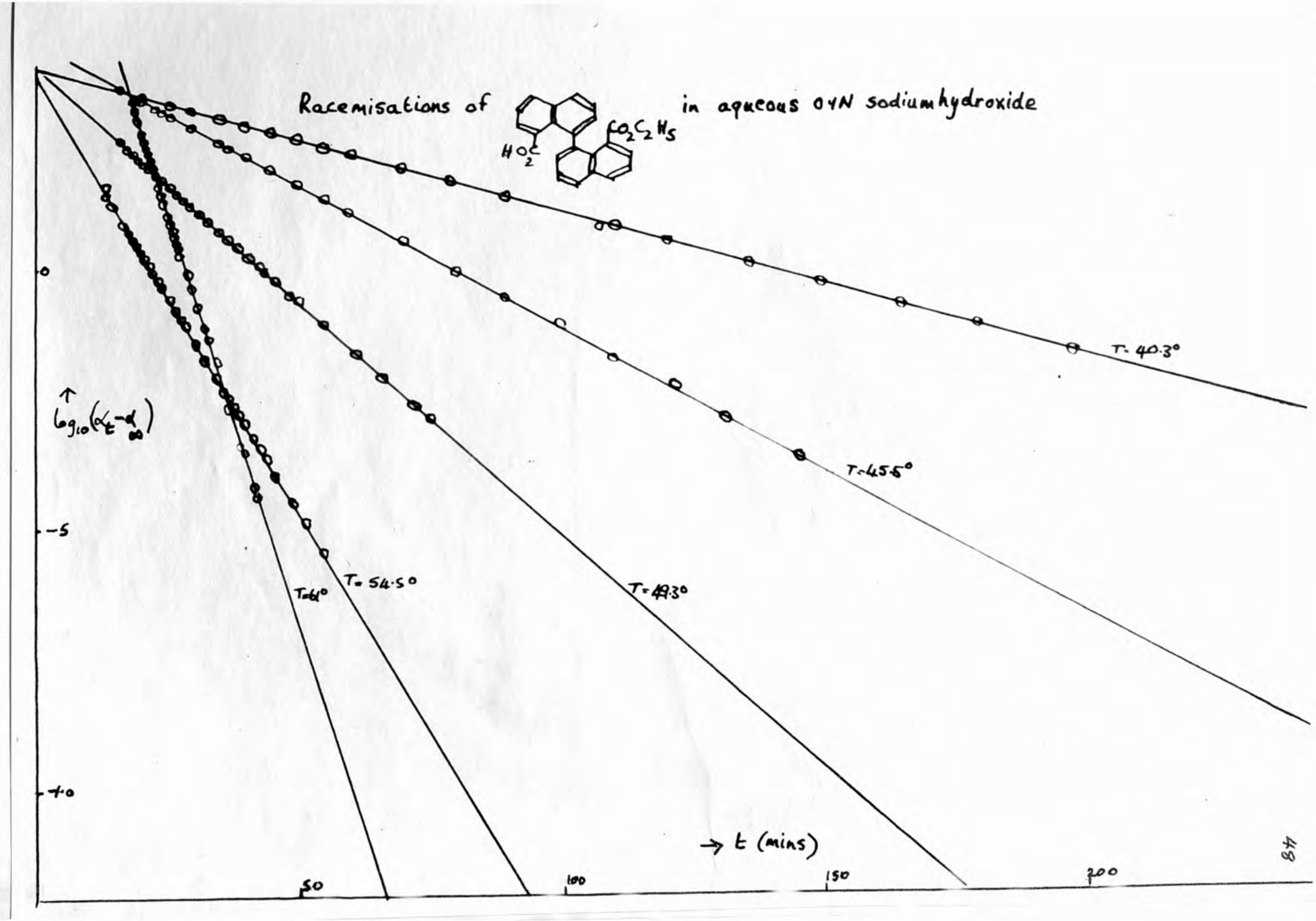
$$\Delta S^{\ddagger} = -8.39 \text{ e.u.}$$

$\Delta H^{\ddagger} = 20.95 \text{ kcal.mole}^{-1} \qquad \Delta F^{\ddagger} = 23.71 \text{ kcal.mole}^{-1}$

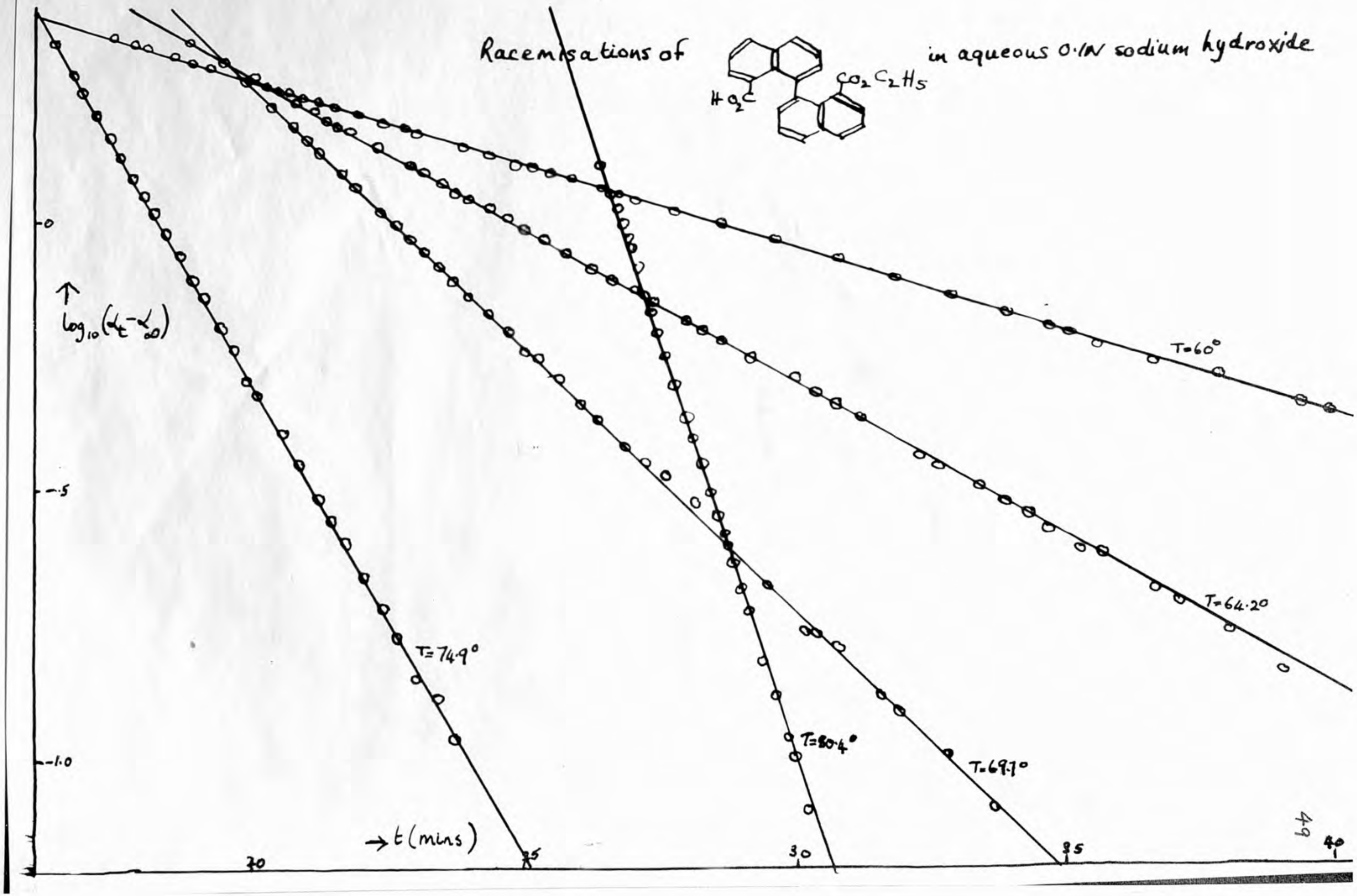
The half life period at 50.7° is 18 mins.

Determination of rate coefficients for racemisation of ethyl hydrogen 1,1'-binaphthyl-8,8'-dicarboxylate in 0.1N aqueous sodium hydroxide.

Temperature in °C	Time of 1st reading	First reading	No. of reading	Time during which readings taken	10^3 k$_{sec}^{-1}$
40.3	16	(+)2.24°	24	180	0.109
45.5	16	(+)2.26°	24	130	0.211
49.3	16	(+)1.79°	27	58	0.354
54.5	15	(+)1.44°	41	40	0.653
60	17	(+)2.23°	41	25	1.20
64.2	19	(+)2.16°	42	20	2.22
69.1	20	(+)1.82°	34	13.6	3.49
74.9	16	(+)2.21°	28	7	6.54
80.4	26	(+)1.26°	25	3.5	12.1



Racemisations of in aqueous 0·4N sodiumhydroxide



Racemisations of in aqueous 0·1N sodium hydroxide

Determination of Arrhenius parameters and the entropy of activation $\Delta S^{\ddagger}$ for ethyl hydrogen 1,1'-binaphthyl-8,8'-dicarboxylate in 0.1^N aqueous sodium hydroxide.

T^o	$10^3/T$	$10^3 k_{sec}^{-1}$	$\log_{10} k_{sec}^{-1}$
313.3	3.192	0.109	$\bar{4}.0380$
318.5	3.140	0.211	$\bar{4}.3237$
322.3	3.103	0.354	$\bar{4}.5490$
327.5	3.053	0.653	$\bar{4}.8148$
333	3.003	1.20	$\bar{3}.0786$
337.2	2.9665	2.22	$\bar{3}.3464$
342.1	2.9230	3.49	$\bar{3}.5425$
347.9	2.874	6.45	$\bar{3}.8153$
353.4	2.830	12.1	$\bar{2}.0814$

The best straight line taken graphically gives:

$\Delta E = 25.64$ kcals.mole^{-1} (see p. 45)

Mean square calculation.

T°	y	x	xy	x^2
313.3	3.191828	1.03782	3.312543	1.07707
318.5	3.139717	1.32366	4.155918	1.752076
322.3	3.102699	1.54900	4.806081	2.399401
327.5	3.063453	1.81478	5.541313	3.293426
333	3.003003	2.07882	6.242703	4.321493
337.2	2.965599	2.34635	6.958333	5.505358
342.1	2.923121	2.54245	7.431889	6.464052
347.9	2.874388	2.81531	8.092296	7.925970
353.4	2.829654	3.08135	8.719154	9.494718

$n = 9$ $\Sigma y = 27.083445$ $\Sigma x = 18.58954$

$\Sigma xy = 55.260230$ $\Sigma x^2 = 42.233564$

$$\therefore b = -\frac{6.126714}{34.531079}$$

$\Delta E = 25.79$ kcal.mole^{-1}

Thus the average value for E is 25.71 kcals.mole^{-1}

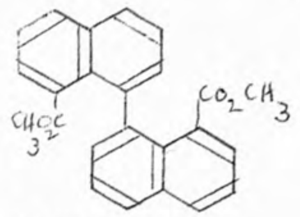
$$A = 10^{13.97} \text{ sec}^{-1}$$

$$\Delta S^{\ddagger} = +3.2 \text{ e.u.}$$

$\Delta H^{\ddagger} = 25.06$ kcal.mole^{-1} $\Delta F^{\ddagger} = 24.40$ kcal.mole^{-1}

and the half life period at 49.3° is 33 minutes.

Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate.

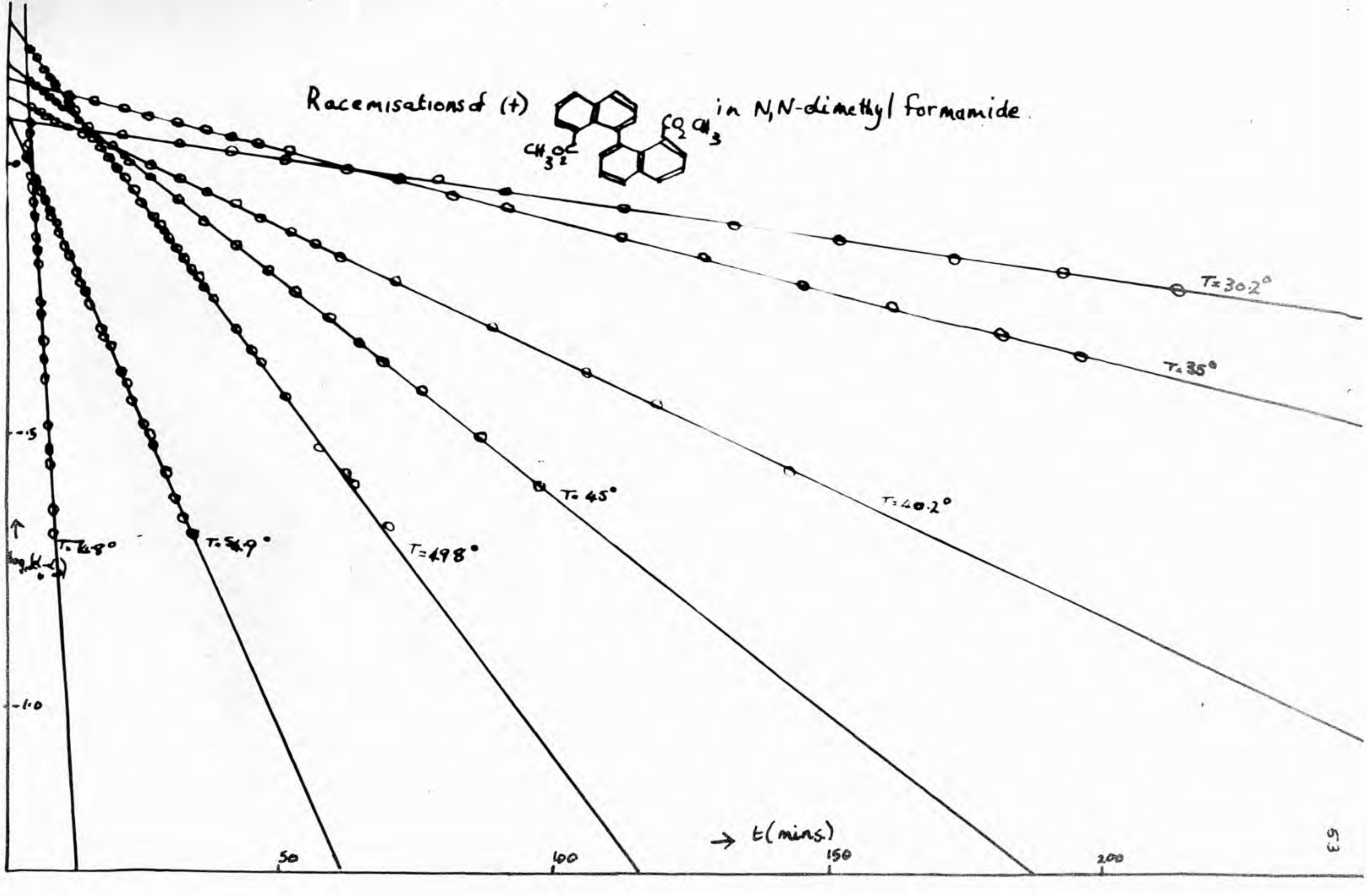


This ester was obtained in its dextro- and laevo-rotatory forms by the method described in the experimental synthetic section (p. 139).

(+)-ester.

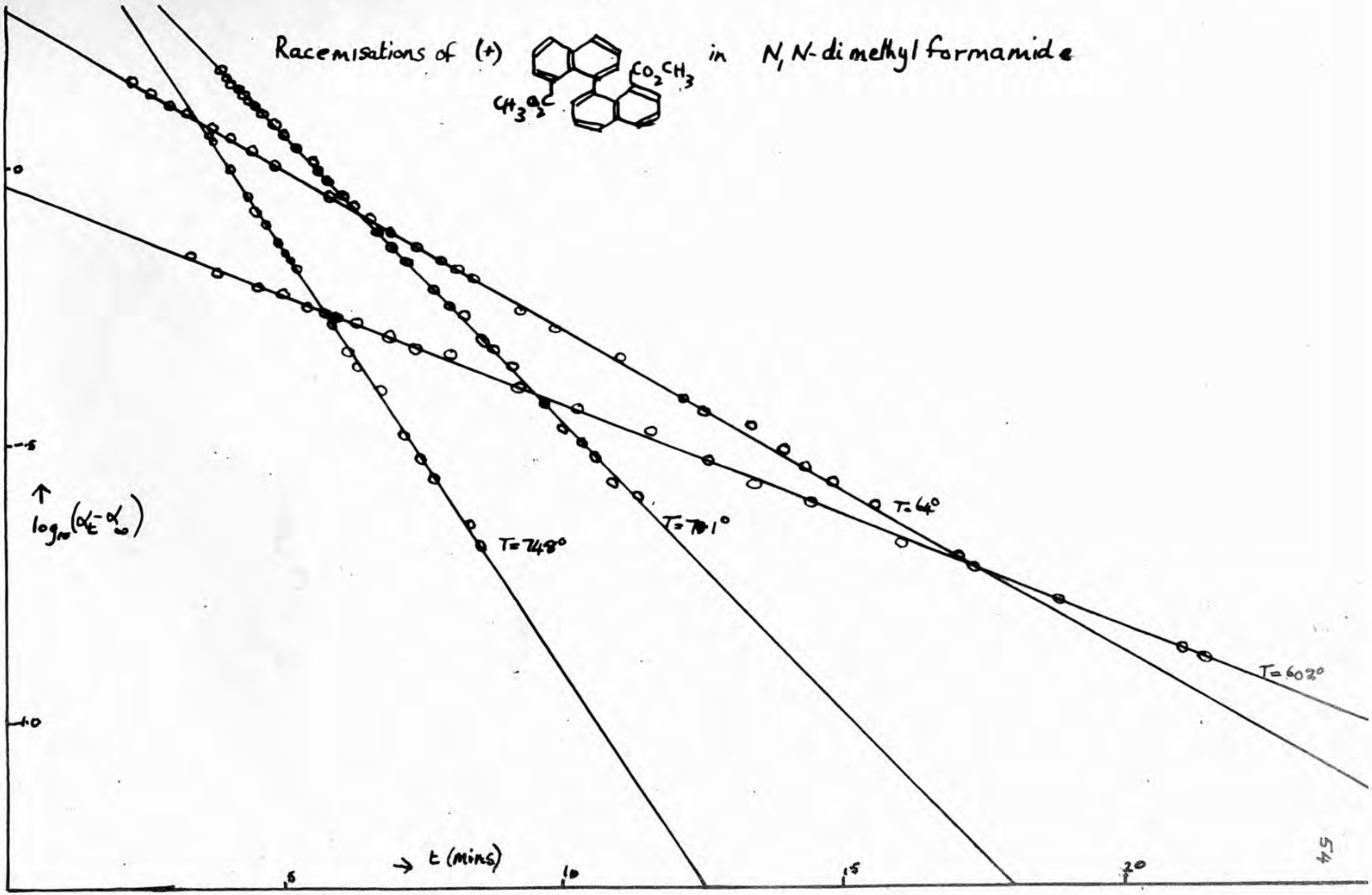
Determination of rate constants for racemisation in N,N-dimethyl formamide.

Temperature in °A	Time of 1st reading	First reading	No. of readings	Time during which readings taken	$10^4k_{sec}{}^{-1}$
303.2	4 mins	(-)1.20°	17	247 mins	0.562
308	4 mins	(-)1.39°	22	190 mins	0.978
313.2	4 mins	(-)1.27°	23	140 mins	1.83
318	4 mins	(-)1.41°	25	92 mins	3.02
322.8	3 mins	(-)1.63°	37	66 mins	5.24
327.9	3 mins	(-)1.0°	27	30 mins	8.68
333.2	3 mins	(-)0.70°	21	18 mins	15.5
337	2 mins	(-)1.42°	28	15 mins	22.1
343.1	4 mins	(-)1.53°	30	8 mins	40.5
347.8	4 mins	(-)1.15°	18	4 mins	58.3



Racemisations of (+) in N,N-dimethyl formamide

Racemisations of (+) in N,N-dimethyl formamide



Determination of the Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

T^{o}	$10^{3}/T$	$10^{4}k_{sec}^{-1}$	$\log_{10}k_{sec}^{-1}$
303.2	3.298	0.562	$\bar{5}.7499$
308	3.246	0.978	$\bar{5}.9903$
312.2	3.193	1.83	$\bar{4}.2625$
318	3.145	3.02	$\bar{4}.4796$
322.8	3.098	5.24	$\bar{4}.7194$
327.9	3.050	8.68	$\bar{4}.9385$
333.2	3.001	15.5	$\bar{3}.1892$
337	2.967	22.1	$\bar{3}.3451$
343.1	2.915	40.5	$\bar{3}.6076$
347.8	2.875	58.3	$\bar{3}.7656$

The best straight line taken graphically (see p.57) gives:

$$\Delta E = 22.16 \text{ kcal.mole}^{-1}$$

Mean square calculation.

T°	y	x	xy	x^2
303.2	3.298153	0.7499797	2.4735477	0.5624695
308	3.2467532	0.9903553	3.2154392	0.09808036
313.2	3.1928480	1.2624606	4.0308448	1.5938067
318	3.1446540	1.4796185	4.6528882	2.1892709
322.8	3.0978934	1.7194398	5.3266412	2.9564732
327.9	3.0497102	1.9385547	5.9120300	3.7579943
333.2	3.0012004	2.1592476	6.57037077	4.7928050
337.2	2.9655998	2.3451521	6.9547807	5.4997383
343.1	2.9146021	2.6075944	7.6001001	6.7995485
347.8	2.8752156	2.7656254	7.9517692	7.6486838

$n = 10$ $\Sigma y = 30.7866289$ $\Sigma x = 18.0480281$

$\Sigma xy = 54.6884118$ $\Sigma x^2 = 36.7815938$

$$b = -0.20800504$$

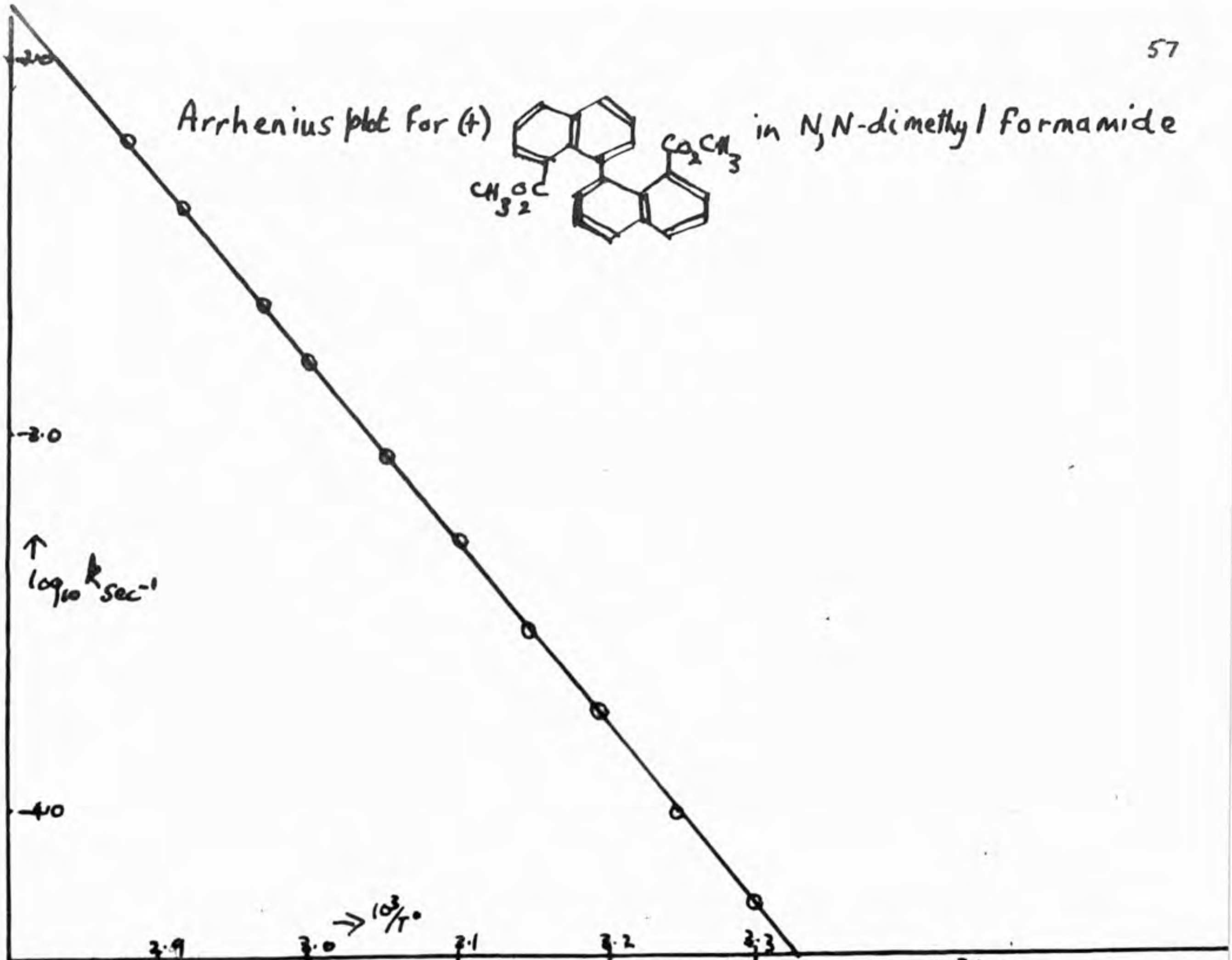
$$\therefore \Delta E = 21.99 \text{ kcal.mole}^{-1}$$

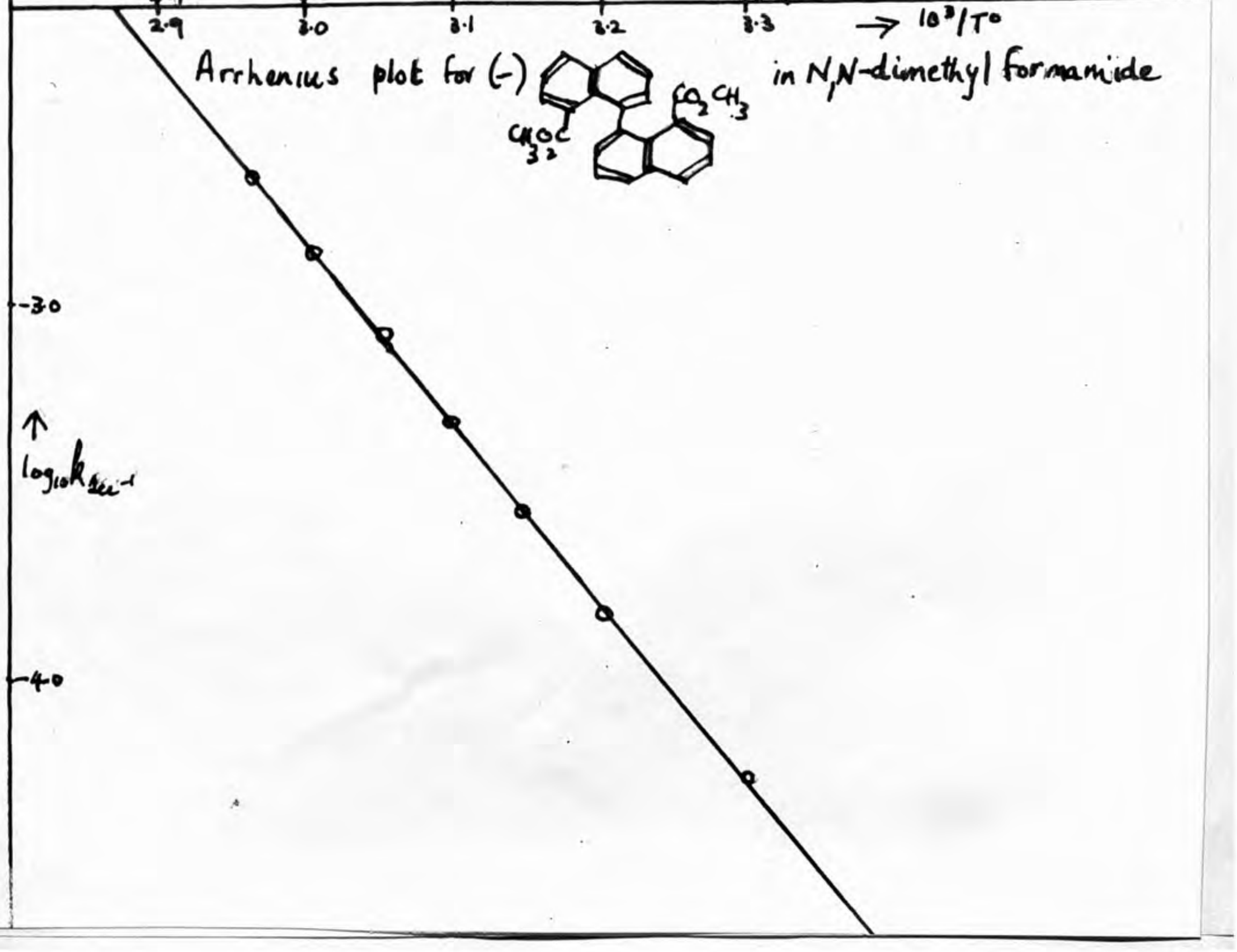
The average value for ΔE is 22.07 kcal.mole^{-1}

$A = 10^{11.65}$ sec^{-1} $\Delta S^{\ddagger} = -7.4$ e.u.

$\Delta H^{\ddagger} = 21.40$ kcal.mole^{-1} $\Delta F^{\ddagger} = 23.88$ kcal.mole^{-1}

The half life period at 49.8° is 22 mins.


Arrhenius plot for (+)
CH3O2C
CO2CH3
in N,N-dimethyl formamide
-2.0
-3.0
-4.0
↑ log10 k sec-1
2.9
3.0
3.1
3.2
3.3
→ 10³/T°

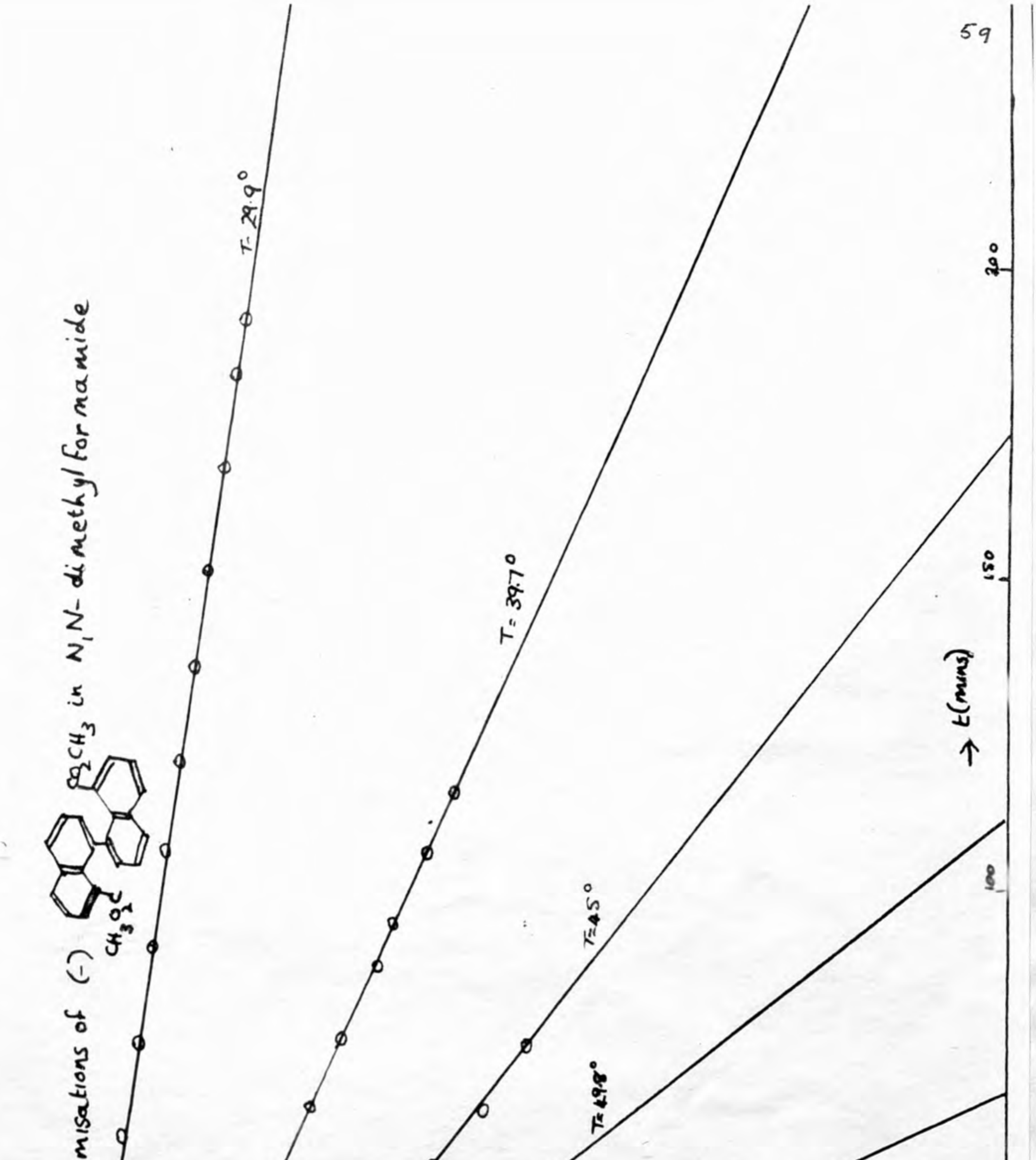

2.9
3.0
3.1
3.2
3.3
→ 10³/T°
Arrhenius plot for (-)
CH3O2C
CO2CH3
in N,N-dimethyl formamide
-3.0
-4.0
↑ log10 k sec-1

Determination of the rate coefficients for racemisation for (−)dimethyl 1,1'-binaphthyl 8,8'-dicarboxylate in N,N-dimethyl formamide.

Temperature in °C	Time of 1st reading	1st reading	No readings	Time during which readings taken	$10^4k_{sec}^{-1}$
29.9	2 mins	(+) 0.99°	20	360 mins.	0.555
39.7	3 mins	(+)0.79°	20	113 mins.	1.46
45	2 mins	(+)0.69°	20	73 mins.	2.82
49.8	3 mins	(+)0.76°	20	50 mins.	4.94
54.7	4 mins	(+)0.80°	26	28 mins.	8.47
60	3 mins	(+)1.12°	28	18 mins.	14.2
64	2 mins	(+)0.83°	25	13 mins.	21.8

Determination of the Arrhenius constants A and ΔE and the entropy of activation $\Delta S^{\dagger}$

T^{o}	$10^3/T$	$10^4K_{sec}^{-1}$	$\log_{10}k_{sec}^{-1}$
302.9	3.301	0.555	$\bar{5}.7441$
312.7	3.197	1.46	$\bar{4}.1648$
318	3.145	2.82	$\bar{4}.4502$
322.8	3.098	4.94	$\bar{4}.6935$
327.7	3.052	8.47	$\bar{4}.9281$
333	3.003	14.2	$\bar{3}.1523$
337.4	2.964	21.8	$\bar{3}.3390$


Racemisations of (−) in N,N- dimethylformamide

The best straight line drawn graphically (see p. 57) gives:

$\Delta E = 21.94$ kcal.mole^{-1}

Mean square calculation.

T^o	y	x	xy	x^2
302.9	3.3014190	0.7420571	2.4498414	0.5506487
312.7	3.197953	1.1649631	3.7248576	1.3566731
318	3.44654	1.4502491	4.5605316	2.1032224
322.8	3.097893	1.6935027	5.2462851	2.8679514
327.7	3.051571	1.9280633	5.9634835	3.8190301
333	3.003003	2.1523437	6.4634945	4.6325834
337.4	2.963841	2.3390278	6.9325065	5.4710510

$n = 7$ $\Sigma x = 11.4700068$ $\Sigma y = 21.760334$

$\Sigma xy = 35.2611387$ $\Sigma x^2 = 20.6995581$

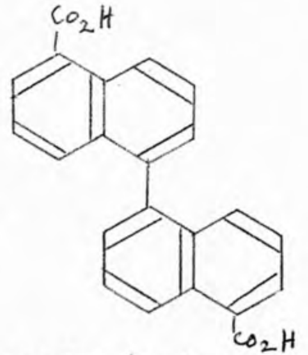
$b = -.20720151$

$\therefore \Delta E = 22.08$ kcal. mole^{-1}

The average value of ΔE is 22.01 kcal.mole^{-1}

$A = 10^{11.60}$ sec^{-1} $\Delta S = -7.6$ e.u. $\Delta F = 23.87$ kcal.mole^{-1}

$\Delta H = 21.40$ kcal.mole^{-1} Half life period at 49.8° is 23 minutes.



1,1'-Binaphthyl-5,5'-dicarboxylic acid.

Preparation of brucine salt (Hall, Ridgwell and Turner, J., 1954, 2498).

The 1,1'-binaphthyl-5,5'-dicarboxylic acid (1.4 g., 1M) and anhydrous brucine (3.2 g., 2M) were dissolved in 80 c.c. of ethyl cellosolve and the solution filtered hot. To this hot filtrate were added 160 c.c. of hot water. 3.3g., of the brucine salt crystallised as faintly yellow, needle-like prisms, m.p. 198-200°, $[\alpha]_{5461}^{21.4}$ -23.99 in solvent X. [Ridgwell (loc.cit.) gave $[\alpha]_{5461}^{20} = -23°$ in chloroform for the salt and $[\alpha]_{5461}^{20} = +56.6$ for the acid in sodium hydroxide.] The active acid had m.p. 367° (inactive 360°) and $[\alpha]_{5461}^{17} = +68.8°$ in dimethyl formamide.

Determination of rate coeffícients in N,N-dimethyl formamide.

The rate coefficients could not be found in the usual way as the acid had virtually no rotation on the mercury green line in N,N-dimethyl formamide, although if alkali was added there was a reading of +0.5 and therefore a different technique was adopted. The rate was carried out in N,N-dimethyl formamide but read in 0.1N aqueous sodium hydroxide. A concentrated solution of the acid in N,N-dimethyl formamide was made and 5 c.c. of it were pipetted into each of 10 ampoules, which were sealed and placed in a thermostat. They were taken out at timed intervals and plunged into a freezing mixture. When they were ice cold 15 c.c. of cold 0.1 N aqueous sodium hydroxide was added from a burette. This solution was filtered into a polarimeter tube thermostated at 15°. Thus three rate coefficients were obtained over a temperature range of 20°.

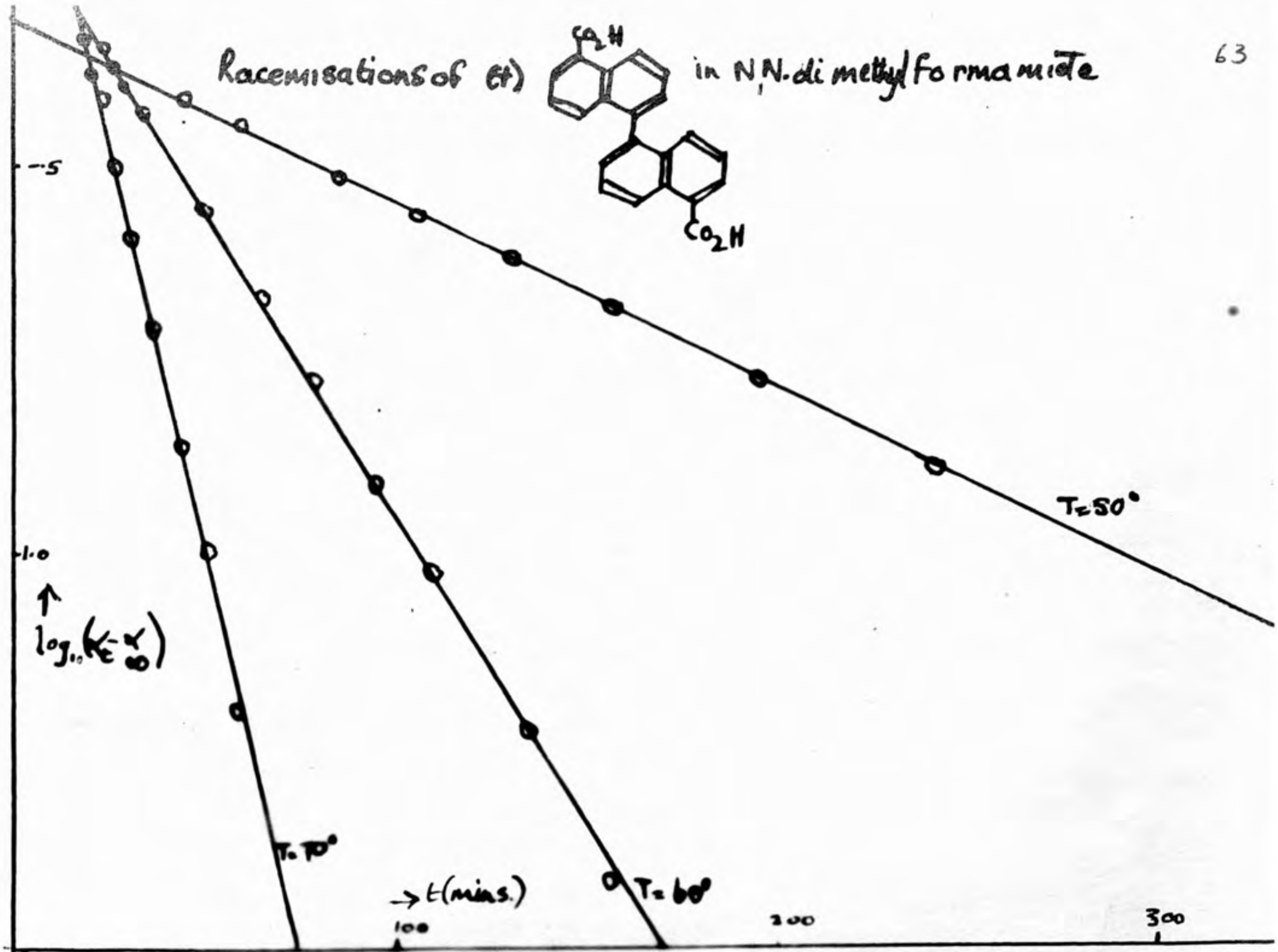
Temperature	Time of 1st reading	First reading	Number of readings	Time during which readings taken	$10^4 k_{sec}^{-1}$
50°	20 mins	(+)0.428°	9	215 mins	0.425
60°	25 "	(+)0.462°	9	135 "	2.94
70°	21 "	(+)0.420°	8	37 "	8.17

Determination of the Arrhenius parameters. A and ΔE and entropy of activation $\Delta S^{\ddagger}$

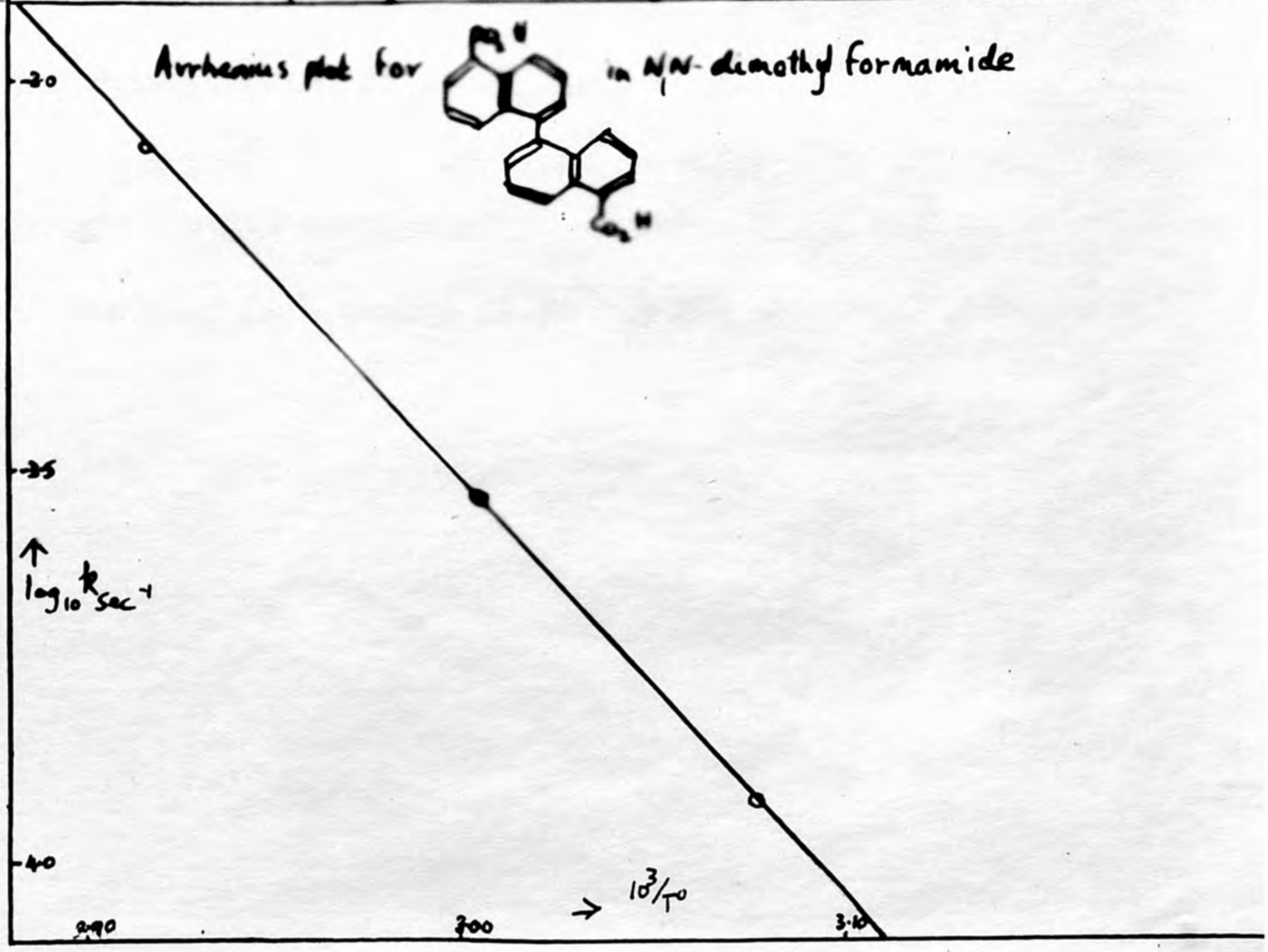
T^o	$10^3/T$	$10^4 k_{sec}^{-1}$	$\log_{10} k_{sec}^{-1}$
323	3.096	0.425	$\bar{5}.9664$
333	3.003	2.94	$\bar{4}.4690$
343	2.915	8.17	$\bar{4}.9120$

The best straight line taken graphically (see p. 63) gives:

$$\Delta E = 24.28 \text{ kcal.mole}^{-1}$$



Racemisations of (+) in N,N-dimethylformamide



Arrhenius plot for in N,N-dimethylformamide

Mean square calculation.

T°	y	x	xy	x^2
323	3.0959752	0.96638	2.991888	0.933890
333	3.003003	1.46894	4.411231	2.157785
343	2.9154518	1.91201	5.574373	3.655782

$n = 3$ $\Sigma x = 4.34733$ $\Sigma y = 9.0144300$

$\Sigma xy = 12.977492$ $\Sigma x^2 = 6.747457$

$$b = \frac{-0.256226}{1.343093}$$

$$\therefore \Delta E = 23.99 \text{ kcal.mole}^{-1}$$

The average value of ΔE is 24.13 kcal.mole^{-1}

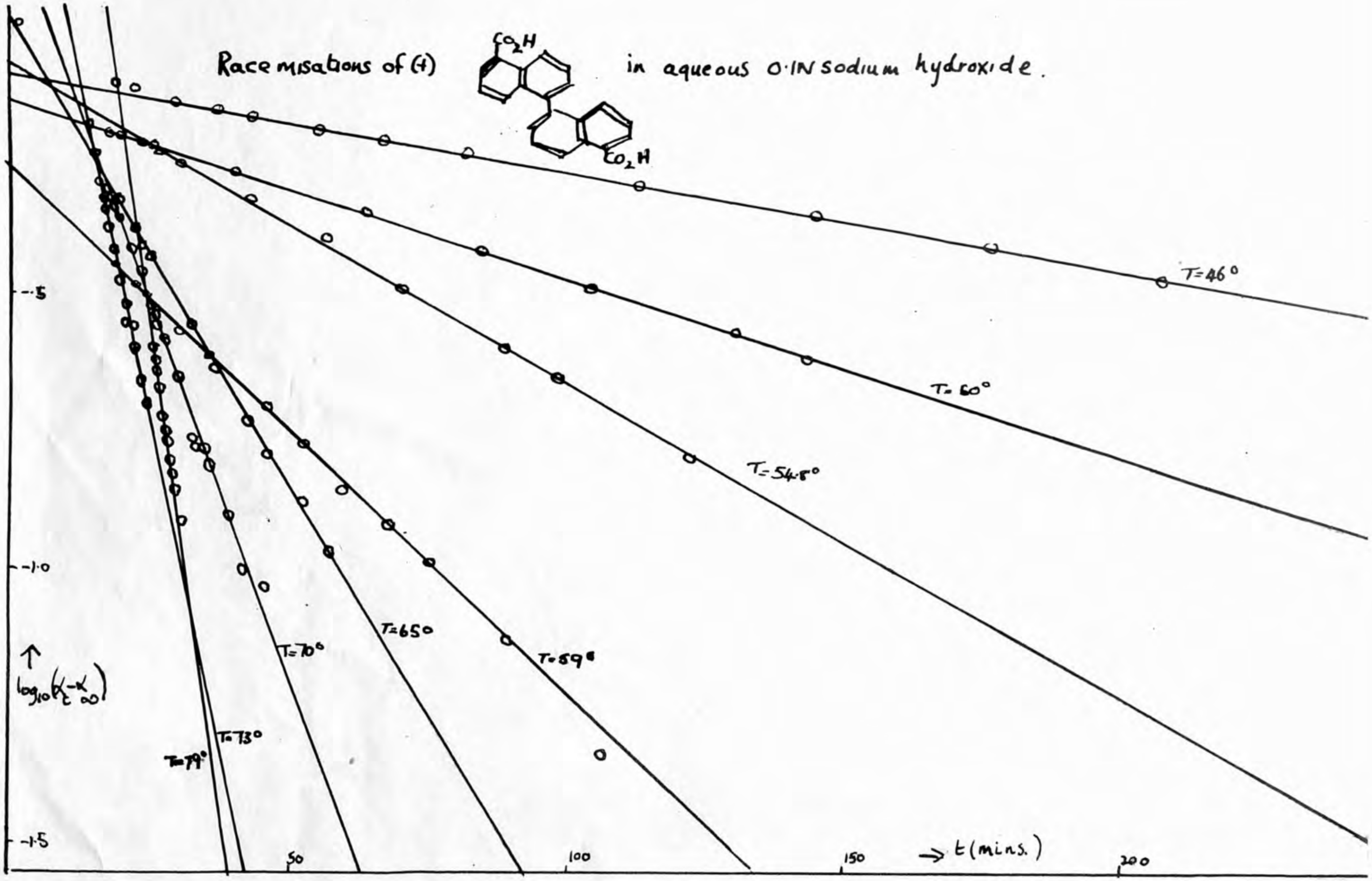
$A = 10^{12.29}$ $\Delta S^{\ddagger} = -4.48$

$\Delta H^{\ddagger} = 23.47 \text{ kcal.mole}^{-1}$ $\Delta F^{\ddagger} = 24.95 \text{ kcal.mole}^{-1}$

The half life period at 50° is 272 minutes.

Determination of the rate coefficients for racemisation of 1,1'-binaphthyl-5,5'-dicarboxylic acid in 0.1N aqueous sodium hydroxide.

Temperature in °C	Time of 1st reading	First reading	No. of readings	Time during which readings taken	$10^4 k_{sec}^{-1}$
46	19 mins	(+)0.77°	16	310 mins.	0.705
50	19 mins	(+)0.61°	10	248 mins.	1.22
54.3	22 mins.	(+)0.62°	11	100 mins.	2.27
59	22 mins	(+)0.33°	10	83 mins.	3.63
65	19 mins.	(+)0.47°	11	40 mins.	6.75
70	16 mins.	(+)0.49°	15	30 mins.	10.6
73	15 mins.	(+)0.64°	16	10 mins.	16.7
79	22 mins.	(+)0.42°	16	8 mins.	30.4



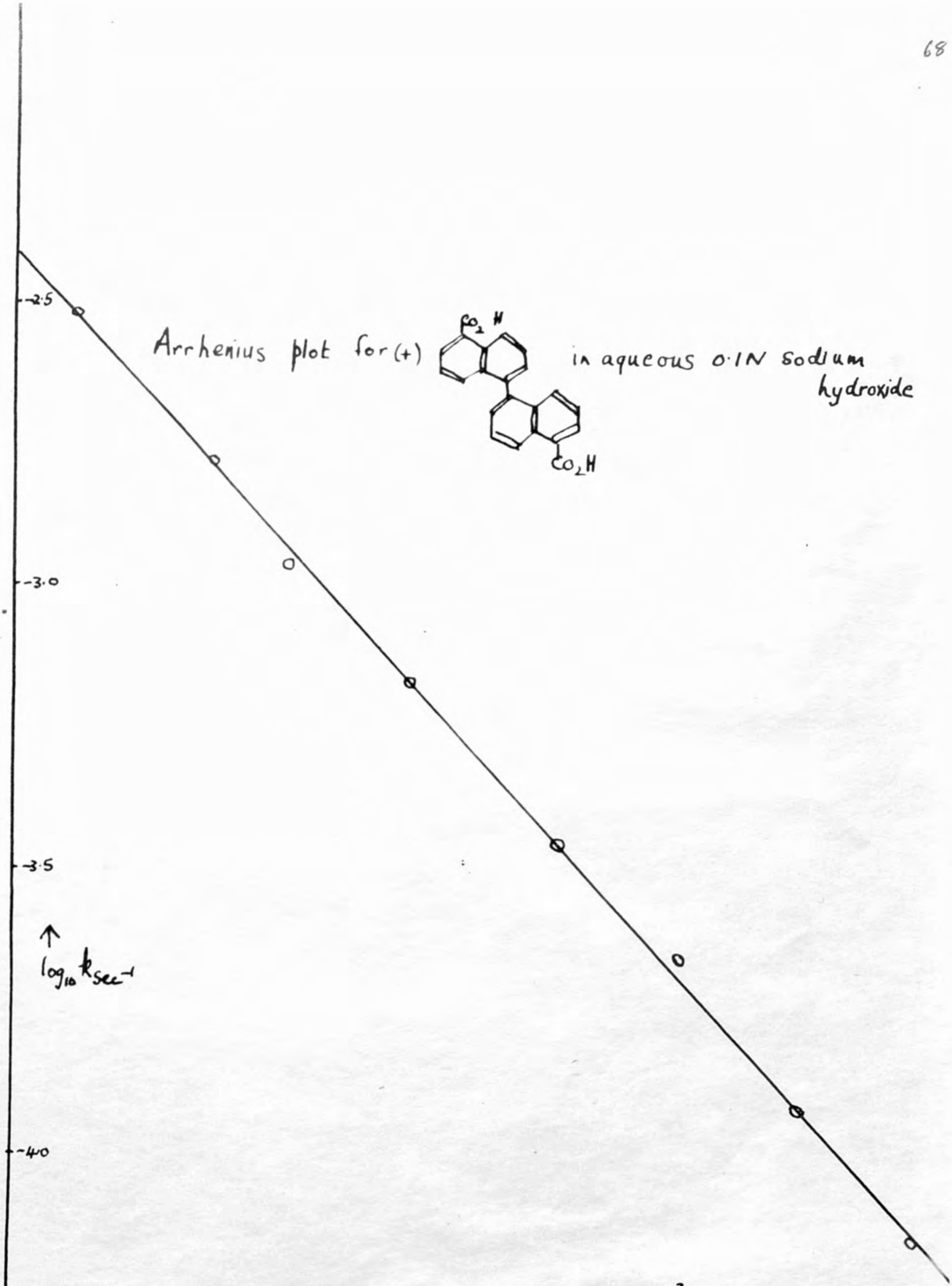
Racemisations of (+) in aqueous 0·1N sodium hydroxide.

Determination of Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

T°	$10^3/T$	$10^4\ k_{sec}{}^{-1}$	$\log_{10}k_{sec}{}^{-1}$
319	3.135	0.705	$\bar{5}.8479$
323	3.096	1.23	$\bar{4}.0859$
327.3	3.055	2.27	$\bar{4}.3559$
332	3.012	3.63	$\bar{4}.8597$
338	2.959	6.75	$\bar{4}.8292$
343	2.915	10.64	$\bar{3}.0262$
346	2.890	16.74	$\bar{3}.2237$
352	2.841	30.4	$\bar{3}.4822$

The best straight line taken graphically (see p. 68) gives:

$$\Delta E = 24.91\ \text{kcal.mole}^{-1}$$



Arrhenius plot for (+) in aqueous 0·1N sodium hydroxide

Mean square calculation.

T°	y	x	xy	x^2
319.2	3.13283	0.84794	2.6564	0.71900
323.2	3.09406	1.08884	3.36757	1.18557
327.5	3.05344	1.35603	4.14056	1.83882
332.2	3.01023	1.55967	4.69497	2.43257
338.2	2.95683	1.82918	5.40857	3.34589
343.2	2.91375	2.02612	5.90361	4.10516
346.2	2.88850	2.22376	6.52333	4.94511
352.2	2.83929	2.48216	7.04757	6.16112

$n = 8$ $\Sigma y = 23.88893$ $\Sigma x^2 = 24.73324$

$\Sigma xy = 39.64263$ $\Sigma x = 13.41370$

$$b = -.183844$$

$$\therefore \Delta E = 24.89 \text{ kcal.mole}^{-1}$$

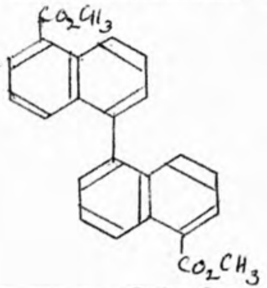
The average value of ΔE is 24.90 kcal.mole^{-1}

$A = 10^{12.935} \text{ sec}^{-1}$ $\Delta S^{\ddagger} = -1.54$ e.u.

$\Delta H^{\ddagger} = 24.25 \text{ kcal.mole}^{-1}$ $\Delta F^{\ddagger} = 24.74 \text{ kcal.mole}^{-1}$

The half life period at 50° is 94 minutes.

Dimethyl 1,1'-binaphthyl-5,5'-dicarboxylate.

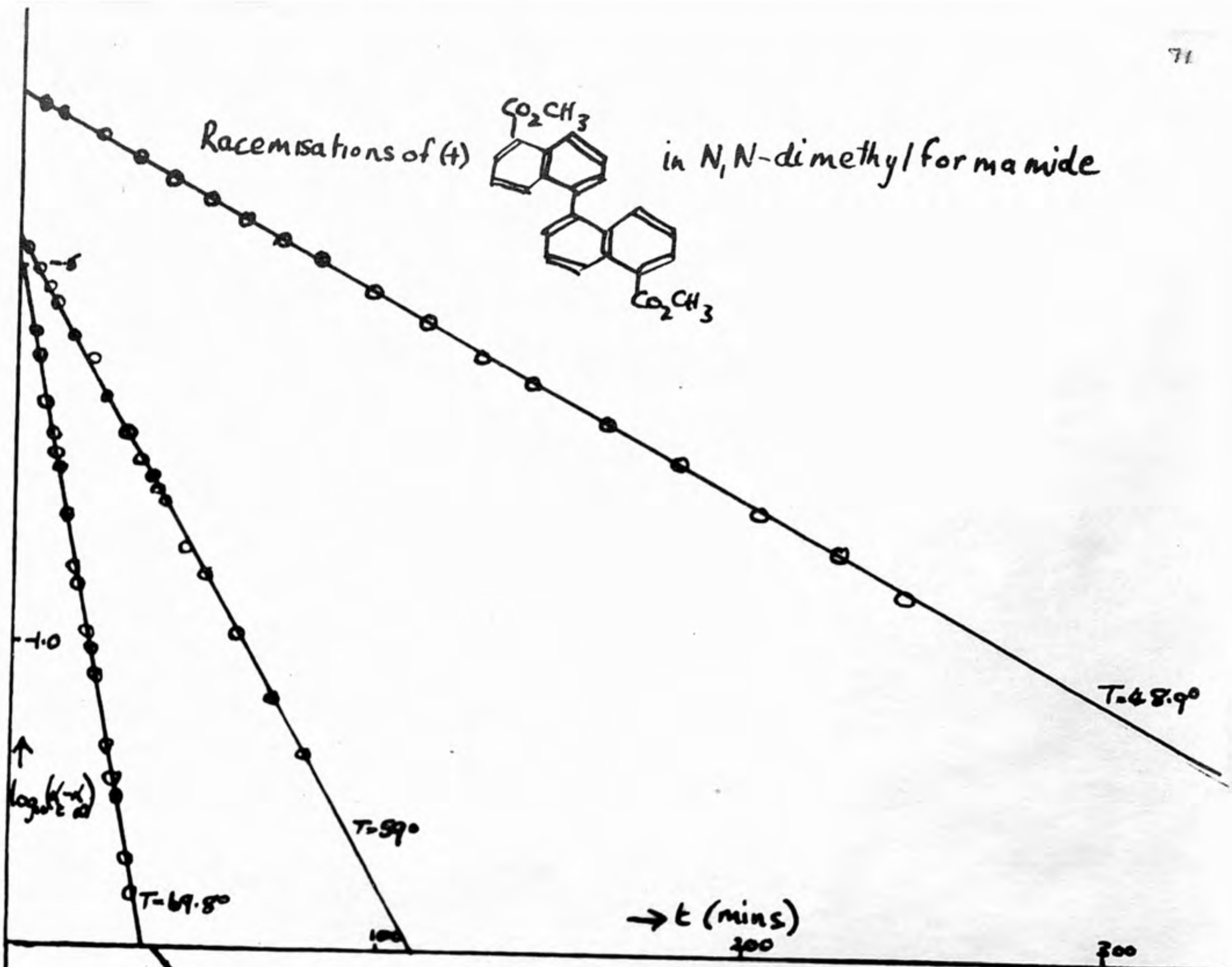


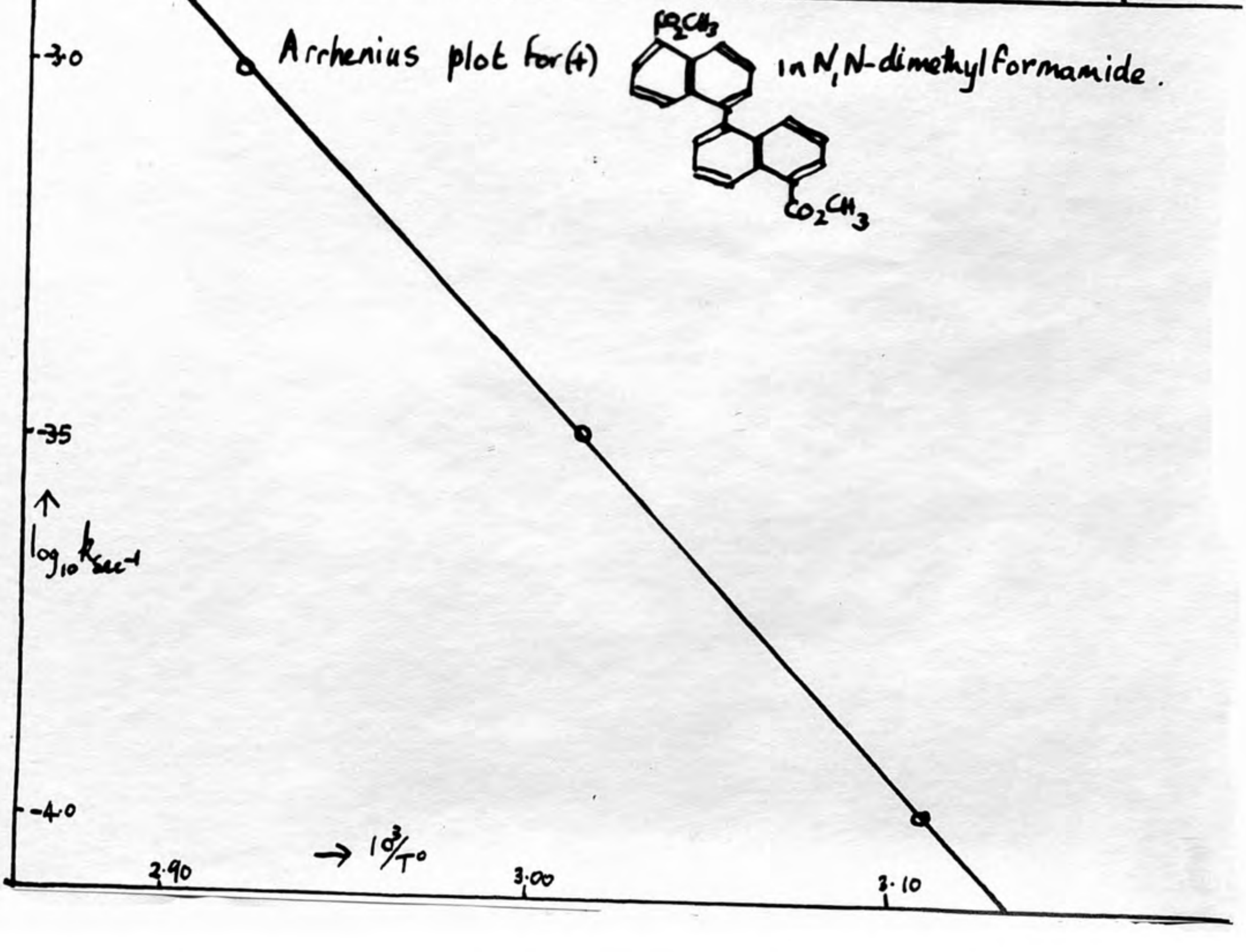
This ester was obtained in an optically active form by the method described in the experimental synthetic section (see p. 140).

This ester also gave a small rotation in dimethyl formamide, 0.1 g. dissolved in 20 c.c. gave a rotation of +0.05, which is much better than that the acid gave in this solvent. It was decided, therefore, to make up a concentrated solution and carry out the rate constant determination normally. As so much material was used in each determination, only three determinations of the rate coefficient could be made.

Determination of rate coefficients for racemisation of this ester in N,N-dimethyl formamide.

Temperature in °C	Time of 1st reading	First reading	No. of readings	Time during which readings taken	$10^4 k_{sec^{-1}}$
48.9	4 mins	0.52°	18	237 mins	1.03
59	2 mins	0.33°	15	78 mins	3.33
69.8	2 mins	0.292°	13	29 mins	9.76


Racemisations of (+) in N,N-dimethylformamide


Arrhenius plot for (+) in N,N-dimethylformamide.

Determination of the Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

T^{o}	$10^{3}/T$	$10^{4}k_{sec^{-1}}$	$\text{Log}_{10}k_{sec^{-1}}$
321.9	3.106	1.032	$\bar{4}.0151$
332	3.012	3.33	$\bar{4}.5222$
342.8	2.917	9.76	$\bar{4}.9892$

The best straight line taken graphically (see p. 71) gives:

$$\Delta E = 24.04 \text{ kcal.mole}^{-1}$$

Mean square calculation:

T^{o}	y	x	xy	x^{2}
321.9	3.1065548	1.0137134	3.1491562	1.0276148
332	3.0120481	1.5222016	4.5849444	2.3170971
342.8	2.9171528	1.9892375	5.8029091	3.9570658

$n = 3$ $\Sigma y = 9.0357557$ $\Sigma x = 4.5251525$

$\Sigma xy = 13.5370097$ $\Sigma x^{2} = 7.397777$

$$b = -.194344$$

$$\therefore \Delta E = 23.54 \text{ kcal.mole}^{-1}$$

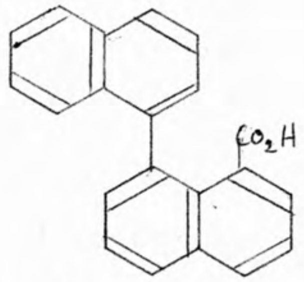
The average value for ΔE from these calculations is $23.78 \text{ kcal.mole}^{-1}$

$A = 10^{12.159} \text{ sec}^{-1}$ $\Delta S^{\dagger} = -5.09$ e.u.

$\Delta F^{\ddagger} = 24.77 \text{ kcal.mole}^{-1}$ $\Delta H^{\ddagger} = 23.12 \text{ kcal.mole}^{-1}$

The half life period at 48.9° is 112 minutes.

1,1'-binaphthyl-8-carboxylic acid.



Resolution via the brucine salt. (Meisenheimer and Beisswenger, *Ber.*, 1932, *65*, 32).

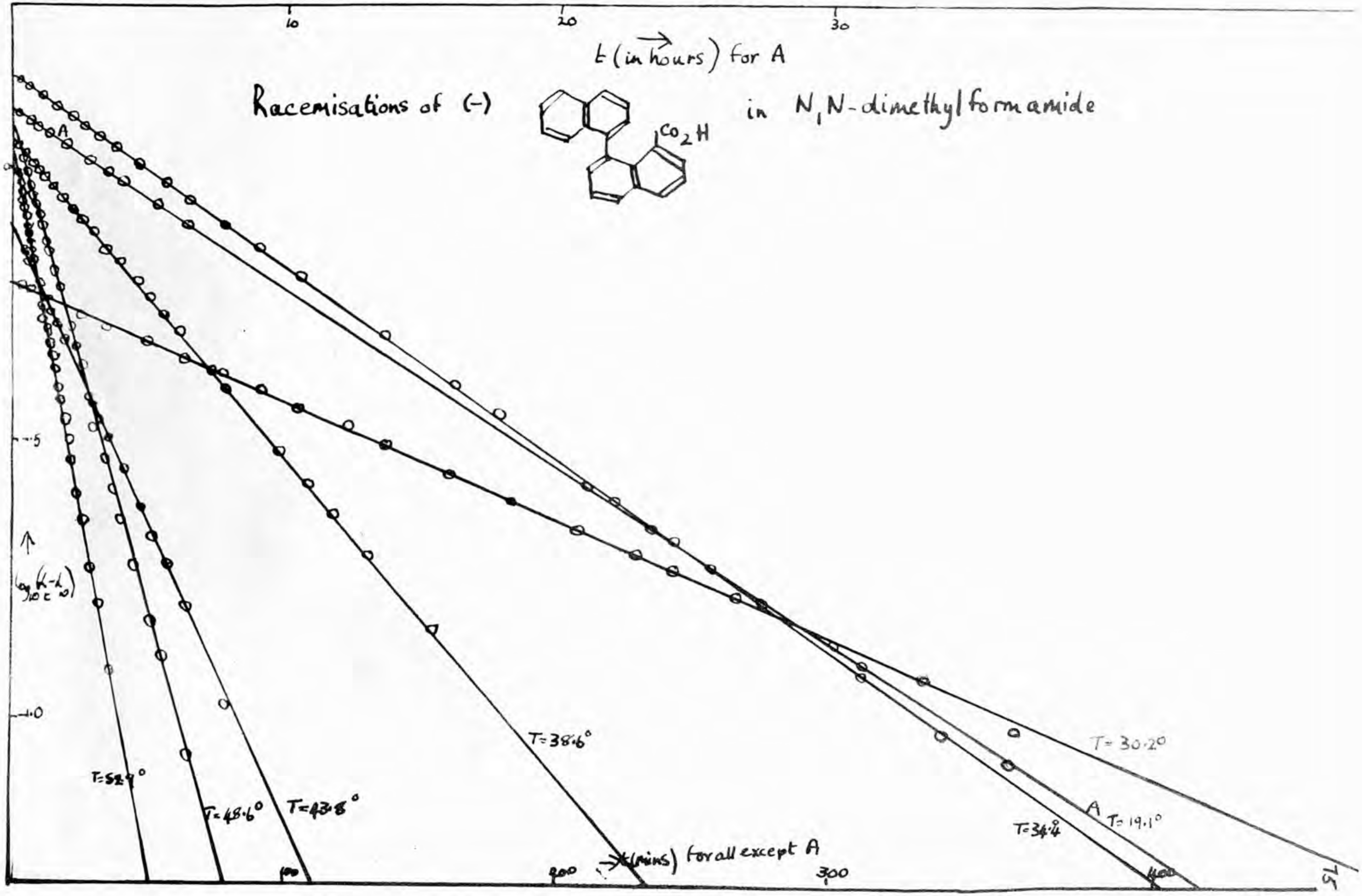
The acid (1.3 g., 1M) and brucine (2 g., 1M) were dissolved in 50 c.c. ethyl acetate with gentle warming. The volume was reduced to about 30 c.c. and the solution was allowed to cool when 6 drops of aqueous methyl alcohol (1 : 1) were added. On scratching 2.1 g. fine white needles crystallised m.p. 150-155°. $[\alpha]_G^{23} = -159.2$.

Resolution via the strychnine salt.

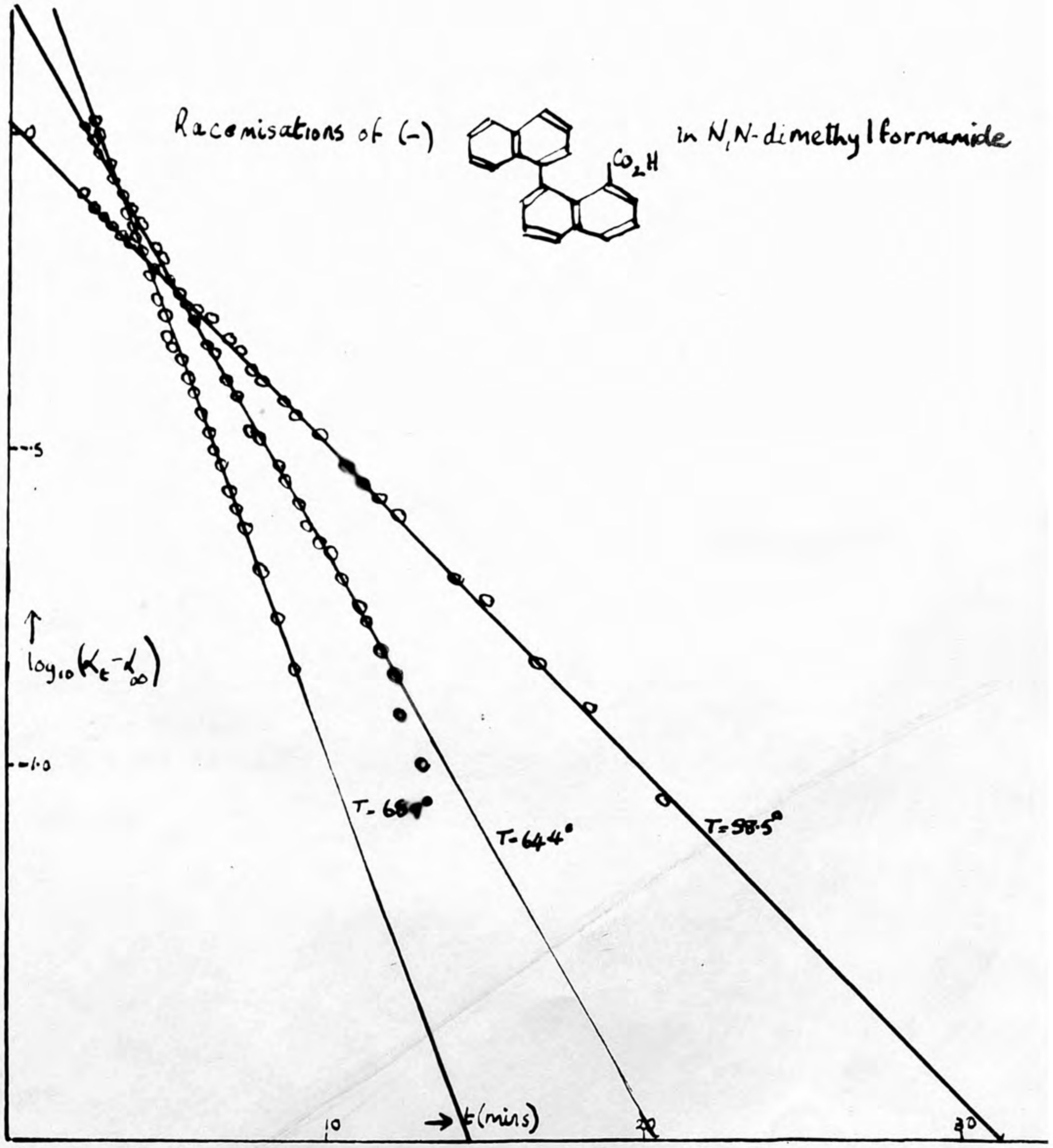
The acid (0.5 g., 1M) and strychnine (0.56 g., 1M) were dissolved by heating in alcohol. This clear solution was then evaporated to dryness and the residue crystallised from 25 c.c. of acetone. The first crop was 0.6 g. of colourless clusters, m.p. 227-230°. $[\alpha]_G^{23} = -240.^{\circ}$

Determination of rate coefficients for racemisation of 1,1'-binaphthyl-8-carboxylic acid in N,N-dimethyl formamide.

Temperature in °C	Time of 1st reading in minutes	First reading	No. of readings	Time over which readings taken	$10^4 k_{sec^{-1}}$
19.1	6	1.26°	15	31 hours	0.204
30.2	3	0.61°	21	360 mins.	0.755
34.4	2	1.45°	23	337 "	1.34
38.6	2	1.10°	25	152 "	2.22
43.8	3	0.70°	19	75 "	4.09
48.6	3	1.03°	24	61 "	6.65
52.9	2	0.92°	33	33 "	10.2
58.5	2	0.81°	32	18 "	19.6
64.4	2	1.03°	36	10 "	36.6
68.8	3	0.89°	25	6 "	52.5
68.9	2	1.06°	27	7 "	52.2



Racemisations of (-) in N,N-dimethylformamide



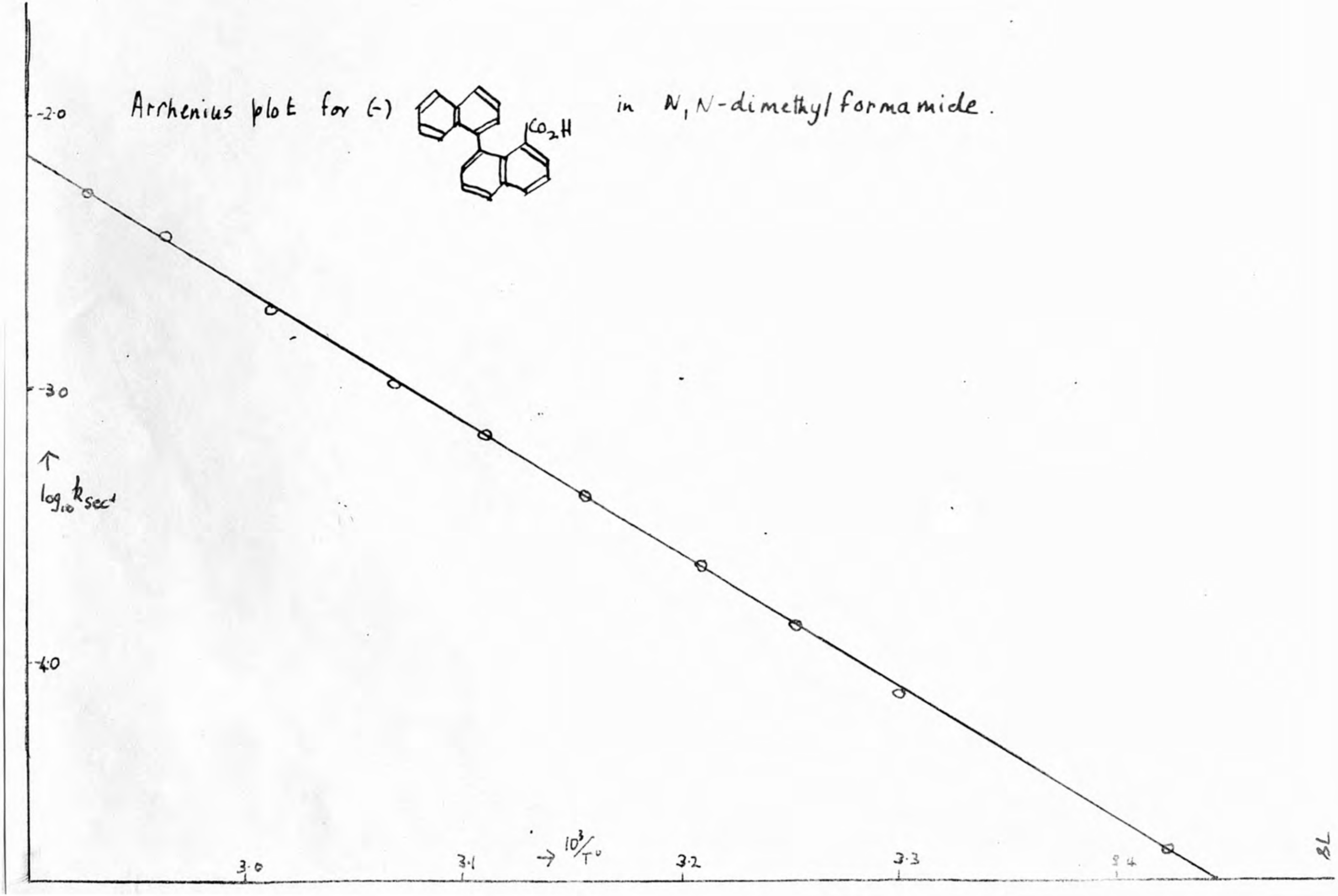
Racemisations of (−) in N,N-dimethylformamide

Determination of the Arrhenius constants A and E and the entropy of activation $\Delta S^{\ddagger}$

T^{o}	$10^{3}/T$	$10^{4}k_{sec}{}^{-1}$	$\log_{10}k_{sec}{}^{-1}$
292.1	3.4234851	0.204	$\bar{5}.3104$
303.2	3.298153	0.755	$\bar{5}.8781$
307.4	3.2530904	1.34	$\bar{4}.1287$
311.6	3.2092426	2.22	$\bar{4}.3455$
316.8	3.1565656	4.09	$\bar{4}.6119$
321.6	3.1094527	6.65	$\bar{4}.8228$
325.9	3.0685258	10.2	$\bar{3}.0107$
331.5	3.0165912	19.6	$\bar{3}.2934$
337.4	2.9638416	36.6	$\bar{3}.5639$
341.8	2.9256875	52.5	$\bar{3}.7199$
341.9	2.9248318	52.2	$\bar{3}.7176$

The best straight line taken graphically (see p. 78) gives:

$$E = 22.49 \text{ kcal.mole}^{-1}$$



Arrhenius plot for (-) in N,N-dimethylformamide.

Mean square calculation.

T°	y	x	xy	x^2
292.1	3.4234851	0.3104681	1.0628829	0.0963904
303.2	3.298153	0.8781867	2.8963941	0.7712119
307.4	3.2530904	1.1287126	3.6718041	1.2739921
311.6	3.2092426	1.3455404	4.3181656	1.8104789
316.8	3.1565656	1.6118921	5.0880431	2.5981961
321.6	3.1094527	1.8228425	5.6685243	3.3227548
325.9	3.0684258	2.0107281	6.1697699	4.0430275
331.5	3.0165912	2.2933803	6.9181908	5.2595932
337.4	2.9638416	2.5639389	7.5991088	6.5737827
341.8	2.9256875	2.7199392	7.9576921	7.3980692
341.9	2.9248318	2.7175698	7.9484345	7.3851856

$n = 11$ $\Sigma y = 34.3493673$ $\Sigma x = 19.4031987$

$\Sigma x^2 = 40.5326824$ $\Sigma xy = 59.2985102$

$\therefore b = -.20474068$

$\therefore E = 22.35$ kcal.mole^{-1}

From these two methods the average value of ΔE is 22.42 kcal.mole^{-1}

$\Delta S^{\ddagger} = -5.53$ e.u. $A = 10^{12.04}$ sec^{-1}

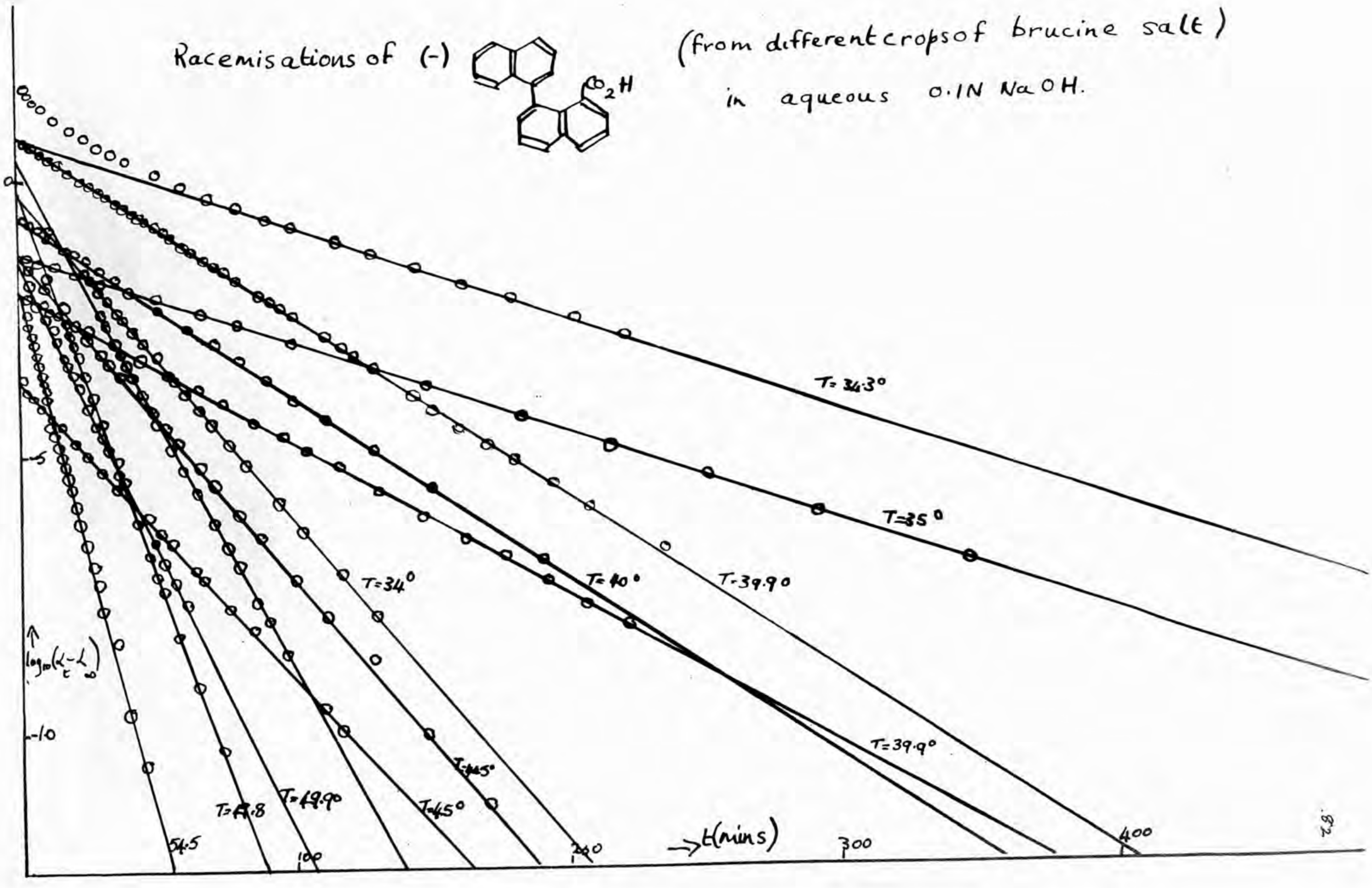
$\Delta F^{\ddagger} = 23.53$ Kcal. mole^{-1} $\Delta H^{\ddagger} = 21.8$ Kcal. mole^{-1}

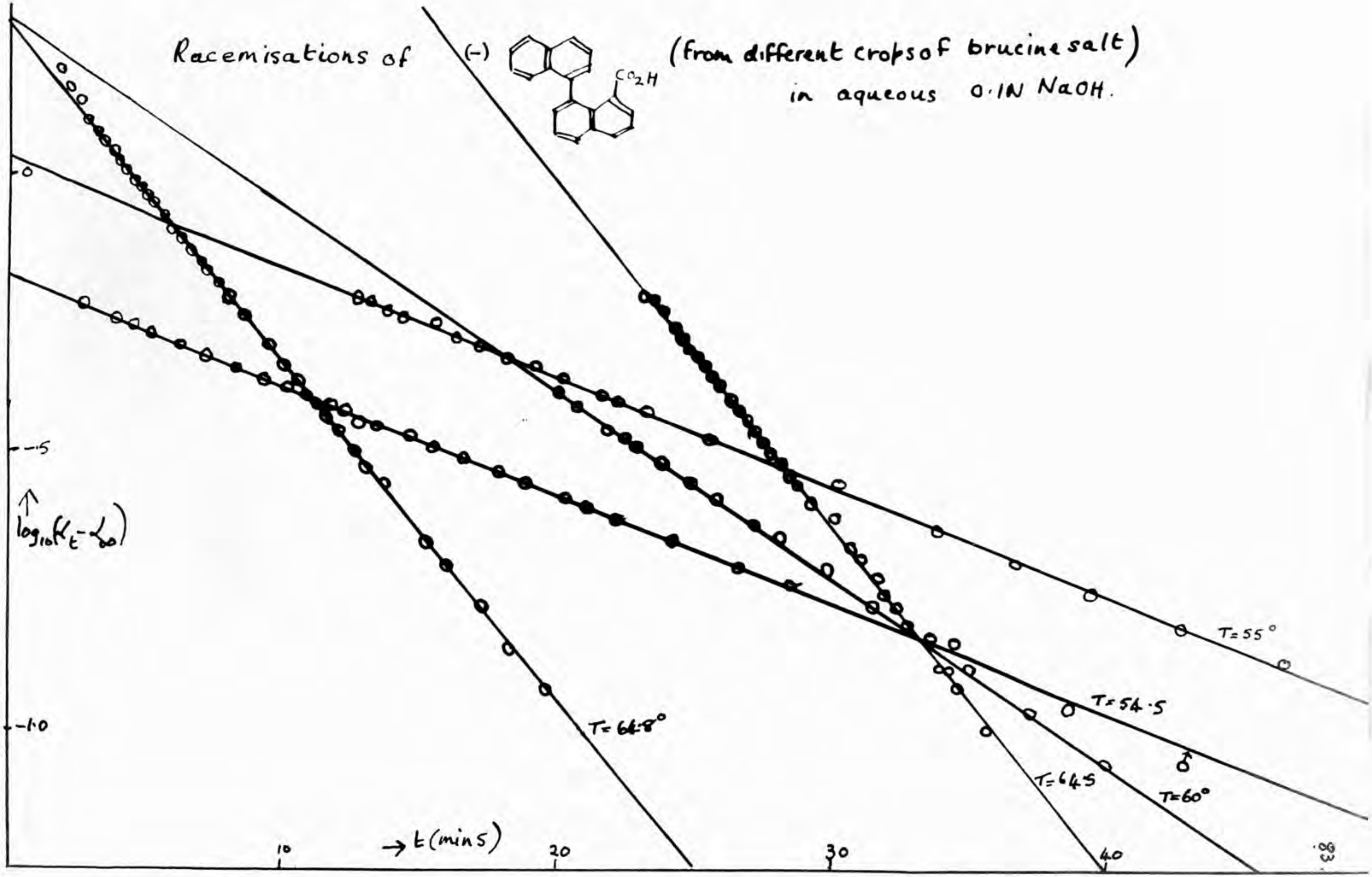
The half life period at 48.6° is 158 minutes.

Determination of rate coefficients for racemisation of 1,1'-binaphthyl-8-carboxylic acid in 0.1 N aqueous sodium hydroxide.

The results obtained in sodium hydroxide were not always reproducible. The polarimetric solutions were checked carefully to see no alkaloid remained in them, the temperature control was also checked and different methods of decomposing the alkaloidal salts were employed. Despite these precautions results were odd, sometimes showing deviations from the normal first order relationship, especially at lower temperatures. The results obtained are set out below.

Temperature in °C	Time of 1st reading in minutes	First reading	No. of readings	Time over which readings taken	$k_{\mathrm{sec}^{-1}}$
34.3	2	1.47°	25	256 mins	$6.561x10^{-5}$
34.5	2	1.26°	27	300 "	$5.805x10^{-5}$
35	4	0.74°	17	340 "	$6.294x10^{-5}$
39.8	2	1.21°	50	236 "	$2.018x10^{-4}$
39.9	4	0.60°	20	220 "	$1.936x10^{-4}$
40	3	0.86°	19	190 "	$1.3007x10^{-4}$
44.3	2	0.70°	24	190 "	$2.2617x10^{-4}$
44	12	0.83°	28	117 "	$2.367x10^{-4}$
45	2	0.44°	17	112 "	$2.1459x10^{-4}$
49.8	18	0.55°	18	55 "	$5.30 x10^{-4}$
49.9	22	0.70°	21	70 "	$3.670x10^{-4}$
49.9	2	0.69°	23	60 "	$4.129x10^{-4}$
54.5	2	0.59°	29	40 "	$7.463x10^{-4}$
55	13	0.60°	22	42 "	$7.622x10^{-4}$
60	20	0.41°	16	20 "	$1.298x10^{-3}$
64.5	23	0.61°	32	13 "	$2.104x10^{-3}$
65	2	0.59°	19	13 "	No zero reading obtained
64.8	2	1.54°	38	117 "	$2.340x10^{-3}$

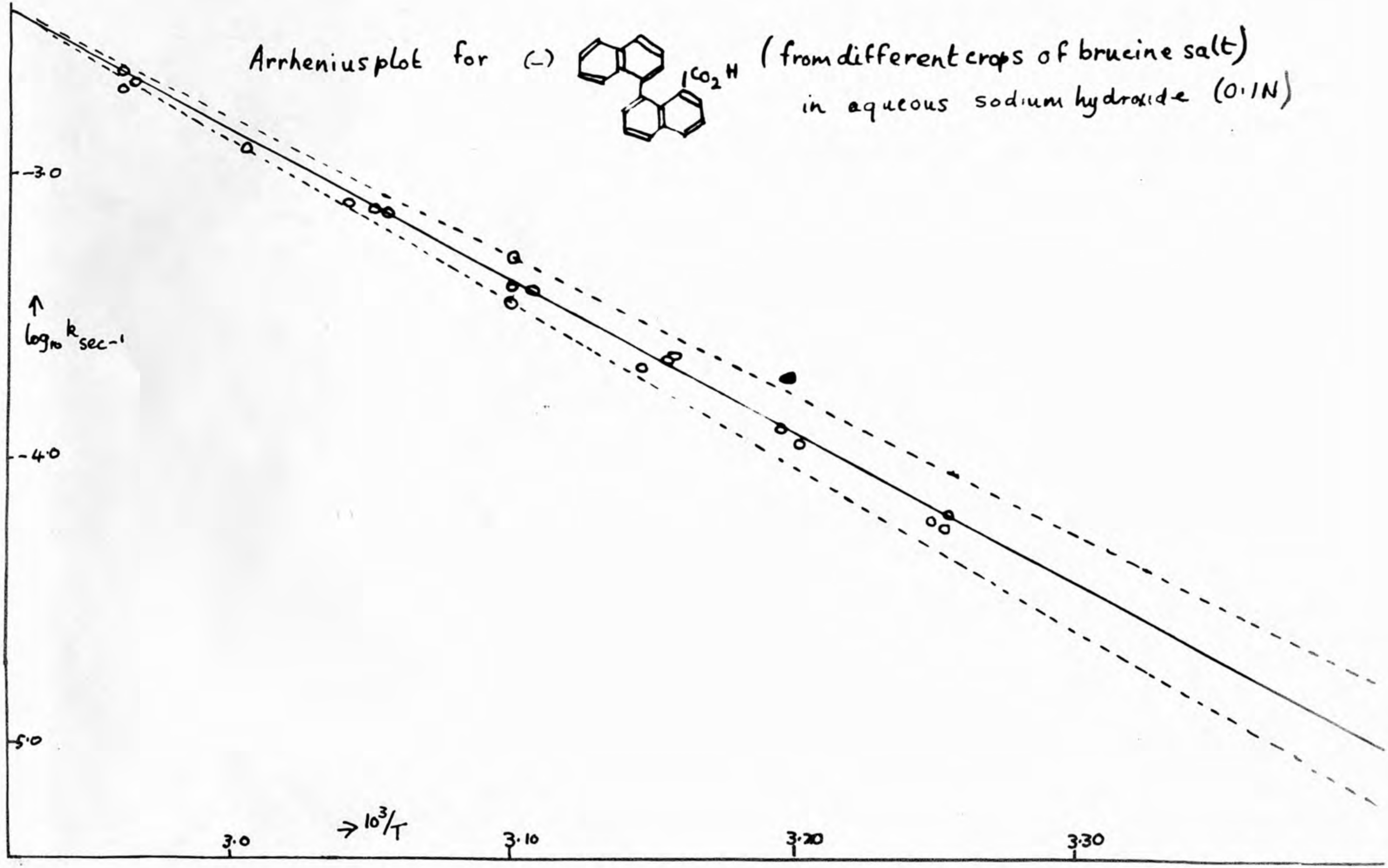

Racemisations of (-) (from different crops of brucine salt) in aqueous 0.1N NaOH.



Racemisations of (−) [structure] (from different crops of brucine salt) in aqueous 0·1N NaOH.

T^{o}	$10^3/T$	$10^4 k_{sec}^{-1}$	$\log_{10} k_{sec}^{-1}$
307.3	3.254	0.656	$\bar{5}.8170$
307.5	3.252	0.581	$\bar{5}.7638$
308	3.246	0.629	$\bar{5}.7989$
312.8	3.197	2.028	$\bar{4}.3050$
312.9	3.196	1.14	$\bar{4}.2869$
313	3.195	1.30	$\bar{4}.1142$
317.3	3.151	2.26	$\bar{4}.3544$
317	3.154	2.37	$\bar{4}.3742$
318	3.145	2.15	$\bar{4}.3316$
322.8	3.098	5.30	$\bar{4}.7247$
322.9	3.097	3.67	$\bar{4}.5647$
322.9	3.097	4.13	$\bar{4}.6158$
327.5	3.053	7.46	$\bar{4}.8729$
328	3.049	7.62	$\bar{4}.8819$
333	3.003	12.98	$\bar{3}.1070$
337.5	2.963	21.0	$\bar{3}.3230$
337.8	2.960	23.4	$\bar{3}.3692$

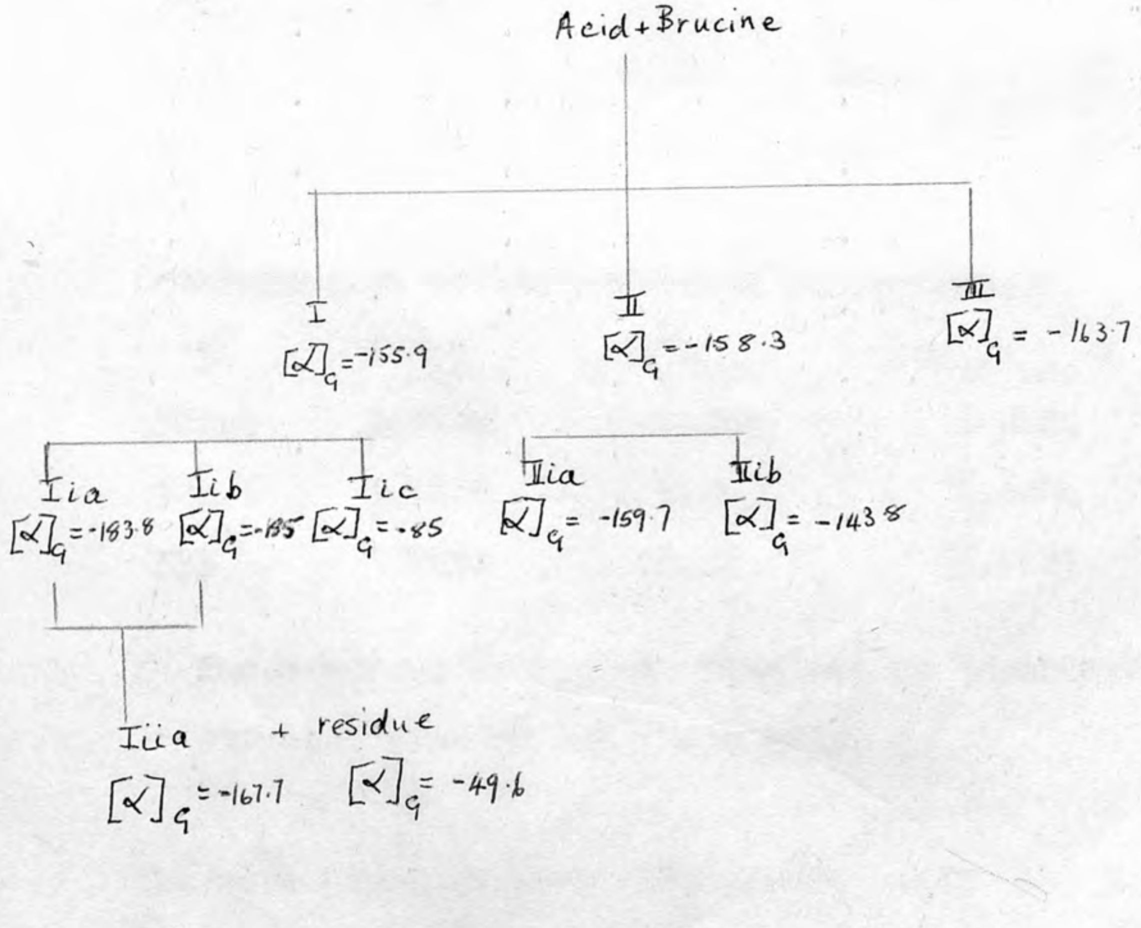
The average value of ΔE from these results is about 24 Kcal. mole^{-1}. (see graph p. 85)



Arrheniusplot for (–) (from different crops of brucine salt) in aqueous sodium hydroxide (0·1N)

It was noted from these results that the size of rotation obtained, using approximately equal weights of acid, varied a great deal. The Arrhenius plot was also very poor and no really good straight line could be drawn through all the points.

It was therefore decided to make a closer examination of the brucine salt. To obtain a pure sample of brucine salt it was decided to recrystallize it until a constant specific rotation was obtained. The following table shows the result.



The specific rotation changed on each crystallisation and was not due to increasing purity as the rotation did not increase consistently in any direction. It was thought that the differences might indicate a crystallisation of different (-) forms of this salt. Some measurements were made using acid from one crop of the brucine salt (IIia) $[\alpha]_G = -159.7$.

These rate coefficients are set out below.

Temperature in °C	Time of 1st reading	First reading	No. of readings	Time over which readings taken	$10^4 k_{sec}^{-1}$ *
39.5	4 mins.	0.61°	30	216 mins.	1.169
49.1	4 "	0.58°	24	62 "	4.057
60	4 "	0.54°	33	21 "	12.89

Determination of the Arrhenius parameters.

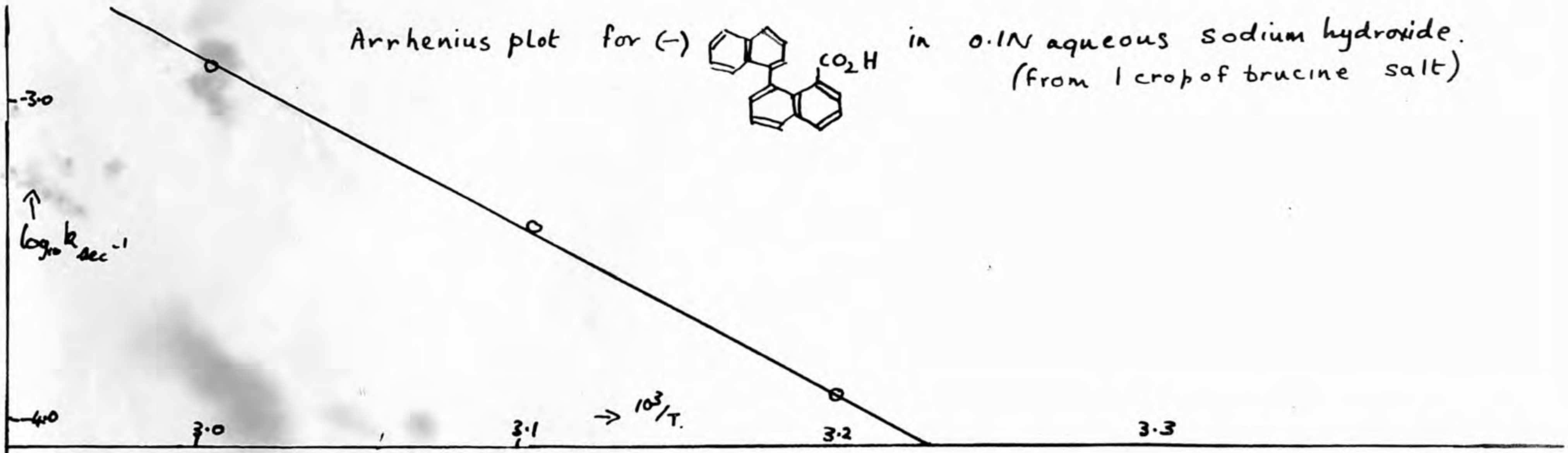
T°	$10^3/T$	$10^4 k_{sec}$	$\log_{10} k_{sec}^{-1}$ *
312.5	3.2000	1.169	$\bar{4}.0682$
322.1	3.1046	4.057	$\bar{4}.6084$
333	3.0030	12.89	$\bar{3}.1103$

* These values of k_{sec}^{-1} obtained by considering the straight part of the graph only.

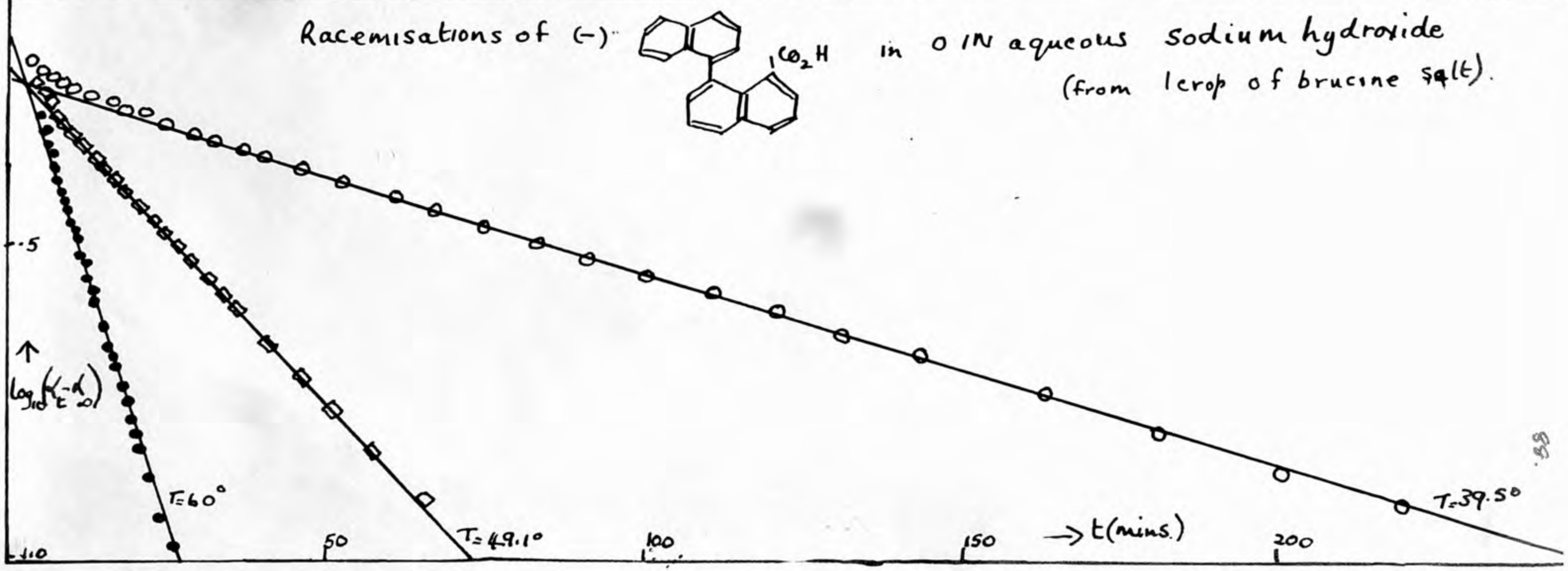
The best straight line taken graphically (see p. 88) gives:

$$\Delta E = 24.72 \text{ kcal.mole}^{-1}$$

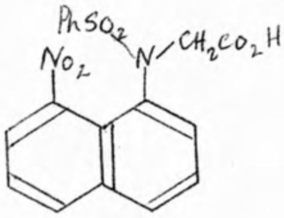
$$\Delta S^{\ddagger} = +0.4 \text{ e.u.} \qquad A = 10^{13.35} \text{ sec}^{-1}.$$



Arrhenius plot for (−) [structure] in 0.1N aqueous sodium hydroxide.
(from 1 crop of brucine salt)



Racemisations of (−) [structure] in 0.1N aqueous sodium hydroxide
(from 1 crop of brucine salt).



Benzene sulphonyl-8-nitro-1-naphthyl-glycine.

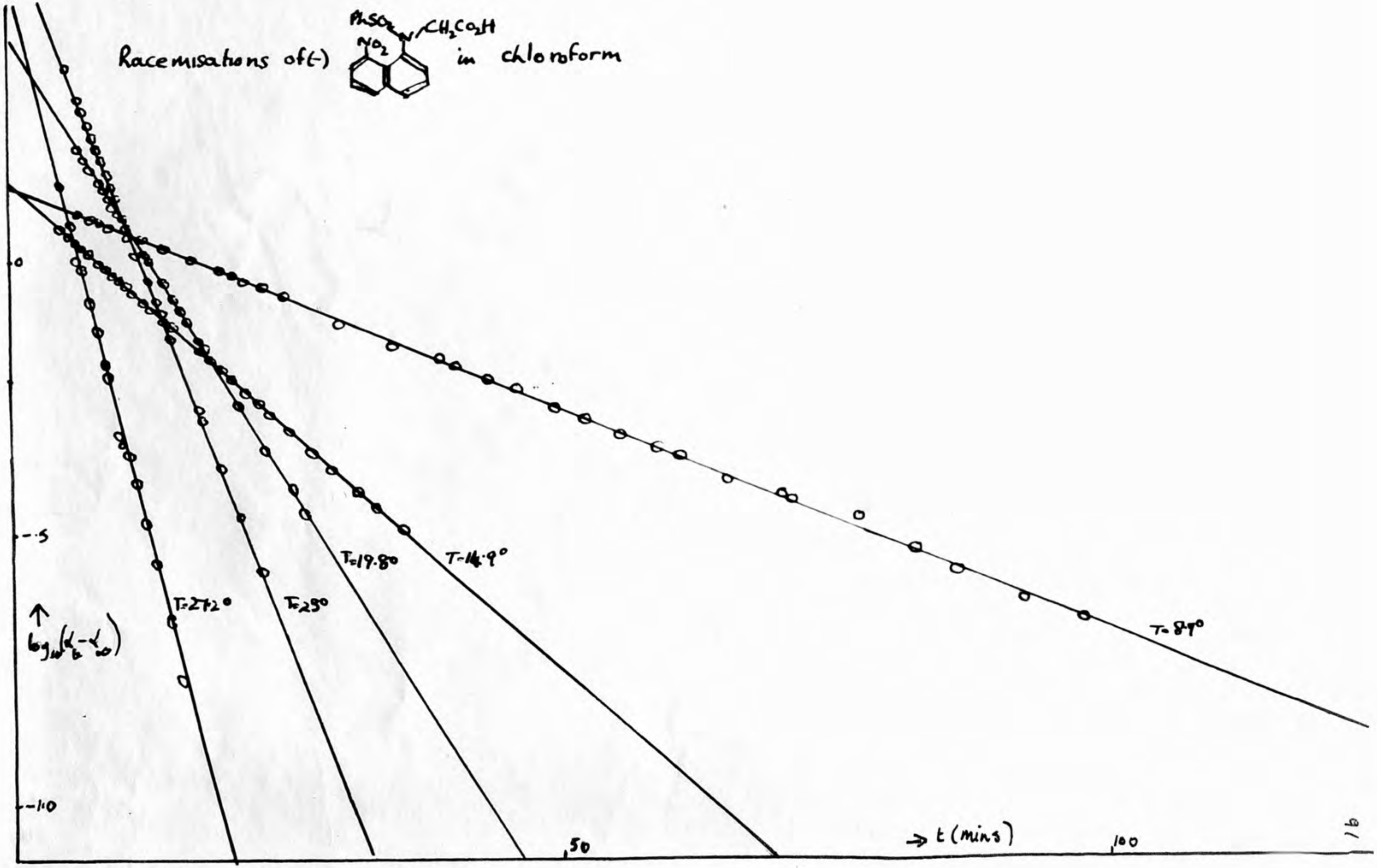
Resolution [Mills and Elliot, J., 1928, 1291]

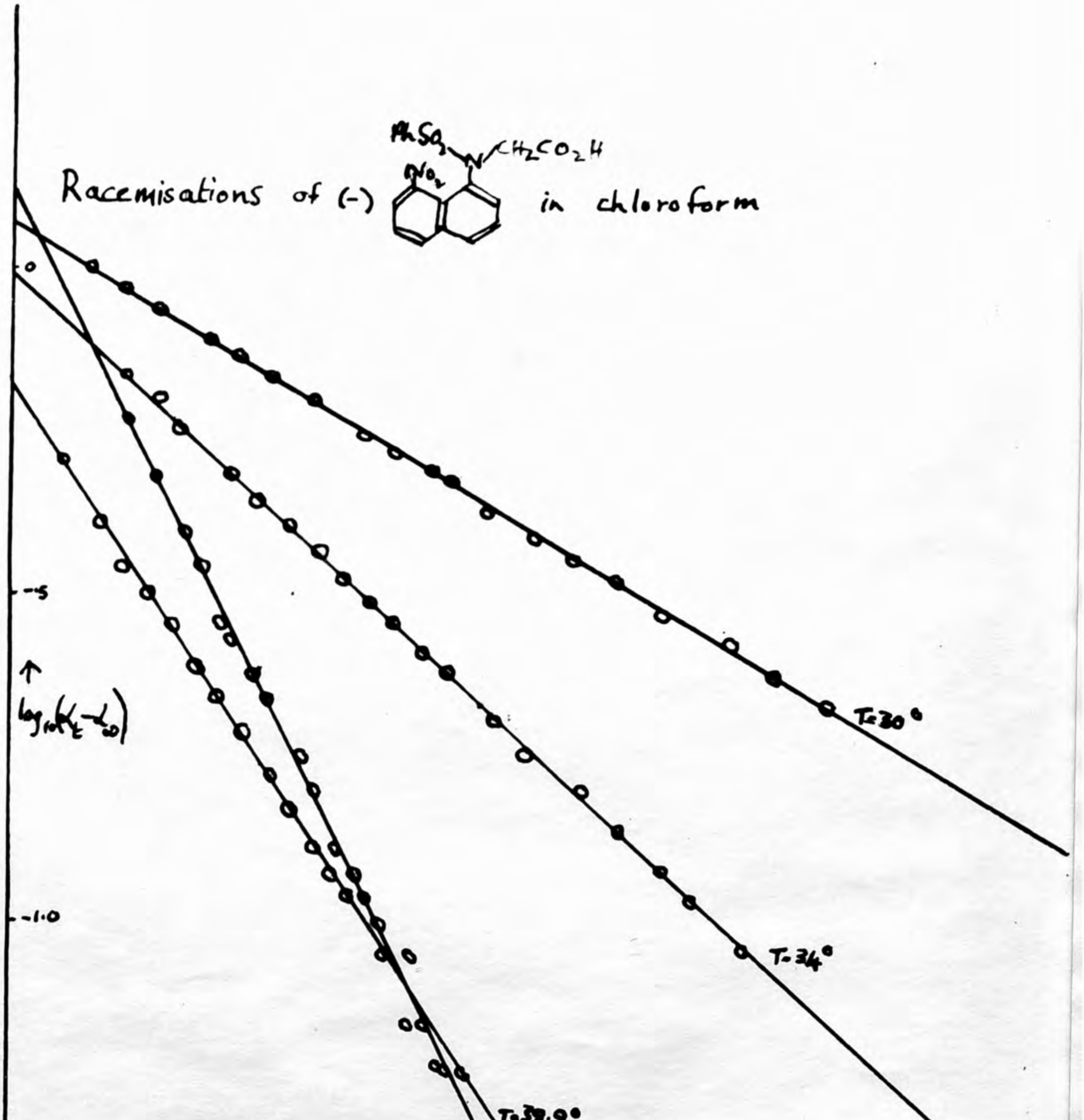
The acid (2g., 1M) was dissolved in a little acetone and mixed with a solution of anhydrous brucine (2g., 1M) also in acetone. The salt (3.3g., 83%) which formed was finely crystalline, m.p. 190 bubbling until 196° [Mills and Elliot, (loc.cit.) reported m.p. 195-6°].

The racemisations were carried out in Solvent X. The brucine salt was dissolved in Solvent X and the solution was then washed twice with dilute sulphuric acid. This washing probably removed any ethanol from the chloroform solution so the point of using a standard solution was somewhat lost. The chloroform solution was filtered directly into the polarimeter tube and readings begun as soon as possible.

Determination of rate coefficients of racemisation of benzene sulphonyl-8-nitro-1-naphthyl-glycine in chloroform.

Temperature in °C	Time of 1st reading in minutes	First reading	No. of readings	Time during which readings taken	$10^3k_{sec}^{-1}$
8.9	6	(−)1.24°	30	100 mins.	0.319
14.9	5	(−)1.14°	35	40 "	0.739
19.5	6	(−)1.59°	25	20 "	1.25
23	5	(−)2.27°	22	20 "	2.01
27.2	5	(−)1.36°	17	10 "	3.09
30	5	(−)1.01°	18	6 "	4.43
34	5	(−)0.69°	20	5 "	6.92
38.9	4	(−)0.51°	17	3 "	11.0
41.8	5	(−)0.59°	19	3 "	15.0


Racemisations of (-)
PhSO₂
N
CH₂CO₂H
NO₂
in chloroform
0
-.5
-1.0
↑ log₁₀(α_t - α_∞)
50
100
→ t (mins)
T=27.2°
T=25°
T=19.8°
T-14.9°
T-8.9°

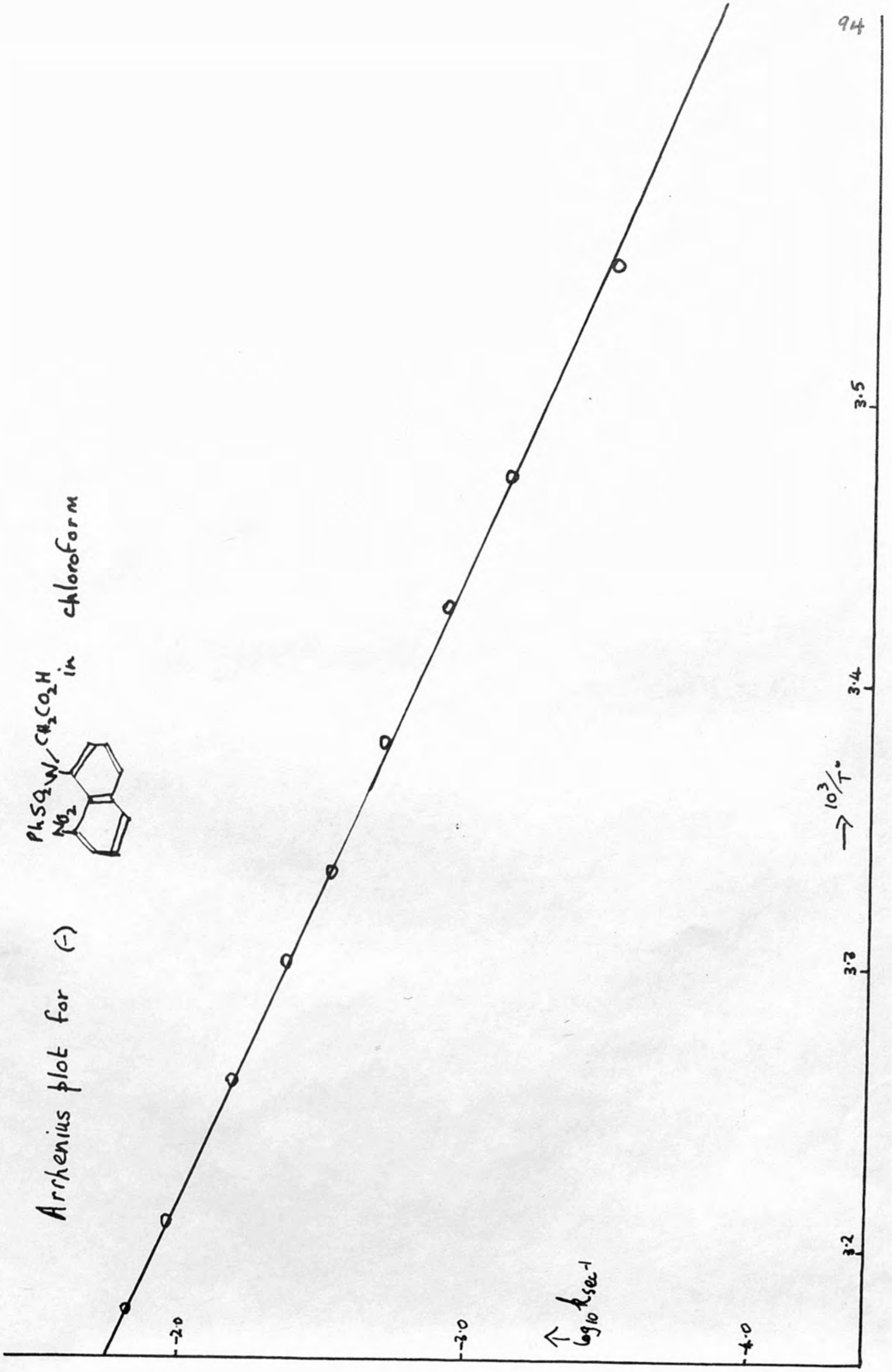

Racemisations of (-)
PhSO2
N
CH2CO2H
NO2
in chloroform
-.5
-1.0
↑ log10(αt - α∞)
→ t (mins.)
5
6
7
8
9
10
11
T=30°
T=34°
T=38.9°
T=41.8°

Determination of the Arrhenius parameters A and ΔE and the entropy of activation $\Delta S^{\ddagger}$

T^o	$10^3/T$	$10^3 k_{sec^{-1}}$	$\log_{10} k_{sec^{-1}}$
281.9	3.548	0.319	$\bar{4}.5042$
287.9	3.473	0.739	$\bar{4}.8690$
292.5	3.425	1.25	$\bar{3}.0950$
296	3.378	2.01	$\bar{3}.3027$
300.2	3.331	3.09	$\bar{3}.4894$
303	3.300	4.43	$\bar{3}.6460$
307	3.251	6.92	$\bar{3}.8399$
311.9	3.207	10.9	$\bar{2}.0407$
314.8	3.177	14.9	$\bar{2}.1755$

The best straight line taken graphically (see p. 94) gives:

$$\Delta E = 20.37 \text{ kcal.mole}^{-1}$$



Arrhenius plot for (-) in chloroform

Mean square calculation:

T	y	x	xy	x^2
281.9	3.547357	1.50379	5.334479	2.261384
287.9	3.473428	1.86904	6.491975	3.493310
292.5	3.418803	2.09500	7.162392	4.389025
396	3.378378	2.2984	7.746080	5.257115
300.2	3.3311125	2.48926	8.292036	6.196415
303	3.300330	2.64673	8.735082	7.005179
307	3.257328	2.84010	9.251137	8.066168
311.9	3.206155	3.04080	9.749276	9.246467
314.8	3.176620	3.17459	10.084466	10.078021

$n = 9$ $\Sigma y = 30.089520$ $\Sigma x = 21.952150$

$\Sigma xy = 72.846923$ $\Sigma x^2 = 55.993084$

$$b = \frac{-4.907349}{22.040867}$$

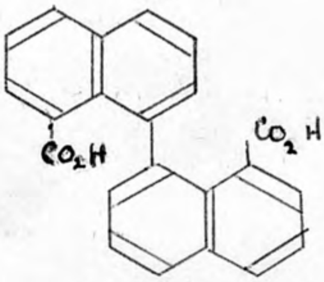
$$\Delta E = 20.56 \text{ kcal.mole}^{-1}$$

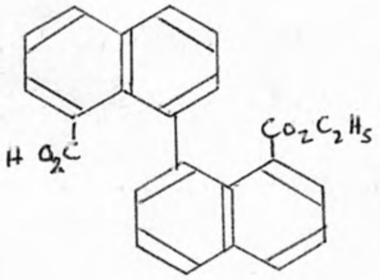
The average value of ΔE is taken as 20.46 kcal.mole^{-1}

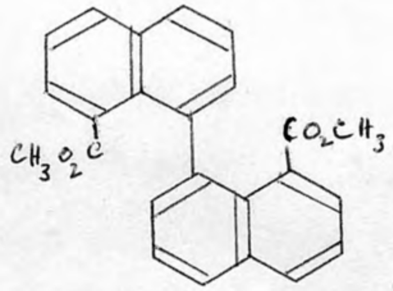
$$A = 10^{12.39} \text{ sec}^{-1} \qquad \Delta S^{\ddagger} = -3.8 \text{ e.u.}$$

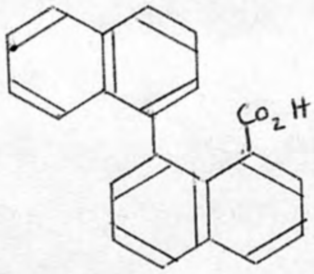
DISCUSSION.

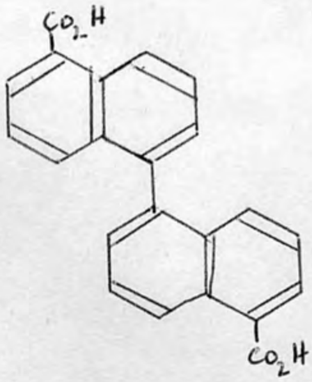
During the work described in this thesis, the following acids and esters have been synthesised, obtained optically active and their rates of racemisation determined:-

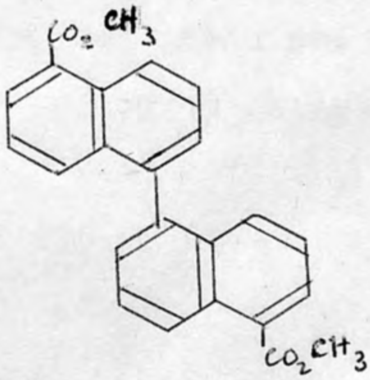


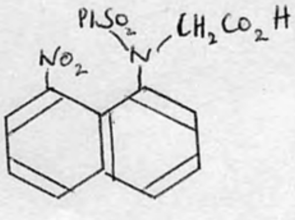












Binaphthyls.

The results obtained in this work are tabulated below:-

Solvent: N,N-dimethylformamide.

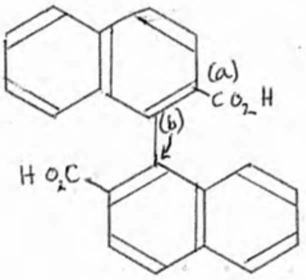
Binaphthyl	ΔE kcal. mole^{-1}	A sec^{-1}	$\Delta F^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$t_{\frac{1}{2}}$ at 50^{0} in mins.
8,CO_2H ; 8', CO_2H	22.1	$10^{11.3}$	24.5	21.4	-9.1	86.1
8,CO_2H; 8', CO_2Et	21.6	$10^{11.4}$	23.7	20.9	-8.4	17.2
8,CO_2CH_3;8',CO_2CH_3	22.0	$10^{11.6}$	23.9	21.4	-7.54	22.7
5,CO_2H; 5',CO_2H	24.1	$10^{12.3}$	24.9	23.5	-4.48	271.5
5,CO_2CH3;5',CO_2CH_3	23.8	$10^{12.2}$	24.8	23.1	-5.09	111.9
8, CO_2H	22.4	$10^{12.0}$	23.5	21.8	-5.5	158
Solvent: 0.1N NaOH.						
8,CO_2H; 8',CO_2H	26.01	$10^{15.2}$	22.7	25.4	+9.2	2.3
8,CO_2H; 8',CO_2Et	25.7	$10^{14.0}$	24.4	25.0	+3.18	32.6
5,CO_2H; 5', CO_2H	24.9	$10^{12.9}$	24.7	24.2	-1.54	94.2
8, CO_2H						

The values of $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ given in this table are average ones taken over the whole temperature range employed.

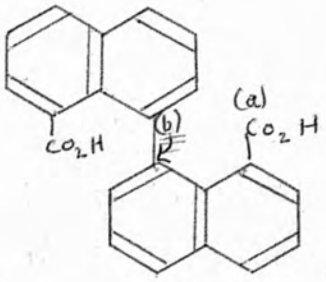
If the ΔE values for the free acids (i.e. those values taken in dimethylformamide) are examined it will be seen that those for the 8,8'-acid and its esters are about 22 kcal.mole^{-1} whilst those of the 5,5'-acid and its ester are about 24 kcal.mole^{-1}. These ΔE values fall in with the order of optical stability obtained by half life periods, i.e. 5,5'-acid > 8,8'-acid. The ΔE values for the acids and their respective esters are very close, and this is what one would expect. The results obtained in sodium hydroxide are, of course, for the dicarboxylate ion. In general the ΔE is larger in sodium hydroxide than in dimethylformamide, substantially larger in the 8,8'-substituted compounds, although the racemisations are in all cases quicker. The order of stability is the same in sodium hydroxide as in dimethylformamide, using half life periods as the criteria as, in sodium hydroxide, the ΔE for 8,8'-acid is larger than that of the 5,5'-acid.

Study of models.

The 1,1'-binaphthyl-8,8'-dicarboxylic acid could not even be made using Leybold models which show the van der Waals envelope. When the $-CO_2H$ group was put in the 8 position the model fell apart. It could, however, be made using the Bedford College scale models in which 14/15" represents 1 Å and no van der Waals envelope is included. These will be called classical models in this discussion.



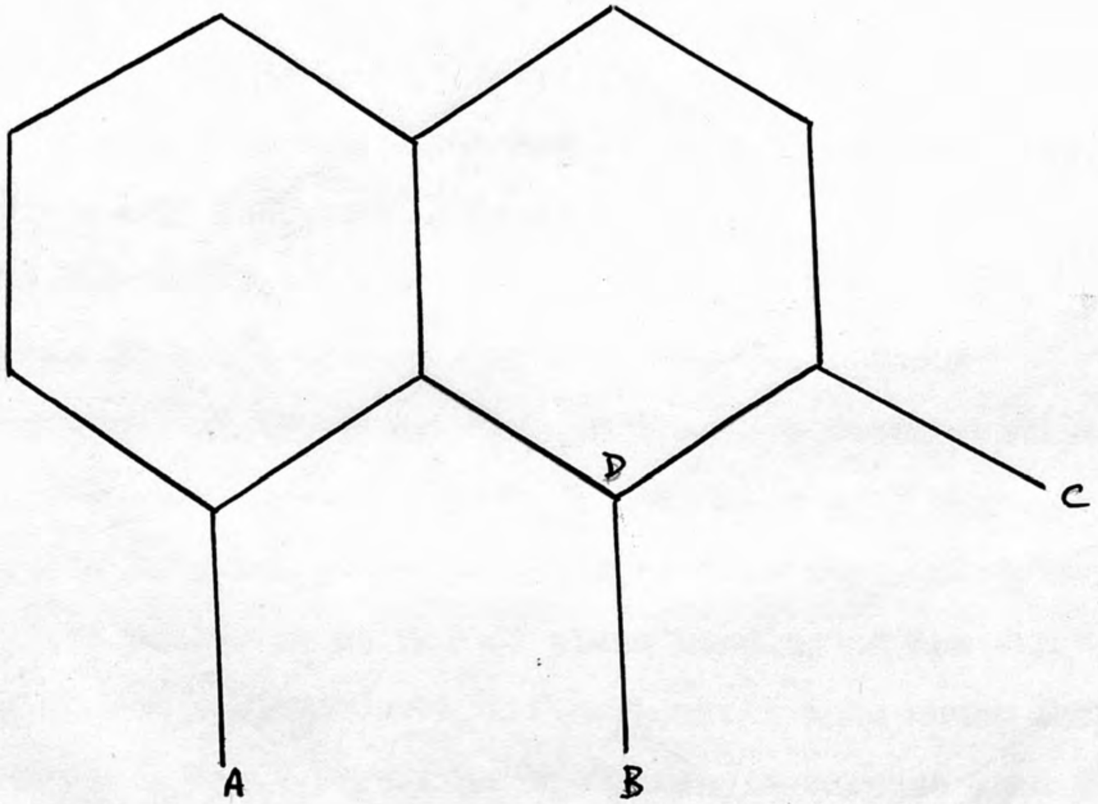
(1)



(2)

Using classical models, attempts were made to see the differences between acid (2) and the geometrically similar acid (1). Several small differences were noted, such as the ability of the carboxyl groups of acid (1) to form hydrogen bonds internally, or each to be coplanar with and conjugated with the naphthalene ring to which it is attached. The acid (2) cannot do either of these things. The major difference, however, was in the distance apart of the carbon atoms $C_{(a)}$ and $C_{(b)}$. In acid (1) the $C_{(a)}-C_{(b)}$ distance was 2.9 Å whilst in acid (2) the $C_{(a)}-C_{(b)}$ distance was 2.4 Å. Using the available data on bond lengths and angles for naphthalene a scale diagram can be constructed to show this.

Diagram constructed using the bond lengths and angles given by Trotter for 1- naphthoic acid (loc. cit)
Interannular bond DB taken as 1·5 Å.



Scale
2 c.m. ≡ 1 Å

AB = 4·9 c.m. ≡ 2·45 Å

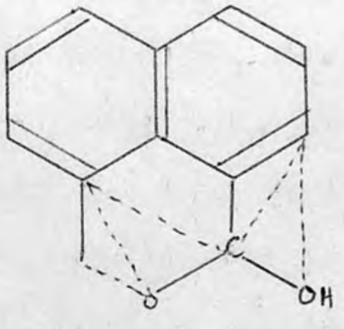
BC = 5·8c.m. ≡ 2·9 Å

Deformation as a consequence of strain in peri-substituted binaphthyls.

In a review by Harnik, Herbstein, Schmidt and Hirschfield (*J.*, 1954, 3288) it is said "Overcrowding begins when the unperturbed structures bring the C-atoms (aliphatic or aromatic) to within 3 Å. When there is overcrowding it tends to find relief principally in an out of plane distortion which tends to be spread over the whole molecule rather than by the stretching of particular bonds." 1,1'-binaphthyl-8,8'-dicarboxylic acid has two C - C distances of 2.4 Å which thus comprise two serious compressions and there are also smaller C - O compressions. It is concluded therefore that this acid, and of necessity its esters too, are intra-molecular overcrowded molecules which find relief by an out of plane bending of the $-CO_2H$ groups. The 1,1'-binaphthyl-8-carboxylic acid comes into this category too. There is no reason to suppose that the 1,1'-binaphthyl-2,2'-dicarboxylic acid or the 1,1'-binaphthyl-5,5'-carboxylic acid are intramolecular overcrowded compounds and thuse these compounds should behave normally, which is what is observed.

There is evidence of this kind of out of plane bending in substituted naphthalene compounds especially those substituted in the peri- (or 1,8) positions. Donaldson and Robertson (J., 1953, 17) studied the crystal structure of octamethyl naphthalene by X-ray crystallography and found an out of plane distortion of the α-methyl group of 0.73 Å which means that the α-methyl group is bent at an angle of 29° to the "plane" of the naphthalene. They also found distortions of 0.38Å from the plane of the β- and other methyl groups which means they are inclined to an angle of 15° to the plane. Adjacent methyl groups are found to be displaced in the opposite direction to each other, thus in octamethylnaphthalene the methyl groups are displaced up and down from the plane all round the molecule but the greatest effect is at the 1,8-positions.

If such out-of-plane distortions are to be found in these naphthalene compounds it is certain that distortions in-the-plane will exist too and this has been recently demonstrated by Trotter (Acta.Cryst., 1960, 13, 732) working on the crystal structure of 1-naphthoic acid.

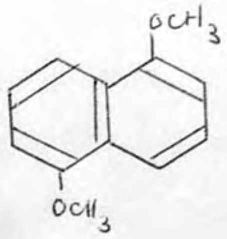


------- overcrowded distances.

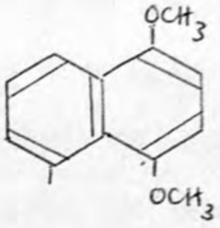
As the diagram shows there are two important C - C compressions as well as C - O and H - O compressions which find relief partly by the twisting of the carboxyl group at an angle of 11° to the naphthalene, and partly by an in plane distortion of the $C_{aromatic}$ - $C_{aliphatic}$ bond away from the peri-positions. In plane distortions cannot, however, be taken up by the whole system in the same way so as to spread the strain and they would therefore be expected to be smaller.

Everard and Sutton (J., 1949, 2312) made some interesting dipole moment measurements on some substituted naphthalenes.

I



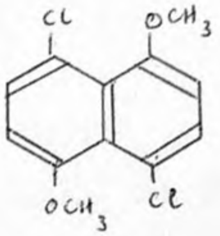
II



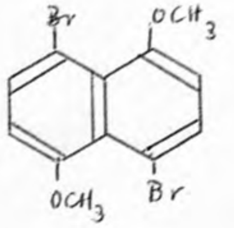
III

The value of 1.73 D for I is assumed to result from the free rotation of the $-OCH_3$ group taking all configurations from cis to trans with equal probability. In II the value of 0.67 indicates the free rotation is much reduced because of the steric effect of the peri hydrogen and the effect of resonance giving a π-bond between the 6_{aryl}-O. Thus it is supposed the $-OCH_3$ groups must lie trans to each other.

The dipole moment of III was measured to test this hypothesis and was found to be 2.09D which was lower than the calculated figure of 2.45. This was said to indicate that the groups cannot be quite coplanar.



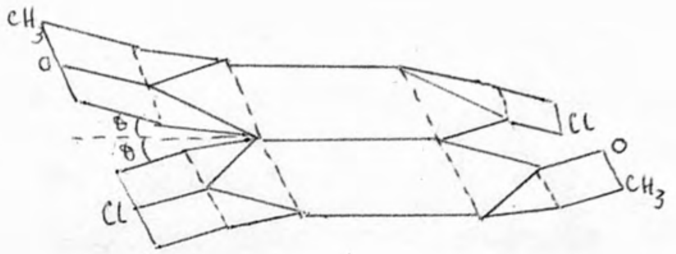
IV



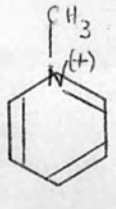
V

In compounds IV and V one would expect the halogen dipoles to cancel and the resultant moment to be that of the parent substance~~s~~ II ~~and III~~ but in fact their dipole moments are 0.95 and 0.93 respectively. Scale diagrams indicate considerable interference between the halogens and the oxygen in IV and V and this strain can be relieved by movement of the substituents in two directions, one in the plane and one out of the plane. The former would not explain the observed moment but an out of plane bending could given an unsymmetrical configuration which would possess a dipole. They calculated the angle of deflection from the plane to be 18° and the theoretical moment to be about 1, which is very close to the observed value.

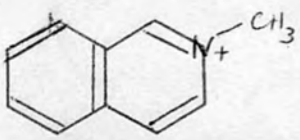
Diagram from Everard and Sutton's paper.



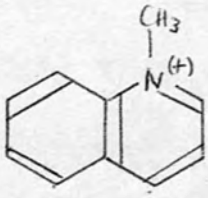
Packer, Vaughan and Wong (J.A.C.S., 1958, 80, 905) attempted to estimate the strain in such compounds by comparing the heats of activation of a series of bases reacting with methyl iodide. The processes were followed by conductivity measurements.



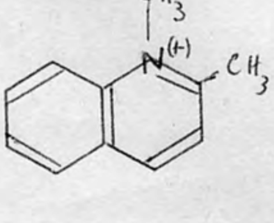
I



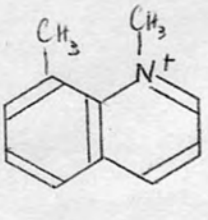
II



III



IV



V

Their results are given in a table set out below. The change in A, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is recorded with respect to the pyridine.

Base	10^5 k (at 30°)	$\Delta \log A$	$\Delta\Delta H^{\ddagger}$	$T\Delta\Delta S^{\ddagger}$
pyridine	50.7	0.00	0.00	0.00
isoquinoline	60	0.03	-0.14	0.04
quinoline	8.0	0.0	1.11	0.00
2-Me-quinoline	0.677	-0.19	2.34	-0.26
8-Me-quinoline	0.0087	-0.06	5.12	-0.08

As the main changes occur in $\Delta\Delta H^{\ddagger}$ this is the main thing to be considered. $\Delta\Delta H^{\ddagger}$ is taken as a quantitative measure of the steric strain in the transition state of the reaction. It can be seen, as might be expected, that $\Delta\Delta H^{\ddagger}$ is biggest in compounds IV and V, the greatest strain being observed in V where both peri-positions are involved. Following some calculations by Brown (J., 1956, 1248) they say that the strain in the corresponding methyl naphthalenes must be even greater and quote a figure of 7.6 kcal.mole^{-1} as the kind of value one would expect for the strain in 1,8-dimethylnaphthalene.

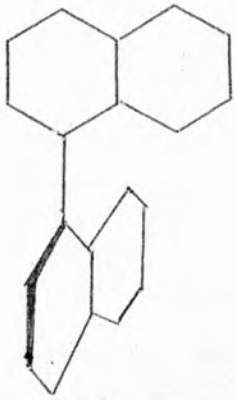
A lot of this evidence, it is true, is given for the solid state. There is, however, no reason to suppose that substituted naphthalenes are any less deformable in solution than in the solid state. In fact it is likely that, in solution when the restricting forces of the crystal lattice are removed, these substituted naphthalenes are even more distorted. Diphenyl, for example, is known to be more twisted in solution than in the solid state.

If the strain in 1,1'-binaphthyl-8,8'-dicarboxylic is relieved by the kind of out of plane bending which exists in octamethyl naphthalene then its structure can be made up from two possible enantiomeric substituted naphthalene units.

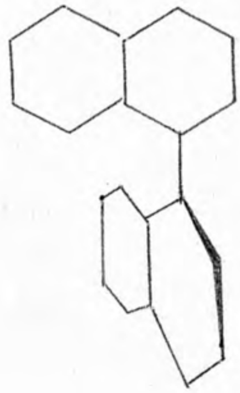

(−)


(+)

When these units are combined there results three possible structures (+)(+), (−)(−) or (+)(−). Each of these structures has an optical isomer corresponding with the *R* and *S* structures of 1,1'-binaphthyl itself.



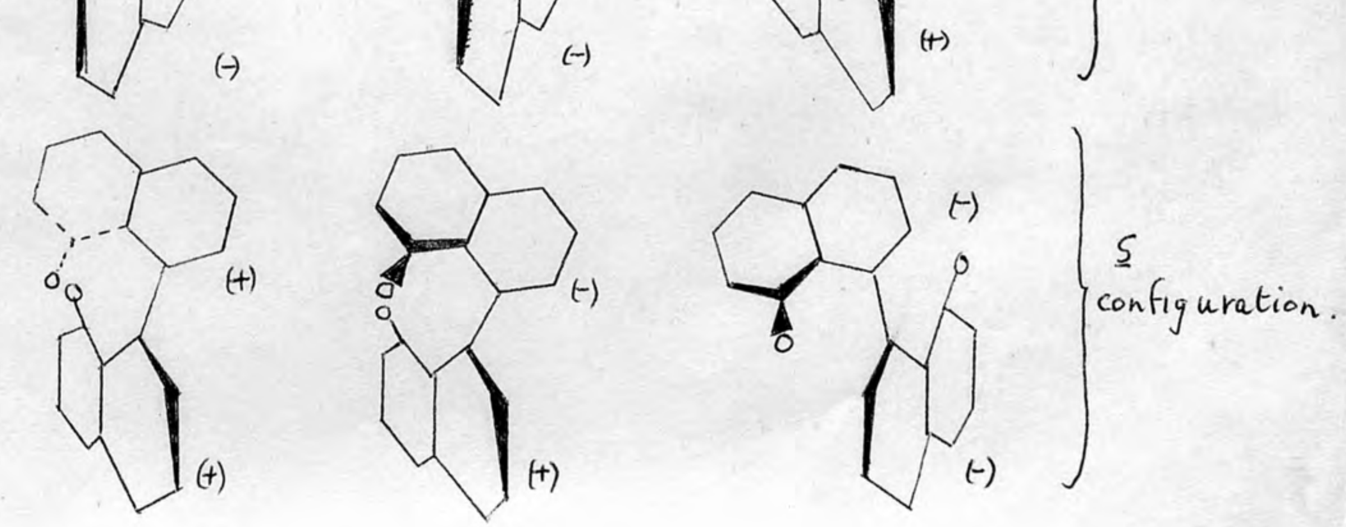
R



S

(This nomenclature introduced by Cahn, Ingold and Prelog in Experientia, 1956, **12**, 8, and applied to biphenyls and related structures by Mislow et al.)

The forms for the 1,1'-binaphthyl-8,8'-dicarboxylic acid are:



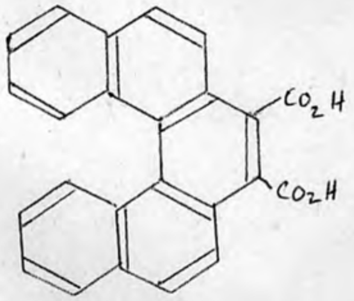
Inversion of each unit [$(+) \rightarrow (-)$, $(-) \rightarrow (+)$] can take place within the framework of each *R* or *S* configuration. There are no significant drifts in the first-order velocity coefficients for racemisation although a deliberate effort has been made to look for deviations. For the 1,1'-binaphthyl-8,8'-dicarboxylic acid measurements of the velocity coefficient were made over a wide temperature range $(14^\circ - 90^\circ)$. The Arrhenius plot so obtained showed very slight deviations at low temperatures (see p. 33 for graph). These deviations are what might be expected over a wide temperature range if E were slightly temperature dependent. (Moelwyn Hughes. Kinetics of Reactions in Solution. Oxford Clarenden Press, 1947, p.56). If these deviations are not significant then it is only the *R* $\rightleftharpoons$ *S* process which is under observation in the polarimeter, the conformational changes in the individual units being too fast to be detectable at the temperature used.

If the deviations are not due to this cause, then they are probably due to the conformational distortions: however, further evidence would be necessary before such an assumption could be made. It should be possible, for example, to design molecules in which the conformational changes would be slower.

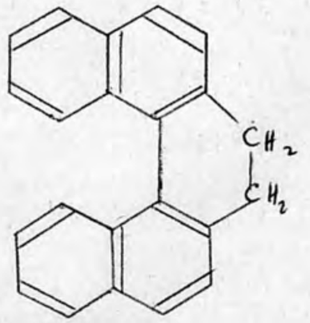
Whichever one of the forms one takes, it is clear that, now the carboxyl groups are bent out of the "planes", they can pass the relevant hydrogen atoms much more easily in the transition state. This would explain the unexpected ease of racemisation. The strain energy required in bending the groups out of the plane has helped to make it easier for the molecule to racemise and therefore the energy barrier for racemisation will be reduced by the strain energy which is why the measured ΔE for 1,1'-binaphthyl-8,8'-dicarboxylic acid is so small.

If one takes Packer, Vaughan and Wong's estimate of 7.6 kcal.mole^{-1} as the strain in 1,8-dimethylnaphthalene, the steric strain in the 8,8'-acid should be, very approximately, at least twice as much, i.e. 15 kcal.mole^{-1}. If this 15 kcal. is added to the value for ΔE measured in dimethylformamide one arrived at a value of 37 kcal.mole^{-1} for ΔE which is what would be expected for an optically stable compound and such a compound should not racemise at all easily. This large value for ΔE fits in with what one would expect for 1,1'-binaphthyl-8,8'-dicarboxylic acid if it is not distorted in any way. In fact this picture of a deformed molecule explains very adequately some of the puzzling features of this acid.

There is some evidence that intramolecular overcrowded compounds, in general, have lower optical stability than one would expect and thus have small ΔE factors. Very few accurate measurements have been made on this type of compound with this idea in mind and so the evidence is not substantial, but it undoubtedly is there in a qualitative sense. A well known example of an overcrowded compound is 3,4,5,6,- dibenzphenanthrene-9,10-dicarboxylic acid (VI) prepared by Bell and Waring (J., 1949, 2689). The morphine salt of this acid was reported to mutarotate rapidly in chloroform at room temperature and so the active acid was never isolated there can however be no doubt about its instability. Hall and Turner (J., 1955, 1242) prepared optically active 9,10-dihydrobenzphenanthrene(VII), which is a structurally similar compound to (VI) but is not an overcrowded compound and which racemised slowly in benzene at 100° in a sealed tube. This demonstrates very clearly the difference in stability overcrowding makes.

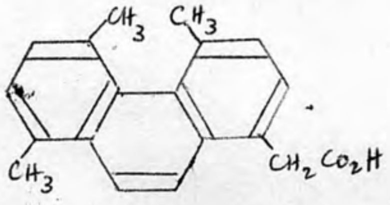


VI

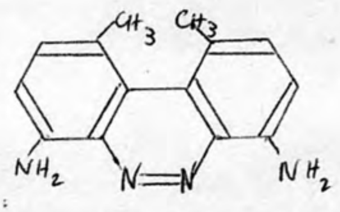


VII

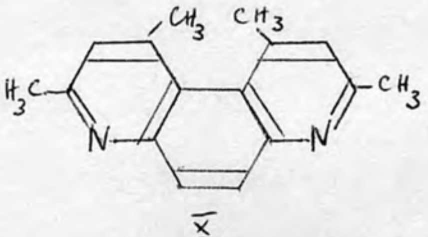
Another well known example of intramolecular overcrowding is 4,5,8-trimethylphenanthryl acetic acid (VIII) prepared by Newmann and Hussey (J.A.C.S., 1947, 69, 3023) which is said to racemise fairly rapidly in chloroform at room temperature. There is also 4,7-diamino-1,10-dimethylbenzocinnolin (IX) prepared and resolved by Theilacker and Boxmann (*Annalen*, 1953, *581*, 117) which must be overcrowded and of which the authors say it racemised quickly in boiling methyl alcohol. In a recent paper Theilacker (*Ber.*, 1959, *92*, 2293) mentioned a compound (X) prepared and resolved by F. Wegner (Dissertat, Tech.Hochshule, Hanover, 1956) which is reported to have a ΔE of 15.9 kcal.mole^{-1}. Theilacker thought this unusually low but perhaps this also is an effect of the overcrowding.



VIII

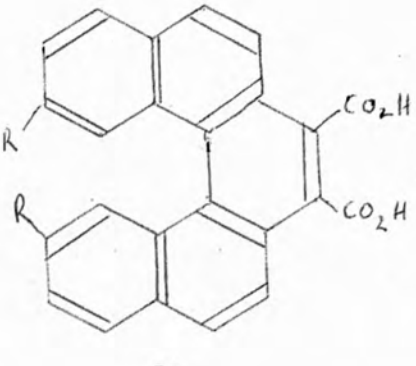


IX



X

There are a number of substituted 3,4,5,6-dibenzphenanthrenes like XI which have been prepared by Bell and Waring, R = CH_3 (*J.*, 1949, 2689) and by Crawford and his co-workers, R = Br (*J.*, 1959, 2807) R = OCH_3 (J., 1960, 3313)



XI

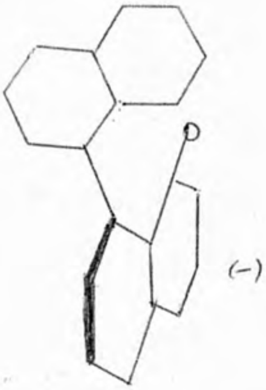
All these compounds are overcrowded and racemise more easily than one would expect on other grounds.

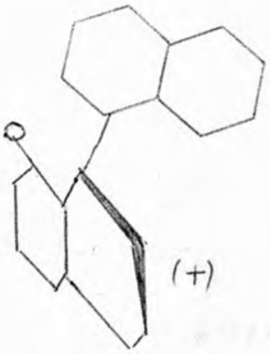
If then it is accepted that 1,1'-binaphthyl-8,8'-dicarboxylic acid has this deformed structure it follows of necessity that its dimethyl ester and its monoethyl ester will possess exactly similar structures. This is borne out by the similarity in the ΔE and A factors for these compounds.

The 1,1'-binaphthyl-8-carboxylic acid has only one substituted naphthalene unit combined with an ordinary undistorted naphthalene. There are two possible combinations of these units:

(+) distorted, naphthalene; (-) distorted, naphthalene

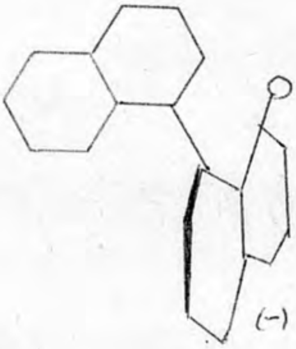
Each of these structures has an optical isomer corresponding to the *R* and *S* configuration of binaphthyl itself.

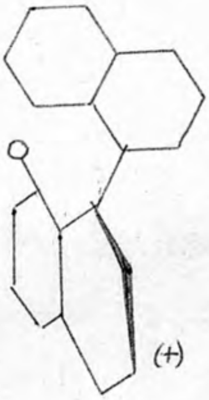




R

configuration





S

configuration.

Here again no drift in the first order velocity coefficient for this acid has been observed in N,N-dimethyl formamide and thus it is thought that here, too, the conformational changes in the individual units is too fast to be detected at the temperatures used and the process under observation in the polarimeter tube is again the R $\rightleftharpoons$ S one.

The measured ΔE, 22.4 kcal.mole^{-1}, is again smaller than one would expect if the acid had a classical structure but it fits in well with the picture of a deformed molecule. If the figure of 7.6 kcal.mole^{-1} for the strain energy of

1 distorted substituted naphthalene is added to this measured ΔE one gets a value of about 30 kcal.mole^{-1} which indicates an optically stable structure of the kind we would expect from classical models. The entropy factor $\Delta S^{\ddagger}$ for this acid is -5.5 e.u. compared to -9.1 for the 1,1'-binaphthyl-8,8'-dicarboxylic acid. This lowering in the entropy is probably due to the fact that the 1,1'-binaphthyl-8-carboxylic acid is less randomly orientated in the resting state than the 8,8'-acid.

In 0.1N sodium hydroxide the values of ΔE were higher than in N,N-dimethyl formamide for all the acids, though the effect was most marked for those compounds with the acid groups in the 8 or 8,8'-positions. In the case of the latter acids, this effect could be plausibly ascribed to solvation.

It has been stated by Hall, Ridgwell and Turner (loc.cit.) that the monoethyl ester of 1,1'-binaphthyl-8,8'-dicarboxylic acid is more stable than 1,1'-binaphthyl-5,5'-dicarboxylic acid in sodium hydroxide but this is based on an erroneous estimate of the half life period of the 5,5'-acid as 600-700 minutes at 20°. By extrapolation of the Arrhenius plot for this acid in sodium hydroxide we found the half life period to be 84 hours at 20°. Using this corrected half life period it is found that the acids have the same order of optical stability in sodium hydroxide as in dimethyl formamide.

The surprising aspects of these results in sodium hydroxide was the large positive entropy factor (+9.2 e.u.) for the 8,8'-acid which is the largest so far reported in restricted rotation racemisations (Harris and Mellor, Chemistry and Industry, 1959, 949, and Hall and Harris, J., 1960, 490). It is thought that this is due to the effect of solvent. Gowenlock (Chemical Reviews, 1960, XIV, 133) said a large positive entropy factor could be ascribed to a transition state which is more disordered (or freer) than the initial state. If the 8,8'-acid is highly solvated in the resting state and on racemisation suffers desolvation then just such a situation occurs when the molecule has more freedom in the transition state. The fact that the monoethyl ester of the 8,8'-acid has a smaller though still positive entropy factor of +3.2 e.u. indicates that this theory is probably correct. This compound has only one $-CO_2^-$ group to interact with the solvent and the effect is therefore bound to be reduced.

The results for 1,1'-binaphthyl-8-carboxylic acid in NaOH are, as will have been noted from the experimental section, difficult to interpret. The lines to determine individual velocity coefficients, in general, are quite good but sometimes, especially at the lower temperatures, deviations occur which indicate a faster process must also be taking place. These

These deviations were not observed in the rates taken in N,N-dimethylformamide at all and the Arrhenius plot of these rate coefficients gave a good straight line (see p. 78) The results in aqueous sodium hydroxide not always appear to be reproducible and the Arrhenius plot for all the results is poor. The general straight line drawn (see p. 85) gives a value for ΔE of about 24 kcal.mole^{-1} but taking the extreme limites the ΔE from such a graph could vary by 4 kcals. from 22 kcal.mole^{-1} to 26 kcal.mole^{-1}.

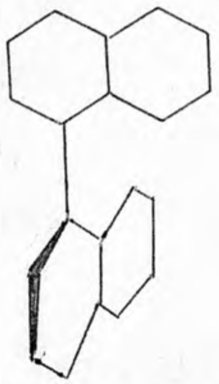
As these results were so odd a closer examination was made of the brucine salt of the acid, taking specific rotations of each crop. It was found that the value of the specific rotation was changed considerably on recrystallisation and not in one particular direction (i.e. not always a larger negative rotation). This would suggest that different (-) forms might be crystallizing out of solution each time. If this is so it could be an explanation of the odd rate coefficients.

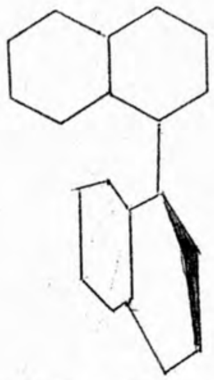
Rates were then determined at three temperatures using acid from the same crop of brucine salt. These three points gave a fairly good Arrhenius plot (see p. 88) and from it ΔE is calculated to be 24.7 kcal.mole^{-1} and $\Delta S^{\ddagger}$ to be +0.4 e.u.

This is obviously not a complete explanation as it is difficult to understand why this anomalous behaviour is not observed in the N,N-dimethyl formamide measurements.

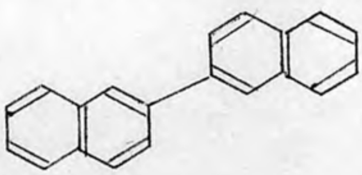
1,1'-Binaphthyl.

It is very possible that 1,1'-binaphthyl itself exists in enantiomeric forms.





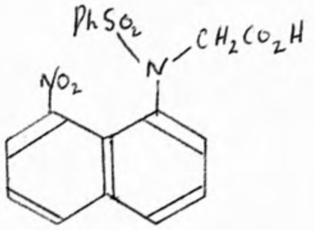
As we have seen, there are a number of 1,1'-binaphthyls substituted in positions other than the blocking ones which have been resolved. Another piece of evidence which indicates that binaphthyl itself is hindered comes from a study of its u.v. adsorption spectrum. This spectrum is very similar to that of naphthalene (Gilliam and Stern, Electronic Adsorption Spectroscopy, p.244), which means that 1,1'-binaphthyl is twisted about the 1,1'-bond. 2,2'-binaphthyl in which there should be no



hindrance to rotation greater than in diphenyl, has quite a different spectrum compared to that of naphthalene.

Attempts have been made before to obtain optically active 1,1'-binaphthyl by deamination of 2,2'-diamino-1,1'-binaphthyl and by decarboxylation of 1,1'-binaphthyl-4,4'-dicarboxylic acid. (Bell and Morgan, *J.*, 1950, 1963).

From the preliminary experiments we have made on optically active naphthidine (see p. 141) it seems that 1,1'-binaphthyl itself does exist in enantiomorphic forms. More work must be done before any more positive conclusions can be drawn.

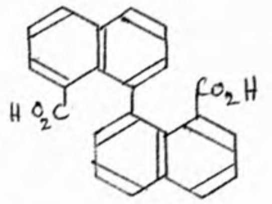


N-benzenesulphonyl-8-nitro-1-naphthyl glycine.

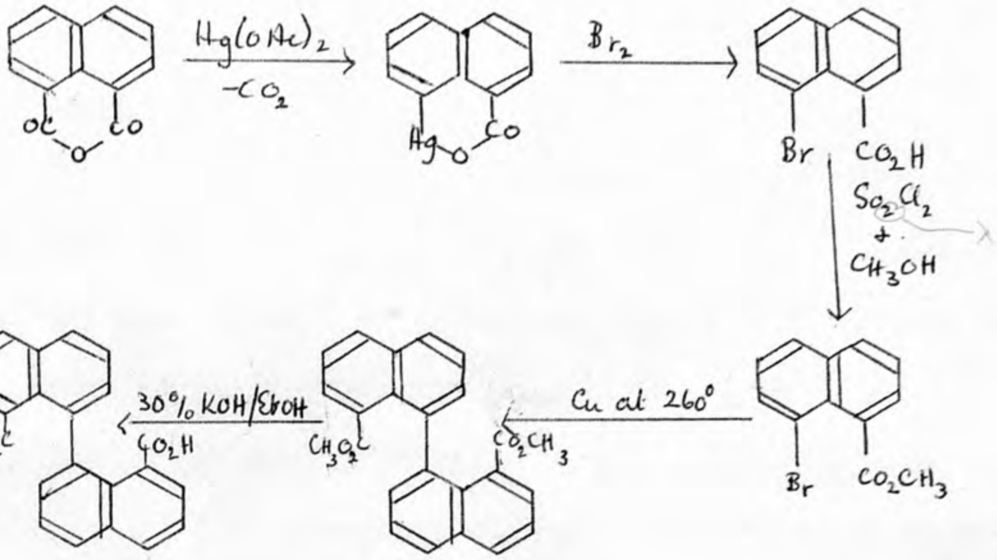
This compound was investigated because of its historical interest as the first peri-substituted naphthalene to be obtained in optically active forms. It was one of the first compounds discovered, other than the biphenyls themselves, which showed optical activity due to restricted rotation. Mills and Elliot (J., 1928, 1291) say that from velocity coefficient measurements on the brucine salt they calculated ΔH for this salt to be about 18.5 kcal.mole^{-1}.

Using the velocity coefficients measured for the acid in chloroform during this work the value of ΔE was found to be 20.5 kcal.mole^{-1}.

1,1'-Binaphthyl-8,8'-dicarboxylic acid.



Scheme



(1) 8-Bromo-1-naphthoic acid [Rule, Pursell and Brown, *J.*, 1934, 165]

1. Mercuri-compound.

The naphthalic anhydride (250 g., 1M) was dissolved in aqueous sodium hydroxide (155 g., in six litres of water) by heating, the solution filtered through glass wool into a 20-litre flask in a large heating mantle and boiled under reflux for 15 minutes. The mercuric oxide (275 g., 1.1 M), dissolved in dilute acetic acid (200 c.c. glacial acetic acid and 750 c.c. water), was then added and the reaction mixture made acid with glacial acetic acid. The solution was then heated for 80 hours. The reaction was complete when a sample gave a clear solution with sodium hydroxide and no mercury was deposited on a clean copper wire held in this solution. The product was filtered off, washed with water, alcohol and ether and then dried. Yield, 475 g. of a pale cream-coloured solid.

(2) Introduction of Bromine.

A suspension of the mercuri-compound (95 g.) in glacial acetic acid and water (300 c.c. glacial acetic acid and 50 c.c. water) was cooled to -10°. Bromine (34 g.) in aqueous sodium bromide solution (150 c.c. of 50% solution) was added gradually with stirring, keeping the temperature below 5°. The reaction was allowed to warm to room temperature and was then heated to 90° when it was poured into three litres of boiling water. The solution was filtered as hot as possible. The residue was extracted with another litre of water and again filtered hot. The combined filtrates were left to cool and then the solid deposited in them was filtered off and dried. Yield: 50 g. (crude)

Crystallisation from benzene gave 40 g. of acid m.p. 173-5° with shrinking at 170°. Percentage yield, 70% calculated on the naphthalic anhydride used in the first stage.

(3) Methyl 8-bromo-1-naphthoate [Rule and Barnet, J., 1932, 175]

The acid (218 g., 1M) was dissolved in benzene (1500 c.c.) by boiling under reflux. Thionyl chloride (74 c.c., 1.2M) was added slowly to the boiling solution and the reaction mixture boiled for 4½ hours. Methyl alcohol (530 c.c.) was then added very cautiously and the reaction mixture boiled for a further 45 minutes. The benzene solution was washed twice with water, twice with 10% aqueous Na_2CO_3 and finally again with water. The solution was dried over calcium chloride and then the benzene removed.

It was found difficult to crystallise this substance (although Rule and Barnet did so from petroleum ether) so it was vacuum distilled, b.p. 190°/2-3 mm. The pale yellow oil solidified into a very pale cream-coloured solid m.p. 35°. Yield, 168 g., Acid recovered from Na_2CO_3 washings 11 g. Percentage yield, 77%.

(4) Ullmann Reaction to prepare dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate. [Hall, Ridgwell and Turner, J., 1954, 2498]

Copper bronze (50 g.) was added gradually to methyl 8-bromo-1-naphthoate contained in a hard glass tube immersed in a metal bath at 260°. During addition the internal temperature rose to 300° whilst the bath temperature was 230°. The cooled mass was extracted with acetone in a Soxhlet apparatus. This solution was boiled with charcoal until it was a pale yellow colour and was then evaporated to about 250 c.c. 23g. of a yellow solid crystallised; recrystallisation from methylated spirit gave beautiful pale yellow plates (sometimes needles).

Yield, 19 g. (55%), m.p. 155-7°.

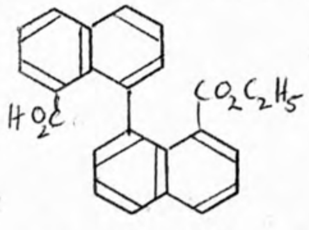
(5) Hydrolysis of methyl ester.

The ester (17 g.) was boiled under reflux with 30% alcoholic potassium hydroxide (500 c.c.) for 30 minutes on a metal bath. The alcohol was then distilled off and the residue heated at 130-140° for 30 minutes. The residue was extracted with boiling water and filtered. The cooled filtrate was acidified with dil. HCl and the precipitate filtered off and dried. This precipitate was extracted with large amounts of methylated spirit in a Soxhlet apparatus - the solution boiled with charcoal, filtered and evaporated to a small volume.

Yield, 13 g. (83%), m.p. 304-6° (decomposition)

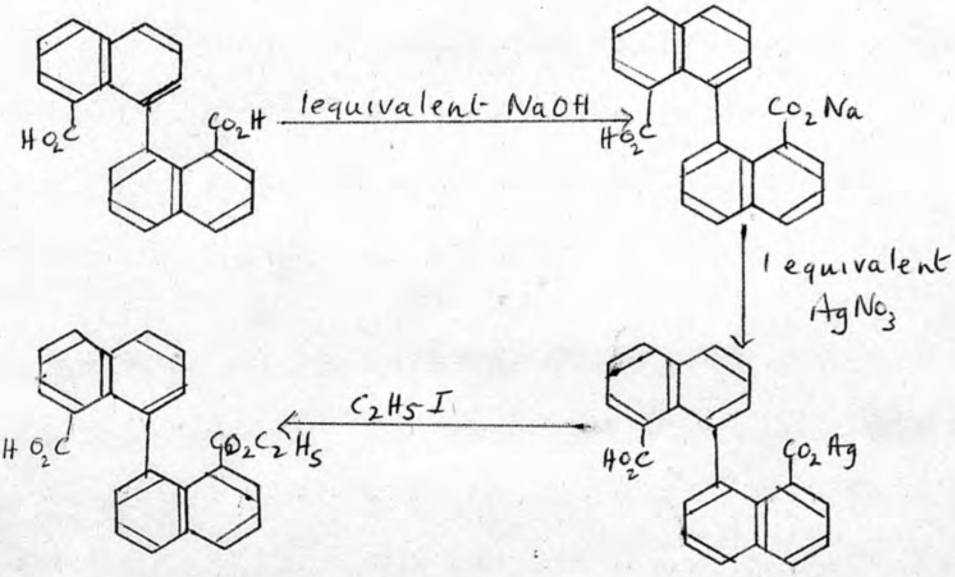
(Found: C, 77.1; H, 4.1; O, 18.7. $C_{22}H_{14}O_4$ requires C, 77,2; H, 4.1, O, 18.7%).

Ethyl hydrogen-1,1'-binaphthyl-8,8'-dicarboxylate.



(Meisenheimer and Beisswenger, Ber., 1932, 65, 32)

Scheme



The acid (10g., 1M) was dissolved in an aqueous 0.1N solution containing the exactly calculated equivalent of NaOH (292 c.c. 1M). To this cold filtered solution the exactly equivalent amount of $AgNO_3$ solution (292 c.c. 0.1N; 1M) was added slowly and with stirring. The fine white precipitate so formed was filtered off and dried carefully away from the light.

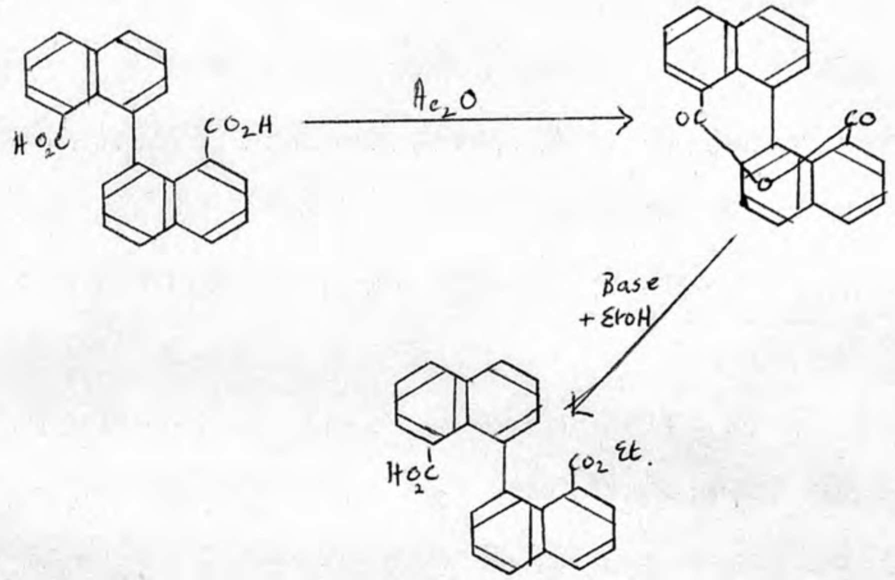
The finely powdered, dry silver salt and excess, freshly distilled ethyl iodide (40 g.) were heated together under reflux for 2 hours. The ethyl iodide was distilled off and the residue extracted twice with aqueous sodium carbonate and finally with acetone.

From the cooled Na_2CO_3 extract, by acidification with dil. HCl, was obtained the crude acid which was crystallised from ethyl alcohol. After two recrystallisations the acid was obtained pure as white prisms, m.p. 193-5°. Yield: 2.4 g. (Found: C, 77.89; H, 4.84; O, 17.18. $C_{24}H_{18}O_4$ requires C, 77.82; H, 4.89; O, 17.27%).

[Meisenheimer and Beisswenger only give analysis figures for the brucine salt not the acid itself. They give m.p. 194-5°].

It was thought a possible alternative method of preparation of 1,1'-binaphthyl-8-ethyl carboxylate-8'-carboxylic acid might be one via the anhydride, if that could be formed.

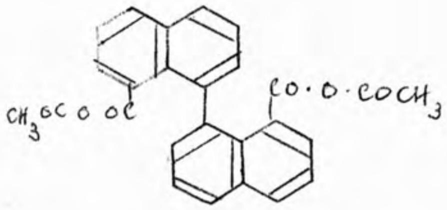
Scheme.



Experiment A.

The 1,1'-binaphthyl-8,8'-dicarboxylic acid (1 g.) was heated under reflux for 1 hour with acetic anhydride (5 c.c.) The solution, which was a clear yellow colour, was poured into a beaker and allowed to cool when yellow needles were deposited. Recrystallisation from ethyl alcohol gave pale yellow needles m.p. 156-7°. The infra-red spectrum of this compound shows peaks at 1808 cm^{-1} and 1721 cm^{-1} indicating a splitting of the carbonyl peak characteristic of an anhydride.

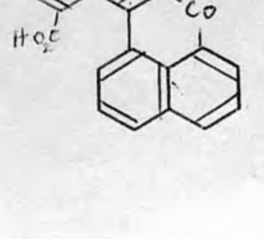
It seems probable that this compound is the hitherto unknown mixed anhydride:-



(Found: C, 73.1; H, 4.6: $C_{26}H_{18}O_6$ requires C, 73.2; H, 4.3%). If this compound is heated above its melting point it begins to bubble and go cloudy, then at 190-200° it resolidifies as an orange solid. If heating is still contimued another melting point with decomposition is obtained at about 300°. It is thought cyclisation must occur with heating to give Anthanthrone.

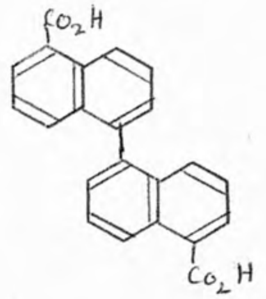
Experiment B.

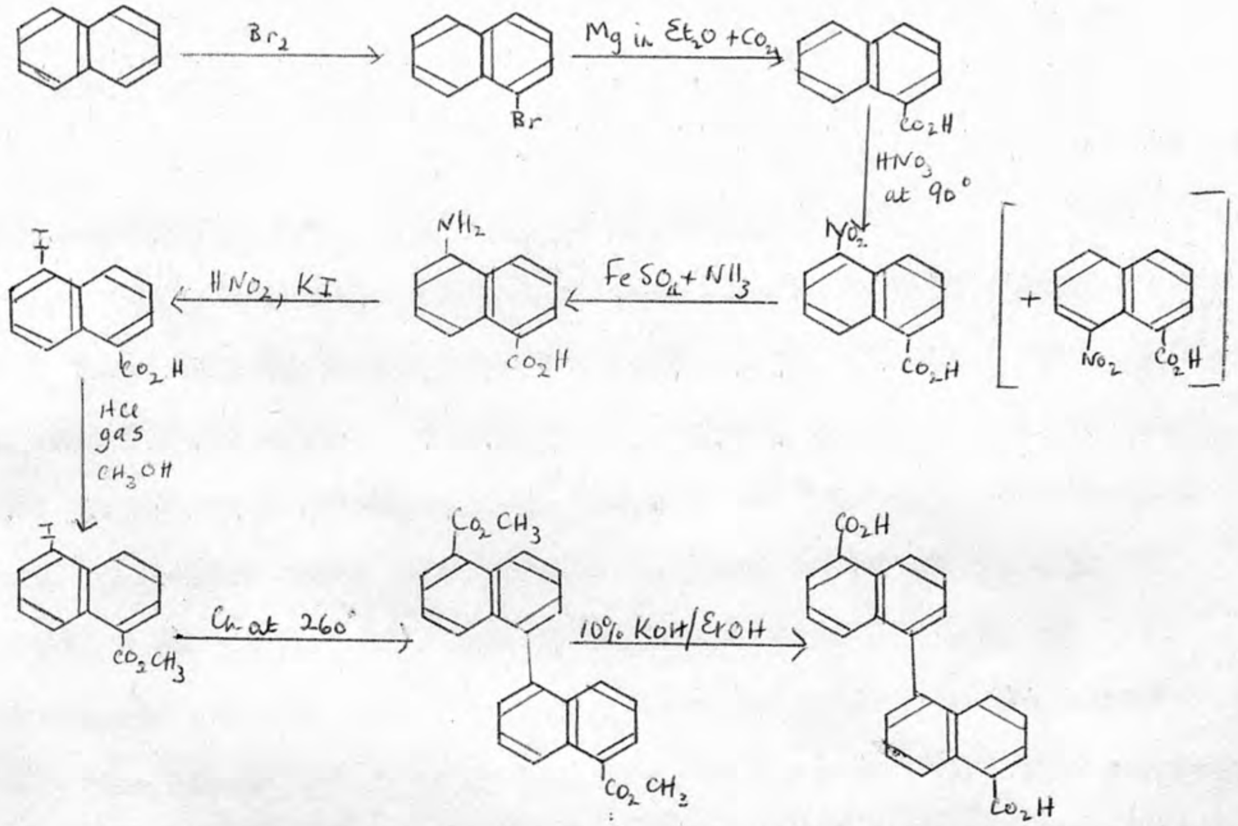
1,1'-Binaphthyl-8,8'-dicarboxylic acid (1 g.,) heated under reflux with acetic anhydride (15 c.c.) for 2 hours when a clear yellow solution was obtained. This was poured into a beaker and left to cool but no crystals formed. By reducing the volume an orange product was obtained m.p. 280°. This was acidic (dissolved in sodium carbonate and was reprecipitated by dil. hydrochloric acid) and had a different infra-red spectrum from the product of experiment A. This new product was thought to be:-



m.p. 180°-1°

1,1'-Binaphthyl-5,5'-dicarboxylic acid.





1-Bromonaphthalene. (Org.Syn., 1930, 10, 14.)

Naphthalene (264 g.) and carbon tetrachloride (90 c.c.) were heated together under reflux with stirring while bromine (254 g.) was added slowly during 4 hours. The mixture was then heated for a further 1½ hrs. Most of the solvent was removed and NaOH (20 g.) was added and the solution was heated on a water bath for 3 hours. The solution was filtered through glass wool and the filtrate vacuum distilled. The distillate was cooled and the naphthalene which crystallised was filtered off. The oil was then redistilled and the fraction b.p. 110-126/5 mm. was collected. Refractive index 1.6580 (1.660 reported). Yield, 277 g. Percentage yield, calculated on amount of bromine used, is 82%.

<u>1-Naphthoic acid</u>. (<u>Orgn.Syn</u>., 1931, <u>11</u>, 80).

The fine magnesium turnings (16.3 g.) and ether (68 c.c. sodium dried) were placed in a 2-litre, three-necked flask fitted with a Hershberg stirrer, dropping funnel and two water condensers one on top of the other. The funnel and condenser were fitted with drying tubes of $CaCl_2$. A crystal of iodine was added together with 10 c.c. of bromonaphthalene and the whole warmed gently to initiate the reaction. The heat was then turned off and the stirrer turned on. The bromonaphthalene in ether (140 g. in 340 c.c. of dry ether all together) was added slowly, the addition taking 2 hours. The reaction mixture was then boiled under reflux for 30 minutes. Dry benzene (340 c.c.) was added to the reaction and the mixture poured on to 600 g. of solid carbon dioxide. When the reaction had finished dilute H_2SO_4 was added until it was in excess. Two layers separated, more ether was used to dissolve up solid and re-extract the acid layer. The ether extracts were then washed with 10% NaOH (aqueous) and the combined sodium hydroxide washings were acidified with dilute hydrochloric acid when the crude naphthoic acid was precipited. This solid was filtered off and dried, then crystallised from toluene. It crystallised in cream plates, 91 g., (68%), m.p. 160°.

5-Nitro-1-naphthoic acid. (Ekstrand, J.pr.Chem., 1888, 38, 156)

Nitric acid (690 c.c. d, 1.42) was poured into a 2-litre three necked flask fitted with a mechanical stirrer, a thermometer, and a joint through which to add solid. The flask was heated on a water bath at 90° and the solid naphthoic acid (100 g.) added slowly. When the addition was completed the mixture was heated for 30 minutes and then cooled and poured onto ice in a 4-litre beaker. After standing for some time the precipitate was filtered off and dissolved in Na_2CO_3 (90 g. in 1 litre H_2O) by heating and then filtered hot. The cooled filtrate was acidified with dilute HCl and the precipitate filtered off and dried. The crude product was crystallised three times from ethyl alcohol and separated as fawn coloured needles, m.p. 236-8°. Yield, 17 g. (15%).

5-Aminol-naphthoic acid. (Pschorr, Annalen, 1912, 391, 23)

Water (220 c.c.) was heated in a 1-litre beaker and stirred mechanically. Ferrous sulphate ($FeSO_4 7H_2O$, 90 g., 7M) was added to the boiling water which contained a little hydrochloric acid. The 5-nitro-naphthoic acid

(10 g., 1M) was dissolved in a little aqueous NH_3 and added. Then NH_3 (100 cc., *d*, 0.88) was added until the solution was alkaline and a black precipitate was formed. This solution was boiled vigorously for five minutes and filtered keeping the pad of filter papers alkaline. Some of the ammonia was boiled off and the filtrate acidified with glacial acetic acid. The precipitate was filtered off, after standing overnight when the colour changed from yellow to deep red. It crystallised as rhombs from ethanol. Yield, 7.5 g. (87%), m.p. 209-212°.

5-Iodo-1naphthoic acid. (Seer and Scholl, *Annalen*, 1913, *398*, 82)

5-Amino 1-naphthoic acid (18 g., 1M) was dissolved in aqueous sodium hydroxide (70 c.c., 10%) and was added to an aqueous solution of sodium nitrite ($NaNo_2$, 8 g., 1.1M) This solution was added dropwise to a solution of sulphuric acid (500 c.c., 2N) at 0° which was mechanically stirred. The cloudy solution filtered on a cold Buchner funnel and poured into a cold solution of KI (34 g., in 180 c.c. H_2O). The solution was left to stand for twelve hours.

The working up of this reaction was modified. The reaction mixture was extracted with ether and the ether layer washed with an acidic solution of sodium meta-bisulphite and then with a large amount of water. The solution was dried over sodium sulphate and finally the ether removed. The crude product was crystallised from glacial acetic acid to give 15.5 g. (54%) of deep red-brown crystals, m.p. 248-50°.

Methyl 5-iodo-1-naphthoate. (Seer and Scholl, loc.cit.)

5-Iodo-1-naphthoic acid (23 g.) was dissolved in methyl alcohol (575 c.c.) and dry hydrogen chloride gas was passed through the solution for seven hours. The reaction mixture was poured into cold water and the solution extracted with ether. The ether extract was washed with aqueous Na_2CO_3 and with water and dried over sodium sulphate. The ether was removed and the residue crystallised from methyl alcohol to give 17 g., (72%) of the ester as pinky-gold plates, m.p. 78-80°.

1.1'-Binaphthyl-5.5'-dicarboxylic acid.
(Seer and Scholl, loc.cit. modified
by Ridgwell, loc.cit.)

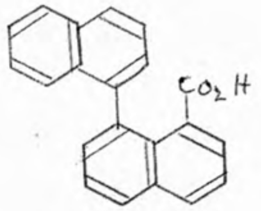
Methyl 5-iodo-1-naphthoate (10g.) was heated in a hard glass tube on a metal bath at 250° under an atmosphere of carbon dioxide. Copper (10 g.) was added slowly when the internal temperature rose to 270°. After the addition of copper, the mixture was heated at 220° for 15 minutes and was then extracted with boiling o-dichlorobenzene. The copper salts were filtered off and the residue, obtained by distilling off the solvent, was hydrolysed directly.

The residue was boiled for six hours under reflux

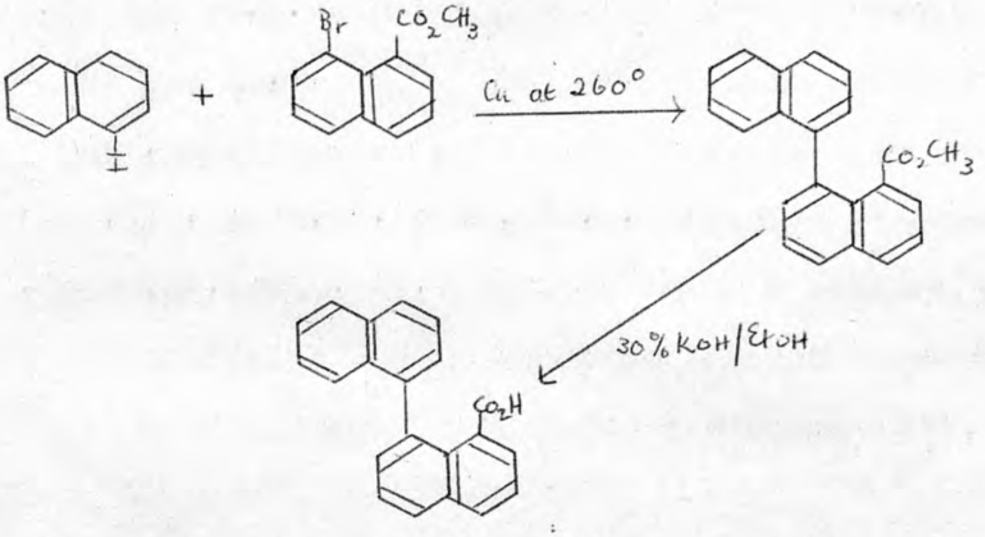
with 10% alcoholic potash. The alcohol was distilled off and the residue extracted with hot water. The cooled solution was acidified with dilute hydrochloric acid. The dried precipitate was extracted with ethyl alcohol using a Soxhlet and the solution so obtained was boiled with charcoal and evaporated to a small volume. Tiny white crystals separated out (4 g., 73%), m.p. 360° with decomposition. This m.p. taken using an electrothermal apparatus. (Ridgwell gives m.p. 358° and Bell, Morgan and Smythe m.p. 355°). Analysis (Bernhardt)
Found: C, 77.0; H, 4.1; O, 18.9. $C_{22}H_{14}O_4$ requires C, 77.1; H, 4.2; O, 18.7%)

The analysis result indicated that this compound was obtained in a higher state of purity than previous workers were able to obtain it.

1.1'-Binaphthyl-8-carboxylic acid.



This compound had been prepared before in low yield by Meisenheimer and Beisswenger (loc.cit.) but this author was unable to repeat their work. Therefore a new method of preparation was developed.



Methyl 1.1'-binaphthyl-8-carboxylate.

Methyl-8-bromo-1-naphthoate (25 g., 1M) and α-iodonaphthalene (24 g., 1M) were heated together in a hard glass tube immersed in a metal bath at 260°. Copper bronze (50 g.) was added gradually and after the addition was completed the reaction mixture was kept at 220° for ten minutes. The cooled mass was extracted with chloroform and the resulting solution filtered off from copper salts and inorganic substances. The chloroform was distilled off and a little ether added to the resulting oil when a solid crystallised out (Fraction I). The solid was filtered off from a dark brown oil which was vacuum distilled to give a light yellow oil. (Fraction II) The residue from the distillation, with acetone, gave a dark brown solid (Fraction III).

Fraction I. 6 g. crude material m.p. 130-145° which was crystallised from methylated spirit using charcoal to give: (a) 1st crop m.p. 140-155° yellow compound.

Recrystallised to give 2.5 g. pale yellow needles mp. 155-7°, i.e. Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate.

(b) 2nd crop. m.p. 110-120° with a residue which melted at 150°. Recrystallisation gave a solid m.p. 110-120° still with a residue which disappeared at 130°.

(c) 3rd crop. m.p. 107-120°.

Fraction II. 9 g. light yellow oil and some white solid which dissolved in the oil. b.p. 100-120/2-3 m.m. This was mainly unreacted compounds and some dehalogenated products such as naphthalene and 1-naphthoic acid.

Fraction III. 6 g. sticky, dark yellow solid which was crystallised from methylated spirit using charcoal to give:

(a) 2 g. pale yellow solid, m.p. 114-121°.

(b) 2nd crop which was sticky so recrystallised

directly to give a yellow solid m.p. 115-120°.
These two crops (III (a) and (~~a~~b)) were taken with crops (b) and (c) from Fraction I and recrystallised from methylated spirits. Yield: 2.45 g., m.p. 118-121°

2nd crop. 1.15 g. m.p. 115-120°

The total yield was 3.6 g., (12% calculated from the amount of methyl-8-bromo-1- naphthoate used).
(Found: C, 84.35; H, 5.25; $C_{22}H_{16}O_2$ requires C, 84.6; H, 5.2%)

1,1'-Binaphthyl-8-carboxylic acid.

Methyl 1,1'-binaphthyl-8-carboxylate (3.8 g.) was heated under reflux on a metal bath, with 30% alcoholic potash. The alcohol was distilled off after 15 minutes and the residue heated at 130-140° for about 15 minutes. The residue was extracted with hot water and filtered. The cooled filtrate was acidified with dilute hydrochloric acid and the precipitate so obtained was filtered off and dried. The crude acid was crystallised from methylated spirit, after boiling with charcoal for some time. After several recrystallisations it was obtained pure, m.p. 246-8°, 2g., (56%) (Meisenheimer and Beisswenger, loc.cit., gave m.p. 242°).
Analysis (Bernhardt).
(Found: C, 84.2; H, 4.85; O, 11.2. $C_{21}H_{14}O_2$ requires C, 84.5; H, 4.7; O, 10.7%).

Preparation of the esters of optically active 1,1'-binaphthyl-8,8'-dicarboxylic acid and 1,1'-binaphthyl-5,5'-dicarboxylic acid.

To prepare the optically active esters of these acids it was necessary to find a method of esterification which worked smoothly and well in the cold. It was found that the reaction of acids with diazomethane was an eminently suitable one.

Diazomethane. (Org.Syn., 1956, 36, 16.)

$$p\text{-}CH_3C_6H_4SO_2N(NO)CH_3 + ROH \xrightarrow{KOH} CH_2N_2 + p\text{-}CH_3C_6H_4SO_2OR + H_2O$$

The joints of the apparatus used were fitted with plastic sleeves to limit the possibility of an explosion.

In a round-bottomed flask were placed 5g. KOH, 8 c.c. water and 25c.c. of 95% ethanol. N-methyl-N-nitroso-p-toluene sulphonamide (21.5 g.), dissolved in 130 c.c. of ether, was placed in a dropping funnel. There were two receiving flasks connected in series and the second one, which contained 40-50 c.c. ether, acted as a trap for any CH_2N_2 which might escape. The N-methyl-N-nitroso-p-toluene sulphonamide was added from the dropping funnel to the KOH solution in the flask which was on a water bath maintained at 65-70°. After the addition, a further 50 c.c. of ether was added and the distillation continued until the distillate was colourless. The ethereal solution was used immediately and was assumed to contain 2.6-2.7 g. of diazomethane.

Optically active esters.

1. (-) Dimethyl-1,1'-binaphthyl-8,8'-dicarboxylate.

The (-)1,1'-binaphthyl-8,8'-dicarboxylate acid (2.5 g.) was added slowly to the cold ethereal solution of diazomethane (35 c.c. ~ 0.61 g. CH_2N_2). There was effervescence and as the reaction proceeded a light coloured solid crystallised at the bottom of the flask. When the reaction was complete the solid was filtered off, washed thoroughly with aqueous sodium carbonate and then with water. It was then dried to give a white crystalline product, 9.8 g., m.p. 123-5° (then solidified and melted at 157° probably because of racemisation on melting). (Found: C, 77.9; H, 5.1. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%).

2. (+) Dimethyl 1,1'-binaphthyl-8,8'-dicarboxylate.

The (+)1,1'-binaphthyl-8,8'-dicarboxylic acid (3.2 g.) was added slowly to a cold ethereal solution of diazomethane (45 c.c. ~ 0.89 g. CH_2N_2). When the reaction finished the solid was filtered off and washed well with aqueous sodium carbonate and water and then dried. 2.8 g. of quite white product was obtained. m.p. 123-5° and then 157° (like the (-) isomer).

(Found: C, 77.75; H, 5.1. $C_{25}H_{18}O_4$ requires C, 77.8; H, 4.9%)

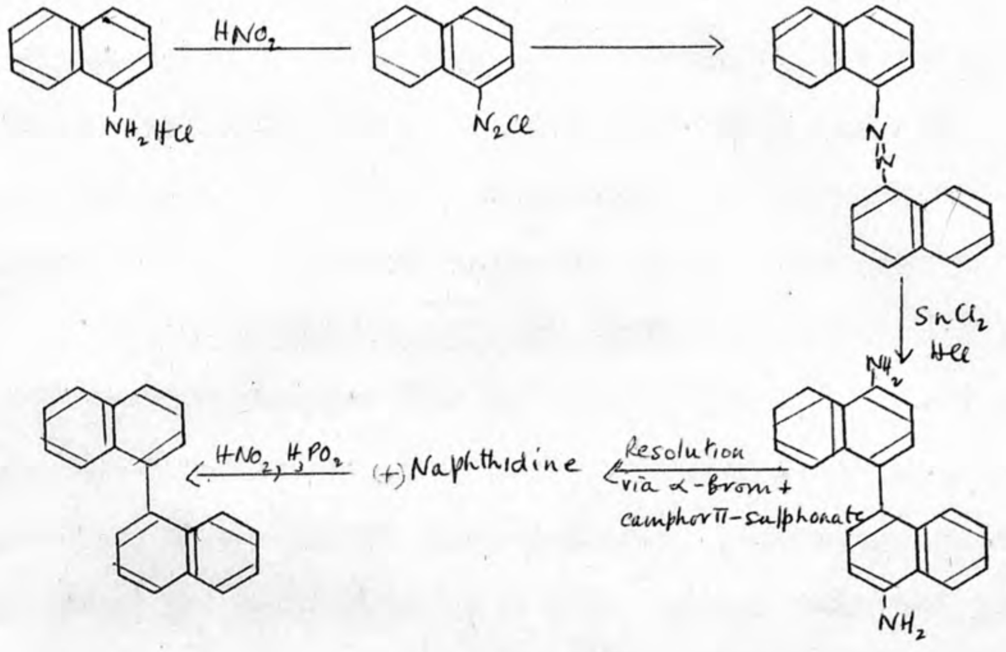
3. (+) Dimethyl 1,1'-binaphthyl-5,5'-dicarboxylate.

The (+) 1,1'-binaphthyl-5,5'-dicarboxylic acid (3 g.) was added slowly to a cold ethereal solution of diazomethane (40 c.c. 0.73 g.). When the reaction was completed the precipitate was filtered off and washed well with aqueous sodium carbonate and water. The product (2 g.) was pale yellow. m.p. 173-4°.

(Found: C, 77.5; H, 5.1. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%)

Attempted preparation of optically active 1,1'-binaphthyl.

Scheme.



Naphthidine. (Cohen & Oesper, Industrial Engineering Chem. Analytical, 1936, 8, 306).

1. Azonaphthalene.

α-Naphthylamine hydrochloride (35 g.) was heated with 500 c.c. of water to get into solution and cooled with stirring. The conc. HCl (5 c.c.) was added and the solution cooled to zero when a mechanical stirrer was started. Cold dilute sulphuric acid (21 c.c. conc. acid and 200 c.c. water) was added and when the solution was again at 0° it was diazotised with sodium nitrite (14 g. in 80 c.c. water). The diazonium solution was left to stand in the ice bath for five minutes and then filtered through a cold Buchner funnel. The filtrate placed in an ice bath and the stirrer started again when a solution of sodium acetate was added keeping the temperature between 0-5°. A cooled solution of sodium sulphite was added slowly when nitrogen was evolved. The solution was warmed on a water bath. The precipitate was washed with water and dried. This precipitate (31 g.) was not recrystallised but used directly in the next stage.

Reduction and rearrangement of azonaphthalene.

Azonaphthalene (40 g.) was suspended in 400 c.c. of ethyl alcohol and brought to a gentle boil. Stannous chloride (80 g. in 200 c.c. conc.HCl) was added slowly with shaking. As soon as a pale salmon coloured precipitate was observed the solution was taken off the heat. The solution was cooled to room temperature and 200 c.c. of conc. HCl was added. The precipitated hydrochloride was filtered off.

Purification of the hydrochloride. (Theilacker and Hopp, *Ber.*, 1959. 2293)

The crude hydrochloride was boiled with two litres of water and filtered hot from the insoluble residue. To the cooled filtrate was added 100 c.c. of conc. HCl when a white precipitate was formed. The brown residue was extracted with more water but very little solid was obtained from the filtrate.

Liberation of the amine.

The purified amine hydrochloride was suspended in 500 c.c. of water and a slight excess of 20% aqueous sodium hydroxide was added. The solution was stirred continuously and the temperature maintained at 40° for 15 minutes. The solution was then cooled and the precipitate filtered off. The amine was recrystallised from 1½ litres of alcohol, boiling the solution with charcoal for some time. The solution was then evaporated to a smaller volume when 9 g. (24% calculated from the amount of amine hydrochloride used) of beige crystals separated as plates.

Optical activation of naphthidine. (Theilacker and Hopp, *loc.cit.*)

Naphthidine (2.8 g., 1M) was dissolved in 50 c.c. hot acetone and this solution was then poured into 400 c.c. of water. 40 c.c. of N-hydrochloric acid was added followed immediately by a solution of ammonium-brom-D-camphor-π-sulphonate (6.5 g., 2M). After standing for some hours the precipitate was filtered off and dried away from the light. It was crystallized from 60% aqueous alcohol.

The first crop was pinky beige crystals (0.8 g.)

$[\alpha]_{5791}^{20} = +105.7^{\circ}$ (in 60% acetone)

The second crop was slightly darker (2.3 g.) $[\alpha]_{5791}^{22} = +95.2^{\circ}$ (in 60% acetone), m.p. 329-331° (shrinks at 280°). (Theilacker gave $[\alpha]_D = +99^{\circ}$).

Liberation of the active amine.

The salt (5 g.) was suspended in 60 c.c. of alcohol and a few pieces of ice added. The solution was made alkaline with ammonium hydroxide when the amine was precipitated. When dry the amine was a light brown colour (1.7 g.) m.p. 204-5°. $[\alpha]_{5791}^{20} = +39.7^{\circ}$ (in dry acetone)

Deamination using hypophosphorous acid (using the method given in Organic Reactions, 1944 , 2, 263).

The reaction was carried out on inactive amine first. The naphthidine (2g., 1M) in 5 c.c. conc.hydrochloric acid and a little water was diazotized with sodium nitrite (1 g., 2M) in a little water, keeping the mixture very cold -20° to -30°. The reaction mixture was poured into 20% aqueous hypophosphorous acid (50 c.c., 15M). A yellow solid was slowly precipitated and eventually filtered off and dried. This solid was dissolved in benzene and this solution washed with sodium hydroxide, dilute hydrochloric acid and water. The solution was dark brown and to purify it without heating it was passed through an alumina column made up in benzene. When the solution was evaporated an orange-yellow compound was obtained, m.p. 148-150°, which was impure 1,1'-binaphthyl (reported m.p. 160° and 156°). This solid dissolved in benzene was passed through a second alumina column made up in petroleum ether (b.p.40-60°) This gave a white product m.p. 156-158°.

The infra-red spectrum was taken to use as a standard.

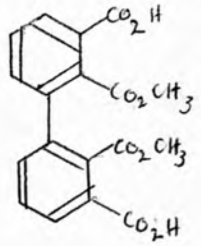
The reaction was repeated using optically active amine in the same quantities.

The amine was diazotised as quickly as possible and poured on to hypophosphorous acid. To speed up the procedure, in case the hydrocarbon should be very labile, it was decided, 30 minutes after pouring into hypophosphorous acid, to extract the reaction mixture with benzene even though the reaction was not complete. The extraction was difficult because of the formation of emulsions but the benzene solution was separated and washed with sodium hydroxide, dil. hydrochloric acid and water. The benzene solution was passed directly through an alumina column made up in petroleum ether (40-60°). The first fraction out was an almost colourless solution 18 c.c. of which was filtered into the polarimeter tube. The observed rotation $\alpha^{13.1}_{5791} = +0.085^{\circ}$ in a benzene petroleum ether mixture. The solution and washings were transferred to a weighed evaporating dish and the solvent removed. By reweighing the evaporating dish the amount of solid in the solution was found and an approximate value of the specific rotation calculated: $[\alpha]^{13.L}_{5791} = +105^\circ$.

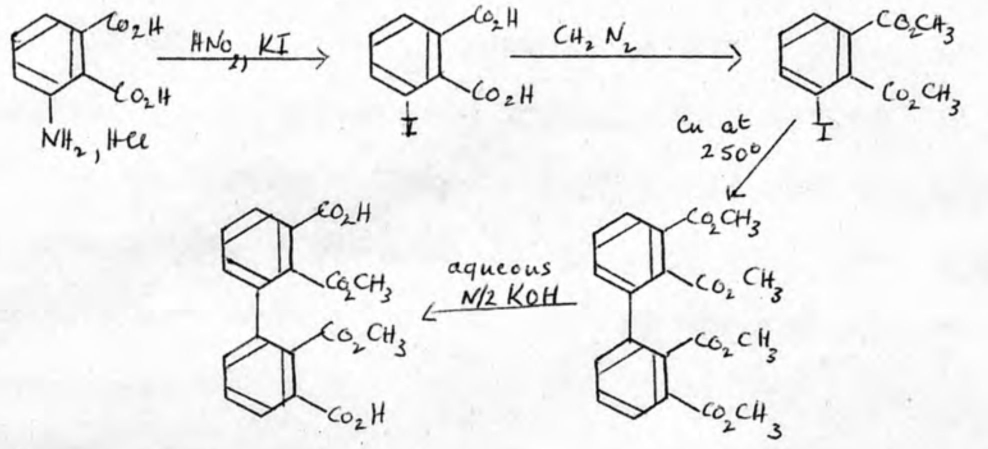
The melting point of this solid taken on an electrothermal apparatus was 151-154° with shrinking at 138°. The infra red spectrum of this residue was also taken and it corresponded well with that of 1,1'-binaphthyl and also showed beyond all doubt that no amine groups were present. This would seem to be the (+) form of 1,1'-binaphthyl which at room temperature seemed to be reasonably stable in benzene and petroleum ether. In dimethyl formamide at 21° it had a half life period of about five hours.

Biphenyls.

2,2'-carbomethoxy-biphenyl-3,3'-dicarboxylic acid.



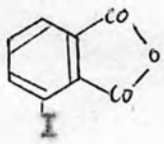
Scheme.



o-Iodo-phthalic acid. (Kenner, J., 1914, 2477)

The hydrochloride of o-amino-phthalic acid (30 g., 1M) was dissolved in concentrated hydrochloric acid (22.5 c.c. 1½M) and water (50 c.c.) without heating. To this solution was added a solution of sodium nitrite in water (10.4 g., 1M) keeping the temperature between -10 and -5°. A yellow solid appeared during the course of the reaction. The reaction mixture was poured into a solution of potassium iodide (36 g., 1½M) which contained a little dilute hydrochloric acid. After being warmed on a water-bath for some time sulphurous acid was added and the yellow precipitate filtered off. This precipitate crystallised from water as cream-coloured plates (18 g., 50%) m.p. 176-8°. The melting point given in the literature is 206° for a solid with three molecules of water of crystallisation. To confirm the structure of this product it was decided to prepare its anhydride which was also known, m.p. 160-1°.

The acid (2.5 g.) prepared by the previously described diazotisation was heated under reflux for 15 minutes with acetic anhydride (2.5 c.c.) and the mixture was then poured into a beaker. On cooling prismatic crystals appeared which were filtered off and recrystallised from alcohol. m.p. 160-1°.

i.e.  had been formed.

Thus the diazotisation product was thought to be o-iodo-phthalic acid and the analysis figure are close to those required for the anhydrous acid. (Found: C, 32.8; H, 1.5; I, 43.7. Calculated for $C_8H_5IO_4$, C, 32.9; H, 1.8; I, 43.45%).

Kenner prepared the ester by the silver salt but here diazomethane was used.

Esterification.

The diazomethane was prepared by the standard method.

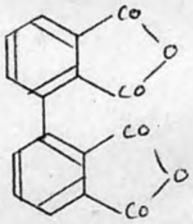
The finely powdered acid (18 g.) was added slowly to an ethereal solution of diazomethane(6g.) A little acetic acid was added to remove any excess diazomethane and the solution allowed to stand in the fume cupboard overnight. The ethereal solution was washed with sodium carbonate solution and water. The ethereal solution was dried over calcium chloride, the solution was then filtered and the ether distilled off. The residue crystallised from petroleum ether in golden plates. (17.5 g., 89%), m.p. 89-90°.

Tetra-methyl biphenyl-2,2',3,3'-tetracarboxylate.

The methyl ester of o-iodo-phthalic acid (20 g.) in a hard glass tube was immersed in a metal bath at 260°. Copper bronze (20 g.) was added gradually when the internal temperature rose to 280°. When all the copper was added the reaction mixture was heated at 260° for 15 minutes. The cooled mass was crushed and extracted with chloroform. The solution was filtered and the chloroform distilled off. The residue was crystallised from benzene and gave a white product (8.7 g., 72%), m.p. 163-4°.

2,2'-carbomethoxy-biphenyl-3,3'-dicarboxylic acid.

The tetra methyl biphenyl-2,2',3,3'-tetracarboxylate (7.5 g.) was dissolved in methyl alcohol (250 c.c.) by heating under reflux. To this solution was added an aqueous solution of N/2 potassium hydroxide (79 c.c.) the quantity calculated to hydrolyse two ester groups only. The mixture was heated for 30 minutes when the solution was found to be neutral. The alcohol was distilled off and water added to extract the residue. The solution was filtered, cooled and then acidified with dilute hydrochloric acid. The white precipitate obtained was filtered off and dried and then crystallised from methyl alcohol when white prismatic crystals separated (5 g., 71%) m.p. 191° but on remelting 265° because of the formation of the anhydride:-



Optical Activation.

Attempts were made to form alkaloid salts of this acid ester with brucine, quinine and cinchonidine. Only the brucine salt was formed which could be crystallised.

Brucine Salt.

The acid (0.5 g., 1M) was dissolved in 5 c.c. ethyl alcohol and added to a solution of anhydrous brucine (1.1 g., 2M) in 5 c.c. ethyl alcohol. Before the solution could be filtered crystals began to form and on heating to try to redissolve these crystals more were deposited. In this way most of the brucine salt crystallised (1.4 g. m.p. 215-219°.

It was thought this might be an asymmetric transformation of the second order but in fact the acid liberated from the salt was inactive. The rotation of salt itself had a small temperature coefficient.

SOCIETY OF CHEMICAL INDUSTRY

Founded 1881. Incorporated by Royal Charter, 1907

President: SIR ROBERT ROBINSON, O.M., F.R.S.

THE ENTROPY FACTOR IN THE OPTICAL STABILITY OF A 1:1′-~~C~~INAPhTHYL

D/

By Margaret M. Harris and Ann S. Mellor

Department of Chemistry, Bedford College, Landon

Reprinted from Chemistry and Industry,
July 25, 1959

LONDON: 14 BELGRAVE SQUARE, S.W.1

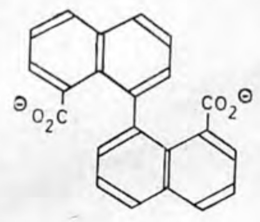
REPRINTED FROM CHEMISTRY AND INDUSTRY, 1959, pp. 949—950

THE ENTROPY FACTOR IN THE OPTICAL STABILITY OF A 1:1′-DINAPHTHYL

By Margaret M. Harris and Ann S. Mellor

Department of Chemistry, Bedford College, London

Several 1:1′-dinaphthyls are known which are optically active owing to restricted rotation about the 1:1′-bond. When their relative stabilities are compared on the basis of rate constants for racemisation it is not by any means obvious on what factors their optical stability depends.[1,2] As the beginning of a programme to investigate this problem further, the rate constants for racemisation of (+)- and (−)-1:1′-dinaphthyl-8:8′-dicarboxylic acid[3,1] have been measured in 0·1N aqueous sodium hydroxide solution at several temperatures between 20° and 52°. The Arrhenius parameters for racemisation corresponding to the formula $k_{racem}=Ae^{\frac{-E}{RT}}$ have been obtained (E by the graphical method) and $\triangle H\ddagger$ and $\triangle S\ddagger$, the activation enthalpy and entropy of the absolute reaction rate theory, calculated.[4]



The results are E, 26·1 kcal. mole^{-1}; $\log_{10}A$, 15·2(sec.$^{-1}$); $\triangle H\ddagger$, 25·5 kcal. mole^{-1}; $\triangle S\ddagger$ +9·2 e.u.

This appears to be the only compound of the non-bridged diphenyl type which is known to have an entropy factor for racemisation which is positive; optically labile diphenyls previously investigated all show negative entropy factors.[5–8] A positive entropy factor for racemisation has, however, been reported for an optically active ring compound, the bridged diphenyl *cis*-1:2:3:4-dibenz-1:3-*cyclo*octadiene-6:7-dicarboxylic acid[9] in 2·32N aqueous sodium hydroxide: the same compound in ethanol solution had a more usual negative entropy factor.

Received June 8, 1959

References

[1] Hall, D. M., Ridgwell, S. & Turner, E. E., *J. chem. Soc.*, 1954, 2498

[2] Harris, M. M., "Progress in Stereochemistry," Vol. II, 1958, *p.* 191 (London: Butterworths)

[3] Meisenheimer, J. & Beisswenger, O., *Ber. dtsch. chem. Ges.*, 1932, **65**, 32

[4] Glasstone, S., Laidler, K. J. & Eyring, H., "The Theory of Rate Processes", 1941, (New York: McGraw-Hill)

[5] Li, C. C. & Adams, R., *J. Amer. chem. Soc.*, 1935, **57**, 1565

[6] Rieger, M. & Westheimer, F. H., *ibid.*, 1950, **72**, 19

[7] Brooks, J. W., Harris, M. M. & Howlett, K. E., *J. chem. Soc.*, 1957, 1934

[8] Wittig, G. & Petri, H., *Liebigs Ann.*, 1933, **505**, 17

[9] Dvorken, L. V., Smyth, R. B. & Mislow, K., *J. Amer. chem. Soc.*, 1958, **80**, 487

PRINTED BY RICHARD MADLEY LTD., 54 GRAFTON WAY, LONDON, W.1, ENGLAND