CLXXI.—*Molecular Dissymmetry Dependent on Restriction of Rotation about a Single Bond. Optically Active Benzenesulphonyl-8-nitro-1-naphthylglycine.*

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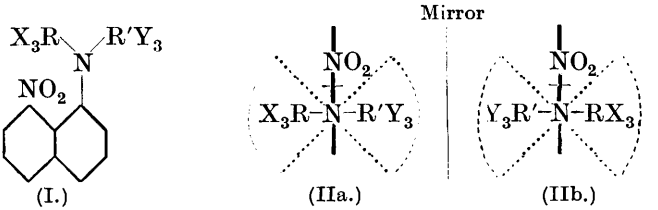
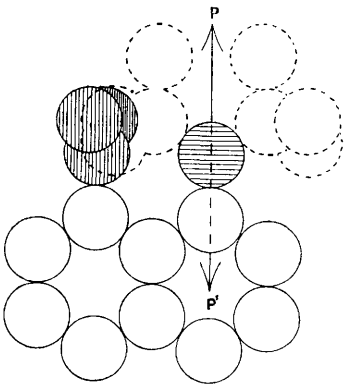
IF, as appears probable (see, for example, Mills, *Chemistry and Industry Review*, 1926, **45**, 884), the molecular dissymmetry of certain diphenic acids, discovered by Kenner and his co-workers (J., 1922, **121**, 614, and subsequent papers) is due to obstruction of the rotation of the two benzene nuclei of the diphenyl molecule about a common axis by substituent groups in the 6- and 6′-positions, it should be possible to obtain evidence of a similar restriction of rotation in other classes of compounds and especially among the *peri*-disubstitution derivatives of naphthalene.

Thus, it seemed that in a compound of formula (I) derived from 1 : 8-nitronaphthylamine by replacement of the hydrogen atoms of the amino-group by two groups RX_3, $R'Y_3$, the rotation of the complex radical $X_3R—N—R'Y_3$ about the carbon-nitrogen bond by which it is linked to the naphthalene nucleus must be restricted by the presence of the nitro-group to a comparatively limited arc, as is indicated by the diagrams IIa, IIb (which are intended to represent I viewed from above, the thick line denoting the naphthalene nucleus viewed edge-wise).



It is clear that if the rotation is in fact thus limited a compound of the above type should exist in two enantiomorphous modifications, and if, as is probable, their resistance to intertransformation through thermal agitation were considerable these modifications should show considerable persistence at moderate temperatures.

FIG. 1.



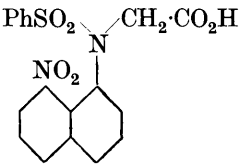
The probability that the rotation of the $-N(RX_3)(R'Y_3)$ complex will be obstructed by the nitro-group is perhaps more clearly indicated in the diagrammatic representation of the compound given in Fig. 1, which is constructed on the assumption that the atoms of carbon, nitrogen, and oxygen may be regarded for this purpose as spheres of diameter approximately 1·5 Å.U.

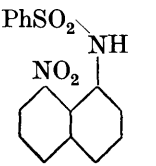
The ten carbon atoms of the naphthalene nucleus are shown in the lower half of the figure and the hydrogen atoms are omitted to simplify the diagram. The group of three vertically shaded spheres attached to the naphthalene nucleus in the 8-position represents a nitro-group; the horizontally shaded sphere represents the nitrogen atom of the $-N(RX_3)(R'Y_3)$ complex, and the $-RX_3$ and $R'Y_3$ groups are indicated with broken outlines. It will be seen that the nitro-group projects far into the space that the $-RX_3$ and

$-R'Y_3$ groups would sweep through if the complex $-N(RX_3)(R'Y_3)$ were rotated about the axis PP'. Unless, therefore, the diagram makes the *peri*-positions considerably too close together in comparison with the size of the substituent groups, the passage of the RX_3-group or $R'Y_3$-group over the obstacle presented by the nitro-group would require exceptional distortion of the molecule. It is, however, improbable that the *peri*-positions are more widely separated than represented in this diagram, in which the centres of the carbon atoms of the naphthalene nucleus are shown as 1·5 Å.U. apart, and lying with a regular hexagonal arrangement in one plane. If the molecule of naphthalene has a configuration which differs considerably from this, the difference will almost certainly be in the direction of greater compactness. *X*-Ray analysis would indicate that, at any rate in the crystalline state, the atoms of the naphthalene molecule are more closely packed than represented here; moreover, the structure of aromatic nuclei is not improbably related to that of the hexagonal nets in graphite in which the centres of the carbon atoms are only 1·45 Å.U. apart (Bernal, *Proc. Roy. Soc.*, 1924, *A*, **106**, 760).

A compound of the type under consideration should therefore exist in two enantiomorphous modifications of considerable persistence, as indicated by the formulæ (IIa) and (IIb).

The compound which we selected for testing these views experimentally was the benzenesulphonyl derivative of 8-nitro-1-naphthylglycine (III), the ester of which was readily prepared by the action of ethyl bromoacetate on the sodio-derivative of benzenesulphonyl-8-nitro-1-naphthylamine (IV), there being no indication of appreciable steric hindrance to the entry of the additional substituent group. The sulphonyl group in this compound serves to deprive the nitrogen

(III.) 



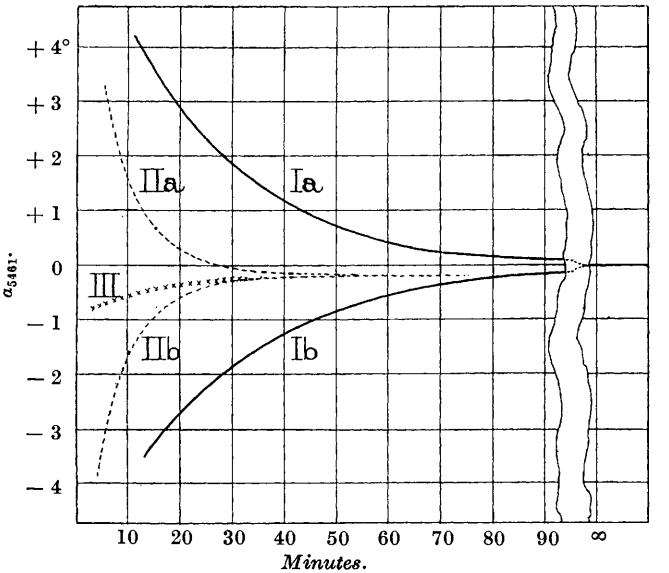
(IV.)

atom of any tendency to pass into the ammonium state and the carboxyl group gives the substance the power of forming salts with optically active bases needed for examining its resolvability into optical antipodes.

Experiments carried out with the brucine salt showed that the acid could in fact be obtained in two antimeric optically active forms. When equivalent quantities of the acid and brucine were mixed in acetone solution a brucine salt crystallised in more than 90% of the theoretical yield and this was the brucine salt of a

lævorotatory modification of the acid. For after its decomposition by extraction of its chloroform solution with sulphuric acid the resulting chloroform solution of the acid was strongly lævorotatory, but the lævorotation gradually disappeared in accordance with the unimolecular law as shown by curve Ib in Fig. 2. The time of half-change at 14·9° was 17 minutes and the average time of persistence of a molecule in either of the two modifications (IIa) or (IIb) was accordingly 25 minutes. The specific rotation, $[\alpha]_{5461}$, when first observed was — 242°, but as this observation was not made until 13 minutes after the salt had been added to the chloroform the

FIG. 2.



initial value of the specific rotation must have been considerably greater, probably at least — 400°.

Moreover chloroform solutions of this brucine *l*-acid salt showed mutarotation, the original strong lævorotation diminishing greatly as the acid component of the salt lost its activity. Thus in a typical experiment, the first reading (taken 4 minutes after bringing the salt into contact with chloroform) showed a rotation, α_{5461}, of — 3·86° and this fell steadily during 48 minutes at 15·5° to —0·19°, the final value reached after equilibrium had become established being — 0·18°. The average period of half-change in this experiment was 5 minutes; the racemisation of the acid is thus much more rapid when in combination with brucine than in the free state. The course of the mutarotation of this salt is shown in Fig. 2, curve IIb. The various

curves in this figure represent observed rotations of mercury green light for equimolecular solutions (0·00947*M*) in chloroform in a 4-dcm. tube plotted against the time in minutes after bringing the substance into contact with the solvent, the temperature being I*a*, 15·3°; I*b*, 14·9°; II*a*, 15·5°; and II*b*, 14·8°.

The *dextrorotatory form* of the acid was obtained in the following manner. The brucine *l*-acid salt was dissolved in methyl alcohol, in which it is easily soluble, but the solution soon deposited a new salt which is sparingly soluble in this solvent. The new salt has 3 molecules of water of crystallisation, the original salt having only 1, and whereas the new salt is less soluble than the original in methyl alcohol, it is much the more soluble in acetone.

Examination showed that this new salt was, as had been anticipated, the brucine salt of the *d*-acid. Its solution in chloroform, observed as soon as possible after preparation, was strongly dextrorotatory, $[\alpha]_{5461} + 103°$, and the rotation gradually sank (Fig. 2, curve II*a*) with an average period of half-change of 5·2 minutes, reaching zero after 22 minutes, and then becoming negative; the equilibrium value finally attained was the same as that for the brucine salt of the *l*-acid.

By removing the brucine from a solution of the salt in chloroform a solution of the *d*-acid was obtained, the first observation, made 11 minutes after bringing the salt into contact with chloroform, giving the reading $\alpha_{5461} + 4·19°$ ($[\alpha]_{5461} + 287°$), and the rotation was seen to sink gradually according to the unimolecular law (Fig. 2, curve I*a*), reaching zero (practically) in about 1½ hours. The temperature was 0·4° higher than in the corresponding experiment described for the *l*-acid and the time of half-change, 15·9 minutes, was accordingly somewhat shorter.

It has thus been established that benzenesulphonylnitronaphthylglycine can exist in two enantiomorphous modifications which possess a limited stability to thermal agitation. Since attempts to resolve nitrogen compounds of the type Nabc by methods similar to that used in this investigation have proved uniformly unsuccessful, it seems justifiable to disregard the possibility that the optical activity of this acid could arise from the presence of the possibly asymmetric nitrogen atom $N(C_{10}H_6{\cdot}NO_2)(SO_2Ph)(CH_2{\cdot}CO_2H)$. For similar reasons the possibility that it might be a consequence of the nonplanar configuration of the naphthalene molecule may also, we think, be considered out of the question.

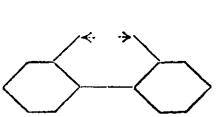
To obtain experimental confirmation of this (although we would not unduly stress the value of such negative evidence) we prepared and examined the corresponding compound in which the nitro-group in the 8-position was lacking, benzenesulphonyl-1-naphthyl-

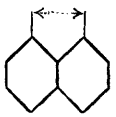
glycine. The brucine salt of this acid unfortunately could not be got to crystallise; quinine, however, gave a crystalline salt, but we could obtain no indication that the acid could be rendered optically active by this alkaloid.

It would seem, therefore, that there is no reasonable alternative to referring the molecular dissymmetry of benzenesulphonylnitronaphthylglycine to its most obvious cause—the restriction of the rotation of the $Ph{\cdot}SO_2{\cdot}N(NO_2){\cdot}CH_2{\cdot}CO_2H$ complex about the bond linking it to the naphthalene nucleus by the obstruction presented by the 8-nitro-group.

The demonstration that this *peri*-disubstitution derivative of naphthalene can exist in optically active modifications evidently serves to confirm the theory that the molecular dissymmetry of the substituted diphenic acids likewise has its origin in steric restriction of rotation.

The naphthalene derivative differs considerably, however, from the diphenic acids in the readiness with which it undergoes autoracemisation; the optical stability of the diphenic acids is much greater (Christie and Kenner, J., 1922, **121**, 614; Bell and Robinson, J., 1927, 2234; Kuhn and Albrecht, *Annalen*, 1927, **455**, 272; **458**, 221). This may be due in part to differences in rigidity of the bonds concerned—in the naphthalene derivative it is a tervalent nitrogen atom that forms the hub of the rotating system—but the chief cause doubtless lies in the fact that the distance between substituent atoms is greater when they are in the naphthalene *peri*-relationship than when in the 6- and 6′-positions (at closest approach) of the diphenyl molecule. Some rough indication of the relationship between these distances may perhaps be obtained by assuming a regular hexagonal arrangement for the carbon atoms of the benzene nucleus. The distances would then be, as the accompanying diagrams show, in the ratio of $1 : \sqrt{3}$, or 1 : 1·73. The temperature





coefficient (for 10°) of the racemisation velocity of the brucine salts in chloroform solution, calculated from the velocity coefficients at 14·8° and 0·6°, was found to be 3·27. This corresponds with a heat of activation of 18,500 cal.

In consequence of their ready autoracemisation the brucine salts of the optically active modifications of the acid are evidently obtained as the result of processes of activation rather than of resolution, similar to those observed, for example, by Pope and

Peachey (P., 1900, **16**, 116) with methylethylpropyltin camphorsulphonate, and by Mills and Bain (J., 1910, **97**, 1866) with the morphine and quinine salts of the oxime of *cyclo*hexanone-4-carboxylic acid.

The acid can also be rendered optically active by brucine in another way in which no separation of a solid phase is involved. When equivalent quantities of brucine and the inactive acid are dissolved separately in chloroform and the two solutions then mixed, the initial lævorotation of the mixture, due to the brucine, is observed to fall gradually to an equilibrium value as shown diagrammatically in Fig. 2, curve III. The amount of change depends on the temperature, being greater at lower temperatures. In an experiment carried out at 1° the lævorotation fell in a little over 1½ hours to 28% of the value first observed. The most probable cause of this mutarotation was partial activation of the acid; though slowness of salt formation in chloroform, which, however, is scarcely to be expected, would give rise to an effect of the kind observed, brucine being much more strongly lævorotatory in the free state than in its salts; slow solvation of the salt also might cause mutarotation. It was possible to show, however, by direct experiment that the phenomenon was actually due to the first of these causes. A chloroform solution of the salt was allowed to attain equilibrium at 0°, and the salt was then decomposed by extracting the solution with dilute sulphuric acid, whereby the brucine was removed and a chloroform solution of the acid was obtained. This solution showed a dextrorotation, similar in magnitude to the fall which had taken place in the lævorotation of the salt, and this rotation gradually fell to zero in accordance with the unimolecular law. The mutarotation must therefore have been due to the establishment of an equilibrium in which an excess of brucine *d*-acid salt was present. The interaction between brucine and the un-nitrated acid, benzenesulphonyl-1-naphthylglycine, was examined in a similar way. Here no trace of mutarotation was observed: the rotation had a constant value which was very nearly the same as the initial value for the brucine salt of the inactive nitro-acid. We regard this difference between the two acids as evidence of some weight that the molecular dissymmetry of the nitro-acid is determined by the nitro-group in the manner suggested and is not due to some other cause.

Since in a solution of the salt the brucine can scarcely have any directive effect on the free acid or on the acid-ion produced by dissociation, it would seem that the inequality of the amounts of the brucine *d*-acid salt and brucine *l*-acid salt present at equilibrium must be due primarily to differences in properties of the undissociated forms of these salts. There must be a difference between the

velocity coefficients of partial racemisation of the undissociated salts, and from the presence of an excess of *d*-acid salt in the equilibrium it is to be inferred that the coefficient for that salt is smaller than that for the brucine *l*-acid salt. The constants of dissociation of the two salts into ions (as well as into acid and base) will also differ to a greater or less extent, for it is evident that the ion of a dissymmetric base may fit more closely to one of the antimeric ions of a dissymmetric acid than to the other. Since the degree of dissociation in chloroform may be assumed to be small, the effect of this on the equilibrium will probably be smaller than that of the inequality of the velocity coefficients of partial racemisation and will be dependent on the relation between the velocity of intertransformation of the *d*- and *l*-free acids and of their ions and the velocities of intertransformation of the undissociated forms of the two salts.* The behaviour of these brucine salts is clearly analogous to that of the hydroxyhydrindamine salts of chlorobromomethanesulphonic acid and chlorobromoacetic acid described by Read and McMath (J., 1925, **127**, 1572; 1926, 2183).

It is evident that the occurrence of molecular dissymmetry dependent on obstructed rotation is also to be expected in other classes of compounds in which similar spatial relationships exist. The investigation of quaternary salts of appropriate 8-substitution derivatives of quinoline is being undertaken from this point of view.

EXPERIMENTAL.

1-Benzenesulphonamido-8-nitronaphthalene (IV).—An excess (nearly 1½ equivs.) of benzenesulphonyl chloride dissolved in anhydrous pyridine was added to a pyridine solution of 8-nitro-1-naphthylamine † (Meldola and Streatfeild, J., 1893, **63**, 1055) and the mixture was left over-night. The liquid was largely diluted with water, made alkaline with sodium hydroxide, filtered, and then acidified with hydrochloric acid. The *benzenesulphonyl* derivative thus precipitated crystallised from alcohol in colourless needles, m. p. 198—199° (Found : C, 58·4; H, 3·6. $C_{16}H_{12}O_4N_2S$ requires C, 58·5; H, 3·7%). Yield, 81%.

* The ratio (p) of the quantities of the *d*- and *l*-acid salts present in solution at equilibrium is easily shown to be given by the equation

$$p = \frac{k_L + a_L(k - k_L)}{k_D + a_D(k - k_D)},$$

where a_D and a_L are the degrees of dissociation of the brucine *d*-acid and *l*-acid salts, k_D and k_L the velocity coefficients of racemisation for the undissociated parts of these salts, and k the velocity coefficient of racemisation for the dissociated part.

† A product melting at 90—91° was found to be sufficiently pure to give a pure benzenesulphonyl derivative.

1-*Dibenzenesulphonamido*-8-*nitronaphthalene*,

$$NO_2{\cdot}C_{10}H_6{\cdot}N(SO_2Ph)_2,$$

was formed as a by-product and was separated on filtering the alkaline solution. It crystallises from much boiling water in short needles, m. p. 199°, mixed m. p. with the monosulphonyl derivative about 170° (Found: S, 13·5. $C_{22}H_{16}O_6N_2S_2$ requires S, 13·7%). The quantity produced was about 7% of the nitronaphthylamine used.

Ethyl N-*Benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate*.—An absolute alcoholic solution of sodium ethoxide (1 equiv.) was added slowly to a suspension of benzenesulphonamidonitronaphthalene in absolute alcohol, and ethyl bromoacetate (slightly more than 1 equiv.) added to the resulting solution of the sodium salt. On cooling after boiling over-night, tufts of short needle-like crystals were formed, which, recrystallised from alcohol, melted at 173° (Found: C, 58·2; H, 4·4. $C_{20}H_{18}O_6N_2S$ requires C, 58·0; H, 4·4%). Yield, 75%.

N-*Benzenesulphonyl*-8-*nitro*-1-*naphthylglycine*.—The ester (12 g.) was dissolved in acetic acid (135 c.c.), dilute sulphuric acid (1 : 12 vols.; 60 c.c.) added, and the mixture kept at the boiling temperature over-night. It was then diluted largely, the *acid* redissolved by adding ammonia, the solution filtered, and the acid precipitated with hydrochloric acid. It crystallised from dilute acetic acid, after being decolorised with charcoal, in needles, m. p. 214° (Found: C, 55·6; H, 3·8; N, 7·1; S, 8·2. $C_{18}H_{14}O_6N_2S$ requires C, 55·9; H, 3·7; N, 7·25; S, 8·2%). Yield of recrystallised product, 81%.

Brucine 1-*Benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate*.—When solutions in acetone of equivalent quantities of the inactive acid and brucine are mixed, the salt of the *l*-acid is deposited after a short time as a fine, heavy powder, m. p. 195—196°. It contains $1H_2O$ (Found: H_2O, 2·1. $C_{41}H_{40}O_{10}N_4S,H_2O$ requires H_2O, 2·25%). Yield, 98 %.

A solution of the salt in chloroform containing 0·378 g. of the monohydrate in 50 c.c. showed at 15·5° the following rotations ($l = 4$), the first observation being made 4 minutes after the salt had been first wetted:

t.	a_{5461}.	*k.*	*t.*	a_{5461}.	*k.*
0	−3·86°	—	13	−0·73°	0·064
3	−2·55	0·064	16	−0·56	0·062
3·5	−2·30	0·066	20·5	−0·39	0·061
4	−2·16	0·067	23·5	−0·33	0·059
5·5	−1·84	0·063	26·5	−0·29	0·057
6	−1·60	0·069	30	−0·27	0·054
7	−1·41	0·068	34·5	−0·23	0·054
8	−1·29	0·065	38	−0·21	0·055
9	−1·13	0·065	48	−0·19	0·054
11	−0·91	0·064	∞	−0·18	—

In this and in the following tables the numbers in the first column give the time (minutes) from the first observation; those in the second column are observed rotations of mercury green light; and those in the third column are calculated with the usual formula for the velocity coefficient of a unimolecular reaction, using decadic logarithms.

Mutarotation of l-*Benzenesulphonyl*-8-*nitro*-l-*naphthylglycine.*—A chloroform solution of the brucine *l*-acid salt containing 0·378 g. of salt in 50 c.c. was extracted twice with dilute (1 : 6) sulphuric acid (30 c.c.) to remove the brucine. The filtered chloroform solution of the acid obtained showed at 14·9° the following rotations ($l = 4$), the first reading having been made 13 minutes after the first wetting of the salt with chloroform :

t.	a_{5461}.	*k.*	*t.*	a_{5161}.	*k.*
0	−3·50°	—	30·8	−1·06°	0·0170
2·2	−3·18	0·0190	37·6	−0·75	0·0180
5	−2·91	0·0161	45	−0·55	0·0182
7	−2·63	0·0179	49·7	−0·46	0·0181
9·3	−2·44	0·0166	54·5	−0·39	0·0179
11	−2·26	0·0174	60·7	−0·30	0·0180
14·4	−2·00	0·0170	71	−0·18	0·0188
20·6	−1·55	0·0173	85·6	−0·15	0·0167
25·5	−1·31	0·0169	∞	−0·02	—

Brucine d-*Benzenesulphonyl*-8-*nitro*-l-*naphthylaminoacetate.* — The brucine salt of the *l*-acid (4 g.) was dissolved in boiling methyl alcohol (400 c.c.) and the solution on cooling deposited the brucine salt of the *d*-acid (3 g.) as colourless needles containing 3 molecules of water of crystallisation (Found : H_2O, 6·4. $C_{41}H_{40}O_{10}N_4S,3H_2O$ requires H_2O, 6·5%). It is soluble in hot acetone and, on standing, the solution deposits the brucine salt of the *l*-acid as a colourless powder, m. p. 195—196°.

A solution of the salt in chloroform containing 0·395 g. of the trihydrate in 50 c.c. showed at 14·8° the following rotations of the mercury green light ($l = 4$), the first observation being made 5 minutes after the salt had been wetted :

t.	a_{5461}.	*k.*	*t.*	a_{5461}.	*k.*
0	+3·25°	—	14·3	+0·31°	0·059
2	+2·43	0·059	21·5	+0·02	0·057
3	+2·04	0·063	26	−0·08	0·059
4	+1·78	0·061	30	−0·11	0·053
5·5	+1·43	0·060	33·5	−0·13	0·055
7·3	+1·03	0·059	36·7	−0·15	0·056
8·5	+0·86	0·061	41	−0·16	0·055
10·7	+0·62	0·059	∞	−0·18	—

On repeating the experiment at a lower temperature (0·6°), the same quantities being used, the following observations of the mutarotation of the salt were made, the first reading being taken 11½ minutes after bringing the salt into contact with chloroform :

t.	a_{5461}.	k.	t.	a_{5461}.	k.
0	+3·85°	—	27	+1·86°	0·0108
2	+3·66	0·0102	32	+1·59	0·0110
3·7	+3·47	0·0115	37·5	+1·34	0·0111
6	+3·30	0·0105	45·8	+1·03	0·0112
8·5	+3·07	0·0109	54·5	+0·80	0·0110
10·5	+2·92	0·0107	64	+0·60	0·0109
14·7	+2·66	0·0102	84	+0·46	0·0093
19	+2·36	0·0104	∞	−0·22	—
23·5	+2·06	0·0107			

Mutarotation of d-*Benzenesulphonyl*-8-*nitro*-1-*naphthylglycine*.—A chloroform solution of the *d*-acid was obtained by removal of the brucine from a solution (50 c.c.) of the brucine *d*-acid salt (0·395 g.) in chloroform by extraction with dilute sulphuric acid. The solution showed at 15·3° the following rotations ($l = 4$), the first having been made 11 minutes after the salt had been wetted :

t.	a_{5461}.	k.	t.	a_{5461}.	k.
0	+4·19°	—	34·9	+0·89°	0·0188
2·7	+3·74	0·0179	45·5	+0·56	0·0185
4·5	+3·47	0·0180	53	+0·35	0·0193
7·3	+3·06	0·0184	61	+0·23	0·0194
10	+2·71	0·0187	69·3	+0·14	0·0195
13·5	+2·30	0·0190	74·5	+0·11	0·0191
16·5	+2·06	0·0184	84·5	+0·04	0·0198
19·7	+1·78	0·0185	∞	−0·05	—
22·5	+1·53	0·0191			
27·7	+1·23	0·0187			

The final slight lævorotation was due to a trace of unremoved brucine.

Activation of the Acid by Brucine in Chloroform Solution.—A solution (25 c.c.) of the inactive acid (0·183 g.) in chloroform and the same volume of a chloroform solution of brucine (0·221 g.) were cooled to 0° and mixed and the mixture was observed in a jacketed 4-dcm. tube, the temperature rising during the experiment from 0·7° to 1·5°. The following readings were made :

t	0	3	8	15	22	25	30
a_{5461}	−0·78°	−0·76°	−0·70°	−0·65°	−0·55°	−0·52°	−0·47°
t	35	42·6	55	68	80	92	∞
a_{5461}	−0·42°	−0·39°	−0·33°	−0·30°	−0·26°	−0·23°	−0·22°

The equilibrium varies considerably with the temperature; when the temperature was allowed to rise to 14° the rotation fell to − 0·43°. The equilibrium rotation is also affected by the addition of an excess of acid; in an experiment carried out at 14·5° with the same quantities as above, an equilibrium rotation of − 0·34° was observed, and this rose to − 0·11° after an additional 0·1 g. of acid had been dissolved in the solution; this may indicate a slight dissociation of the salt in chloroform.

That the rise of rotation was due to the production of an excess of *d*-acid in the solution was proved as follows: A chloroform

solution (50 c.c.) of the inactive acid (0·183 g.) and brucine (0·211 g.) was kept in ice for 3 hours to allow equilibrium to become established and the brucine was then removed as rapidly as possible by extraction with ice-cold dilute sulphuric acid. A little acetone (6 c.c.) was added to keep the acid in solution and the chloroform–acetone solution was observed at 1·2°, the first reading being made 11 minutes after addition of the sulphuric acid. The following observations were made:

t	0	4·3	16	22	32·5
α_{5461}	+0·59°	+0·55°	+0·49°	+0·46°	+0·41°
t	63	93	173	∞	
α_{5461}	+0·37°	+0·33°	+0·24°	−0·01°	

*Ethyl Benzenesulphonyl-*l*-naphthylaminoacetate.*—This was prepared from benzenesulphon-1-naphthylamide (Witt and Schmidt, *Ber.*, 1894, **27**, 2371), which we obtained, however, similarly to the nitro-derivative, from 1-naphthylamine (9·5 g.), benzenesulphonyl chloride (11·8 g.), and pyridine (75 c.c.); m. p. 170—171° (Witt and Schmidt give 166—167°).

Benzenesulphon-1-naphthylamide (9 g.) was dissolved in a solution of sodium ethoxide, made from sodium (0·73 g.) and alcohol (110 c.c.), ethyl bromoacetate (5·4 g.) was then added, and the mixture left over-night. The product, isolated in the same way as the nitro-derivative, formed colourless, flat, rhombic prisms, m. p. 89°; yield of recrystallised substance, 83·5% (Found: S, 8·7. $C_{20}H_{19}O_4NS$ requires S, 8·7%).

*Benzenesulphonyl-*l*-naphthylglycine.*—The hydrolysis of the ester was carried out similarly to that of the nitro-ester. The ester (7·4 g.) was boiled with a mixture of acetic acid (100 c.c.), water (50 c.c.), and dilute sulphuric acid (20 c.c.). The resulting acid, crystallised from dilute acetic acid, formed short needles, m. p. 188—189°; yield, 89% (Found: C, 63·4; H, 4·5; N, 4·4; S, 9·3. $C_{18}H_{15}O_4NS$ requires C, 63·3; H, 4·4; N, 4·1; S, 9·4%).

When equivalent quantities of the acid and quinine dissolved in acetone are mixed, the quinine salt is rapidly deposited in almost theoretical amount. It melts at 230° and is unaltered in melting point after crystallising from a large volume of methyl alcohol. Solutions of this salt in chloroform showed no mutarotation, neither could any indication be obtained that the acid could be activated by brucine. The acid (0·162 g.) and brucine (0·221 g.) were each dissolved separately in chloroform (25 c.c.) and the two solutions were mixed at 0°. On examination of the solution in the polarimeter no mutarotation could be detected, the rotation remaining quite constant at −0·94° at 1°.

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