68. *Optical Resolution of Phenyl* 8-*Carboxy*-1-*naphthyl Sulphoxide. The Prediction of Restricted Rotation in* peri-*Substituted Naphthalenes.*

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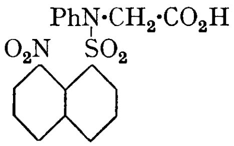
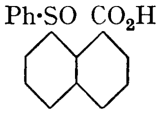
THE existence of stereoisomerism due to restricted rotation has usually been predicted in one of two ways: by the " molecular diagram " method of Mills and Elliott (J., 1928, 1291) and Lesslie and Turner (J., 1932, 2021), in which the atoms are represented as spheres of known radii drawn to scale, or the trigonometrical method of Adams (*J. Amer. Chem. Soc.*, 1930, **52**, 1200), which allows a calculation of the " interference value " by which two groups overlap. Both of these methods are open to criticism, but both have been successfully used for compounds of the diphenyl series. In an attempt to obtain closer concordance between the calculated and the experimental conclusions, Sidgwick (*Ann. Reports*, 1932, **29**, 70; 1933, **30**, 119) has advocated the assumption of an interference envelope around a carbon atom amounting to about 0·5 Å. in extent, although Kleiderer and Adams (*J. Amer. Chem. Soc.*, 1933, **55**, 4220) regard this estimate as excessive. On general grounds it would appear probable that an additional factor varying with the electronic structures of the atoms or groups concerned also enters into the problem.

Unfortunately the above methods are of questionable value when applied to *peri*-substituted naphthalenes, presumably because the distance between the *peri*-carbon atoms is not known with sufficient accuracy. Thus the optical stability of the benzenesulphonyl derivative of 8-nitro-1-naphthylglycine studied by Mills and Elliott proved to be less than had been anticipated from the interference diagram, in which no additional envelope had been assumed. Similarly Steiger (*Bull. Soc. chim.*, 1933, **53**, 1249) has prepared the isomeric compound (I), and by using the envelope method of Sidgwick predicted the existence of comparatively stable, optically active forms. He was not able to resolve the compound, however, nor to detect any mutarotation of the alkaloid salts.

(I.)





(II.)

In the present instance it has been found that phenyl 8-carboxy-1-naphthyl sulphoxide (II) is readily resolvable into highly active enantiomerides, having $[\alpha]_{5463}^{20^\circ} + 605^\circ$ (in acetone). By using the active acid it was considered possible that the fixed centre of asymmetry in the sulphoxide group might result in preferential stabilisation of one of the isomeric forms arising from the restricted rotation of the *peri*-substituents, and so render this type of isomerism the more easily detected.

No definite information could be found in the literature concerning the valency angles in the sulphoxide group, but Bergmann (*Ber.*, 1932, **65**, 457) has deduced values for the sulphone group from dipole moment measurements. Assuming that the angles so obtained also hold without modification for the sulphoxide, it follows that the bonds joining sulphur to the phenyl and naphthyl nuclei enclose an angle of 109°, and those linking sulphur to oxygen and naphthalene make an angle of approximately 112°. On this basis and adopting the atomic dimensions used by Lesslie and Turner (*loc. cit.*) the resulting molecular diagram shows that neither the oxygen atom of the sulphoxide group nor the carbon atom of the benzene ring attached to sulphur is capable of clearing the carboxylic carbon atom. It thus follows that definite evidence of restricted rotation is to be anticipated without any assumption of an atomic envelope. Even if the above angles are given the improbably high value of 120°, the diagram shows that the carboxylic carbon atom is practically in contact with the carbon atom of the benzene ring and that it passes within 0·2 Å. of the oxygen atom of the sulphoxide group. Experiment proved, however, that no trace of mutarotation could be observed with the alkaloid salts of the active acid, and that the free acid was unaffected by heat treatment at 100°.

EXPERIMENTAL.

Resolution of Phenyl 8-*Carboxy*-1-*naphthyl Sulphoxide.*—The inactive sulphoxide (see preceding paper), m. p. 200—201°, was dissolved in boiling ethyl acetate (1·12 g. in 80 c.c.), and to it was added a boiling solution of 0·8 g. of brucine in 6 c.c. of ethyl acetate. On cooling, 1·18 g. of salt were obtained, and this was resolved by continued fractionation from chloroform until a sample (0·6 g.) was obtained having $\alpha_D = + 9{\cdot}62^\circ$ ($l = 1$; $t = 20^\circ$; $c = 3{\cdot}458$). A solution of the active salt in pyridine showed no signs of mutarotation.

Liberation of the Active Acids.—A chloroform solution of the above *d*-salt was repeatedly extracted with dilute hydrochloric acid until completely free from brucine, the large volume of acid required (300 c.c.) being very noticeable (cf. Harrison, Kenyon, and Phillips, J., 1926, 2088). The chloroform was removed in a vacuum, and the *d*-acid then separated in hexagonal prisms, m. p. 200—201° (this is the same as that of the inactive material). In moist chloroform, the acid had $[\alpha]_D^{20^\circ} = + 380{\cdot}5^\circ$ and in acetone $[\alpha]_{5463}^{20^\circ} = + 605^\circ$.

The lævo-form of the acid was obtained in a slightly less pure state by removing ethyl acetate from the mother-liquor resulting from the first crystallisation of the brucine salt. The recovered salt (0·7 g.) was decomposed as above without further purification, and yielded an acid of $[\alpha]_{5463}^{20^\circ} = - 500^\circ$ in acetone.

Dispersion.—The graph of $1/\alpha$ and λ^2, plotted from the figures given below, is a straight line, showing that the compound has simple dispersion over the wave-length examined.

Rotation of the d-*acid in acetone.*

$t = 20°$. $l = 1$. $c = 0{\cdot}2000$.

λ, Å	6563	5893	5463	4861	4358
α	+0·76°	+0·98°	+1·21°	+1·67°	+2·38°
$[\alpha]$	+380°	+490°	+605°	+835°	+1190°

The above solutions of the active acid showed no perceptible mutarotation, nor was any racemisation observed when the acid was heated for 1½ hours in glacial acetic acid solution at 94°.

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