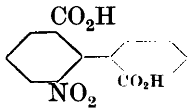
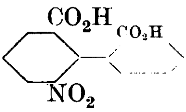
CCXVII.—*Investigations in the Diphenyl Series. Part VI. The Configuration of Diphenyl Derivatives.*

By FRANK BELL and PERCY HARRY ROBINSON.

THE normal and the acid quinine salt of 4-nitrodiphenic acid can be crystallised without showing any sign of resolution. 6-Nitrodiphenic acid is readily resolvable, and the optical activity is apparently of a normal degree of permanence. This striking difference in behaviour of two such similarly constituted acids can be accounted for only by the assumption that the presence of the nitro-group in position 6 is essential to prevent the interchange of the enantiomorphs (I) and (II). The fact that it has so far proved impossible to prepare tetranitrofluorenone (III) or tetra-

(I.)

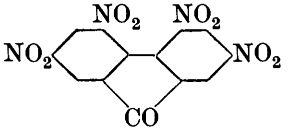


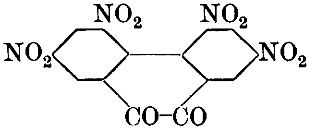


(II.)

nitrophenanthraquinone (IV), whilst diphenic acid and benzil readily yield tetranitro-derivatives (V and VI), could be anticipated from this "obstacle" theory. Moreover, it would be expected that diphenic acids unsubstituted in the 6 : 6′-positions should form anhydrides, in spite of many statements to the contrary (*e.g.*, Adkins, Steinbring, and Pickering, *J. Amer. Chem. Soc.*, 1924, **46**, 1918; Underwood and Kochmann, *ibid.*, p. 2069). It is now found that 4-nitro- and 4 : 4′-dinitro-diphenic acids yield anhydrides under suitable conditions; an attempt to prepare the anhydride of 6-nitrodiphenic acid was, however, unsuccessful. According to the present hypothesis, a diphenyl derivative with two sufficiently large groups in the 2- and 2′-positions, that is, groups which, owing to size or electrical character, are unable to pass the 6′- and 6-positions, respectively, should be capable of resolution (VII and VIII). Suitable derivatives for testing this point have not yet been obtained. The dicamphorsulphonyl derivative of 2 : 2′-diaminodiphenyl was a viscous mass, and the camphor(and bromocamphor)-sulphonates of several 2 : 2′-derivatives of tetramethylbenzidine proved unsuitable for crystallisation. Menthyl hydrogen and di-*d*-β-octyl diphenates were not obtained in a solid condition, but dimenthyl and *d*-β-octyl hydrogen diphenates were crystallised from several solvents without showing any indication of resolution. The resolvability of such compounds is therefore still an open question.

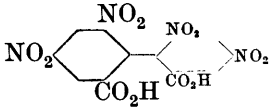
(III.)

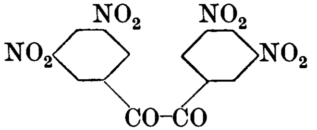




(IV.)

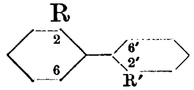
(V.)

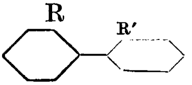




(VI.)

(VII.)





(VIII.)

EXPERIMENTAL.

Optically Active 6-*Nitrodiphenic Acid.*—Morphine hydrate (7·7 g.) was added to a boiling solution of 6-nitrodiphenic acid (7·2 g.) in alcohol (500 c.c.). The precipitated salt (7·8 g.; m. p. 224°) (Found: C, 63·6, 63·7; H, 5·4, 5·3%. $[\alpha]_{5461}$ −87·5° in pyridine,

$c = 4{\cdot}99$; $l = 2{\cdot}0$) was extracted repeatedly with boiling alcohol, and the product ($[\alpha]_{5461}$ −91·5° in pyridine; $c = 4{\cdot}81$; $l = 1{\cdot}0$) was dissolved in a large bulk of boiling water and decomposed with a slight excess of hydrochloric acid. The solution was extracted with ether, and the extract was repeatedly washed with dilute hydrochloric acid, dried with sodium sulphate, and then evaporated to dryness. The residue was further purified by reprecipitation from solution in ammonia by hydrochloric acid. The *d* + *dl*-6-nitrodiphenic acid melted indefinitely at 240—245°, and had $[\alpha]_{5461}$ +56·2° ($c = 5{\cdot}91$; $l = 1{\cdot}0$) in absolute ethyl alcohol.

The alcoholic mother-liquor containing the more soluble salt ($[\alpha]_{5461}$ −84·6° in pyridine solution; $c = 5{\cdot}0$, $l = 1{\cdot}0$) was concentrated and poured into dilute hydrochloric acid, and the precipitated *l* + *dl*-acid recovered as described above. The *l* + *dl*-acid melted at 239—245° and had $[\alpha]_{5461}$ −66·7° in ethyl alcohol ($c = 5{\cdot}07$; $l = 1{\cdot}0$). Quinine hydrogen 6-nitrodiphenate was equally suitable and after one crystallisation gave on decomposition the *d* + *dl*-acid with $[\alpha]_{5461}$ +62°.

The acid ($[\alpha]_{5461}$ −66·7°) was dissolved in boiling acetic acid and allowed to crystallise slowly. The acid which crystallised had $[\alpha]_{5461}$ −57·6°, whilst the mother-liquor, on evaporation to dryness, gave an acid with $[\alpha]_{5461}$ −60·3°. Solutions of four different samples of acid having $\alpha_{5461} = -1{\cdot}12°$, −2·90°, −3·38°, and +3·32° respectively in absolute ethyl alcohol were left in corked flasks at laboratory temperature for 6 months; they then had the values $\alpha_{5461} = -1{\cdot}11°$, −2·92°, −3·24°, and +3·24°, respectively.

Dichloride of 4-*Nitrodiphenic Acid.*—The acid was added slowly to warm thionyl chloride, and the resultant solution evaporated to dryness in a vacuum. The residual solid crystallised from benzene–light petroleum as a pale yellow powder, m. p. 90—92° (Found: C, 52·6; H, 2·1. $C_{14}H_7O_4NCl_2$ requires C, 51·8; H, 2·2%).

4-*Nitrodiphenic Anhydride.*—Thionyl chloride was added drop by drop to 4-nitrodiphenic acid, and the resultant solution evaporated to dryness in a vacuum. The residual solid crystallised from acetic anhydride in small needles, m. p. 205—207° (Found: C, 62·8; H, 2·4. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6%).

4 : 4′-*Dinitrodiphenic Anhydride.*—4 : 4′-Dinitrodiphenic acid (1·9 g.) and its acid chloride (2·1 g.) were heated under reflux with acetic anhydride for several hours. On cooling, the liquid filled with small prisms, which sintered at 125° and melted at 232—234° (Found: C, 51·9; H, 3·0; loss on drying to constant weight at 130°, 24·3. $C_{14}H_6O_7N_2,C_4H_6O_3$ requires C, 51·9; H, 2·9; loss, 24·5%). After crystallisation from benzene, the anhydride formed

a powder, m. p. 233—235° (Found : C, 54·1 ; H, 2·1. $C_{14}H_6O_7N_2$ requires C, 53·5 ; H, 1·9%).

Dichloride of 6-Nitrodiphenic Acid (compare 4-nitrodiphenic acid).—This was a pale yellow powder, m. p. 87° (Found : C, 51·8 ; H, 2·2. $C_{14}H_7O_4NCl_2$ requires C, 51·8 ; H, 2·2%). Attempts to prepare the anhydride of this acid resulted in viscous products only.

2 : 2′-*Dibenzamidotetramethylbenzidine*, prepared by interaction of the components in pyridine, separated from benzene as a crystalline powder, m. p. 201° (Found : C, 75·9 ; H, 6·1. $C_{30}H_{30}O_2N_4$ requires C, 75·3 ; H, 6·3%), and 2 : 2′-*di*-p-*toluenesulphonylamidotetramethylbenzidine*, similarly prepared, crystallised from alcohol in leaflets, m. p. 203° (Found : C, 62·8 ; H, 5·8. $C_{30}H_{34}O_4N_4S_2$ requires C, 62·3 ; H, 5·9%).

2-*Aminotetramethylbenzidine*, prepared by the same method as 2 : 2′-diaminotetramethylbenzidine, crystallised from alcohol in plates, m. p. 138° (Found : C, 74·8 ; H, 7·8. $C_{16}H_{21}N_3$ requires C, 75·3 ; H, 8·2%).

d-β-*Octyl hydrogen diphenate*, prepared from diphenic anhydride and *d*-β-octanol in the usual way, formed large needles, m. p. 70—73°, when crystallised from light petroleum (Found : equiv., 349. $C_{22}H_{26}O_4$ requires equiv., 354). It was unchanged in rotatory power ($[\alpha]_D$ +51° ; $c = 5·0$; $l = 1·0$ in absolute ethyl alcohol) by recrystallisation from light petroleum or aqueous ethyl alcohol.

Dichloride of Diphenic Acid.—Diphenic acid (20 g.) was dissolved in warm thionyl chloride (100 c.c.), and the excess of thionyl chloride then removed in a vacuum. The residue was boiled with benzene, and the solution was filtered from diphenic anhydride (2—3 g.) and diluted with light petroleum. A yield of 80% of the dichloride, m. p. 97°, was obtained.

Dimenthyl Diphenate.—(*a*) A solution of equivalent quantities of menthol and diphenic acid dichloride in ether was boiled for 15 hours in the presence of potassium carbonate. Water was then added and the ethereal layer was separated, dried, and evaporated. The oily residue was dissolved in light petroleum, from which it separated in plates (yield 30%), m. p. 123—126°, $[\alpha]_{5461}$ −118·6°, which, after recrystallisation from light petroleum, had m. p. 126° and $[\alpha]_{5461}$ −120·4° in chloroform solution ($c = 4·88, l = 2·0$) (Found : C, 78·5 ; H, 8·3. $C_{34}H_{46}O_4$ requires C, 78·7 ; H, 8·9%). (*b*) A solution of equivalent quantities of menthol and diphenic acid dichloride in pyridine, after standing for 12 hours, was poured into water, and the resulting precipitate crystallised from light petroleum. Successive crops had $[\alpha]_{5461}$ −119·6°, −119·2°, −119·0° (yield 60%), and after recrystallisation from light petroleum or acetic acid the ester had $[\alpha]_{5461}$ $-120{\cdot}3°$ ($c = 4{\cdot}94$, $l = 2{\cdot}0$).

One of the authors (F.B.) is in receipt of a grant from the Department of Scientific and Industrial Research.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, May* 11*th*, 1927.]