20. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part VII. A Further Resolution of 4 : 6 : 4′-Trinitrodiphenic Acid.*

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The benzene compounds of the optically active 4 : 6 : 4′-trinitrodiphenic acids are sparingly soluble in benzene, whereas the inactive complex cannot be prepared. This fact makes it possible to effect further resolutions of the active acids obtained by means of quinine.

In a previous communication (Part II; J., 1935, 1856) it was shown that the resolution of 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acid with brucine (Lesslie and Turner, J., 1930, 1758) is incomplete, but that a further separation of inactive from lævo-acid could be effected by repeated crystallisation from benzene. Owing to the fact that the benzene addition compound of the inactive acid is less soluble than that of the lævo-acid, the mother-liquors became relatively richer in the active form.

We have now examined another case in which it has been possible to effect a further resolution of an internally impeded nitrodiphenyl derivative by means of benzene. Christie and Kenner (J., 1926, 474) resolved 4 : 6 : 4′-trinitrodiphenic acid with quinine and obtained isomers having $[\alpha]_{5461}$ + 23·1° and − 15·1° in ether. We have obtained similar values for the quinine-resolved forms; we find, however, that repeated crystallisation of them from benzene–ether under the conditions described below yields a series of less soluble but more optically active complexes. Allowance being made for the benzene content of the addition compounds, acids were ultimately obtained with $[\alpha]_{5461}$ + 47·8° and − 37·0° in ether. The relation between the solubilities of the active and the inactive benzene complexes is the reverse of that found in the previously recorded case, in which the inactive complex was less soluble than the active form.

EXPERIMENTAL.

4 : 6 : 4′-Trinitrodiphenic acid was prepared and resolved with quinine as described by Christie and Kenner (*loc. cit.*). These workers obtained the *d*-acid as an oil which solidified only after standing for several months. We find that rapid crystallisation can be brought about by solution in chloroform and evaporation to dryness, the operation being repeated 3 or 4 times. Rapid solidification of the *l*-acid, which is much harder to obtain than the *d*-isomer (Christie and Kenner, J., 1923, **123**, 785), was brought about in the same manner. Optically active benzene complexes, $2C_{14}H_7O_{10}N_3,C_6H_6$, were prepared by dissolving specimens of quinine-resolved acid of varying rotatory power in mixtures of benzene and ether (2 : 1 by volume), from which the ether was slowly distilled on the water-bath until the first signs of crystallisation were seen. The distilling flask was then rapidly cooled, and the crystals of benzene complex filtered off (Found for the *d*-acid *complex* having $[\alpha]_{5461}$ 23·14° in ether, m. p. 176° and after resolidification, m. p. 279—281° : C, 49·7; H, 2·5. $2C_{14}H_7O_{10}N_3,C_6H_6$ requires C, 49·1; H, 2·4%).

The molecular rotations of the crystals obtained after successive recrystallisations A, B, C, D, by the above technique and of the solids left after evaporation of mother-liquors were determined in dry ether in a 2 dcm. tube for the line λ = 5461 A. The results are collected in the table, in which the values for $[\alpha]_{5461}$ refer to free acid, having been corrected for the benzene content of the complexes by multiplying the observed rotations by the factor 1·11.

	I.	II.	III.	IV.	V.	VI.	VII.
A. Original complex	24·6°	26·9°	26·9°	13·3°	13·1°	15·3°	−14·7°
B. Recrystallisation of A	42·2	41·5	47·1	36·0	37·0	29·6	−33·0
B′. Mother-liquor	12·2	—	—	—	—	8·0	—
C. Recrystallisation of B	—	48·2	48·1	45·2	—	—	−37·0
C′. Mother-liquor	—	5·0	—	—	—	—	—
D. Recrystallisation of C	—	—	—	48·0	—	—	—

In order to avoid complicating the presentation of the data in the table, actual rotations and the concentrations at which they were determined have been omitted. The measured values for the rotations ranged from 0·35° to 0·9° at concentrations c = *ca.* 0·4 g.-mol./l., giving the molecular rotations recorded in the table.

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