433. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons. Part II. The System 2 : 4-Dinitro-2′-methyldiphenyl-6-carboxylic Acid–Benzene.*

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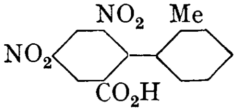
IT was shown in Part I (this vol., p. 580) that methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate interacts at a finite rate with indene in carbon tetrachloride, the recognition and estimation of a compound in solution being possible owing to the fact that the combined indene does not react with bromine. Aromatic hydrocarbons that can be estimated by bromine titration are, however, limited in number, and other methods are needed by which interaction in liquid polynitro-compound–hydrocarbon systems can be investigated. We have therefore examined the possibility, suggested by certain incidental observations by Lesslie and Turner (J., 1930, 1758), of utilising a change in optical activity produced by the combination of an active nitro-compound with a hydrocarbon. The above authors describe solid complexes containing the active 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acids (I) (2 mols.) and benzene (1 mol.) with rotations in alcohol of $[\alpha]_{5791} = \pm 7\cdot8^\circ$, those of the uncombined acids being $[\alpha]_{5791} = \pm 18\cdot7^\circ$. They also state that the complex is recoverable unchanged from alcoholic solution, and that after the removal of the benzene by solution in aqueous alkali, the free acids have their original rotations of $[\alpha]_{5791} = \pm 18\cdot7^\circ$ in alcohol. They found that the racemic acid crystallised from benzene without combining with the latter. It would thus appear that we have here a complex with a characteristic property in solution and suitable for study by polarimetric methods.

(I.)



Repetition of the work of Lesslie and Turner with our particular object in view showed that the racemic acid does, in fact, form solid complexes with benzene in the molar ratios 2 : 1 and 1 : 1, the former complex being much less soluble than the corresponding substance containing active acid. Moreover, although we confirmed the figures for the resolution of the acid by means of brucine, which was used by Lesslie and Turner ($[\alpha] = \pm 18\cdot7^\circ$), yet we found that the use of *d*-α-phenylethylamine * gave an acid of much higher rotation, *viz.*, $+ 89\cdot8^\circ$ in alcohol (all rotations were measured for the line 5791 in alcohol unless otherwise stated). Whether or not this corresponds to an optically pure substance we cannot say with certainty, for we have not attempted to obtain the *l*-form. Examination of the work of Lesslie and Turner shows that they were justified in regarding their resolution as complete, since (*a*) the two pure isomerides were obtained and led to two acids having the same numerical rotation, and (*b*) they obtained the same result by resolution with brucine in acetone as by using the ammonium salt of the acid and brucine hydrochloride in aqueous solution.

We find, moreover, that the most completely resolved *d*-acid we have been able to obtain has the same rotation in alcohol as it has when measured in the same solvent in the form of its benzene complex. Removal of the solvent and the benzene yields the free acid unchanged in rotation. Mixtures of active and inactive acids, such as that obtained by resolution with brucine, give, on recrystallisation from benzene, complexes richer in the less soluble inactive complex than the original mixtures. In all such cases the rotations per g. of acid per c.c. are the same as those of the acids obtained after removal of alcohol and benzene. We must therefore conclude, either that the complex does not exist in appreciable amount in solution, or else that the rotatory power of the acid is the same per g. per c.c. whether it is attached to benzene or not. In either case optical activity is useless as a property by which the complex can be investigated in solution.

We find that inactive and *d*-2 : 4-dinitro-2-methyldiphenyl-6-carboxylic acids form solid complexes with water (1 : 1) and with methyl alcohol (1 : 1). With these substances also the activity of the acid is unchanged by complex formation.

The fact that the inactive is less soluble than the active benzene complex means that the former must be a true racemate. It also makes it possible to bring about a further resolution of a mixture of active and inactive acids by crystallising it from benzene. Since the racemic complex has a finite solubility, it is clearly not possible to obtain a mother-liquor entirely free from racemate. The limit of separation appears to be reached with acids of rotation $[\alpha] = 77\cdot8^\circ$; such acids have been obtained at the end of several independent separations. It is possible that similar sparingly soluble racemates are formed with benzene by other resolvable nitro-diphenyl derivatives, and that further resolutions can be effected by crystallisation from benzene. One example has already been found in this

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* Ingersoll and Littler (*J. Amer. Chem. Soc.*, 1934, **56**, 2123) have drawn attention to the suitability of this active base for resolving internally impeded nitrodiphenic acids.

laboratory by Dr. G. Sixsmith, who has effected a further resolution of 4 : 6 : 4′-trinitrodiphenic acid. Resolved by quinine, this substance has $[\alpha]_{5461} = -24{\cdot}6°$ in ether, but after recrystallisation from benzene, the mother-liquors yielded an acid of rotation $[\alpha]_{5461} = -42{\cdot}2°$ in ether.

EXPERIMENTAL.

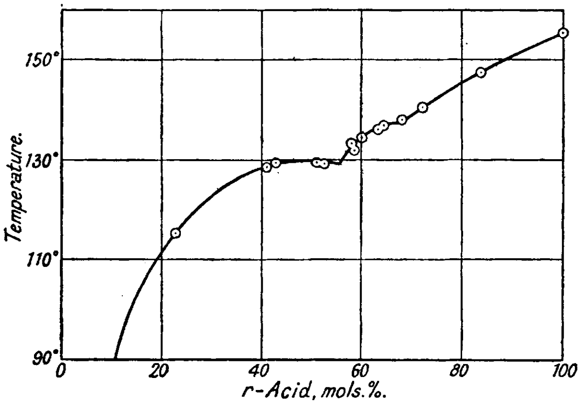
Preparation of 2 : 4-*Dinitro*-2′-*methyldiphenyl*-6-*carboxylic Acid*.—This substance was prepared by a slight modification of the method of Lesslie and Turner (*loc. cit.*). Equivalent quantities of methyl 2-chloro-3 : 5-dinitrobenzoate (26 g.) and *o*-iodotoluene (25 g.) were melted together until a homogeneous liquid was obtained (*ca.* 90°). 26 G. of copper-bronze (Hopkin and Williams) were then added, and the temperature raised slowly (1° per min.), with constant stirring, to 115—120°. Reaction now set in, the liquid becoming viscous, with formation of copper halides. The temperature was raised slowly to 160° and kept there for 2 hours. The cooled mass was extracted by boiling five times with acetone for 15 minutes. After the combined extracts had been boiled with animal charcoal for ½ hour, the acetone was removed, and the brown residue triturated with a little methyl alcohol, in which the coloured impurities were soluble. After filtration, the crude ester (yield, 75%) was twice recrystallised from methyl alcohol (pale yellow needles, m. p. 138·5°).

The ester (10 g.) was hydrolysed by 5 minutes' boiling with methyl-alcoholic sodium hydroxide (25 c.c. of 2*N*-sodium hydroxide, 50 c.c. of water, 300 c.c. of methyl alcohol, giving a homogeneous solution at the b. p.), and the mixture poured into about 2 l. of water, and kept until the oily acid had solidified; yield, 90%; m. p. 156° (from ligroin).

The Ullmann condensation with the methyl ester instead of the ethyl ester (used by Lesslie and Turner, *loc. cit.*) proceeded more smoothly and the product was much easier to work up. The alkaline hydrolysis was also a definite improvement on the method employed by the above authors.

Solid–liquid Equilibria in the System r-2 : 4-*Dinitro*-2′-*methyldiphenyl*-6-*carboxylic Acid–Benzene*.—Weighed quantities of the *r*-acid and pure benzene were sealed into bulb tubes, and the temperatures at which the last trace of solid remained in equilibrium with liquid were observed in a variable thermostat. The data below were obtained, and are plotted in the figure: *C* is the composition in mols. % of *r*-acid of the liquids that are in equilibrium with solid at temperatures *T*°.

T	5·5°	115·3°	128·5°	129·5°	129·6°	129·3°	133·3°	131·9°
C	0·0	22·9	41·0	42·8	51·0	52·5	57·9	58·5
T	134·6°	136·2°	137·1°	138·3°	140·6°	147·8°	155·5°	
C	59·9	63·2	64·3	67·9	72·0	83·7	100·0	



The shape of the temperature–composition curve indicates the existence of two solid complexes, containing *r*-acid and benzene in the molar ratios 1 : 1 and 2 : 1 and melting at about 128° and 138° respectively.

Crystallisation of the *r*-acid from benzene gives monoclinic crystals of the 2 : 1 complex (Found: C, 59·9; H, 4·0; equiv., 339. Calc. for $2C_{14}H_{10}O_6N_2,C_6H_6$: C, 59·8; H, 3·8%; equiv., 341). The m. p. of these crystals when heated in the ordinary m. p. tube is 154—156°, *i.e.*, that of the free acid. No fusion occurs when capillary tubes containing the crystals are dipped into the oil-bath at successive temperatures below 156° (" rapid heating "), and it would thus appear that the benzene of crystallisation is driven off before fusion can occur. In a sealed capillary tube, however, the m. p. is 138—140°.

Resolution of r-2 : 4-*Dinitro*-2′-*methyldiphenyl*-6-*carboxylic Acid*.—The *l*-acid obtained by the use of brucine had [α] − 19·4° (*c* = 1·61), which is near the value [α] ± 18·7° found by Lesslie and Turner (*loc. cit.*); m. p. 156°. The *d*-acid was obtained by means of *d*-α-phenylethylamine of [α] + 40·4° and b. p. 98°/47 mm. To a solution of 23·9 g. of the *r*-acid in 85 c.c. of acetone, a solution of 9·6 g. of the active base in 15 c.c. of acetone was added. The salt (18·3 g.) that separated on boiling was filtered off from the cold solution and digested with successive lots of about 2 parts by weight of boiling acetone for ¼ hour each time, the extracts being filtered in the cold. This treatment was continued until further extraction did not alter the rotation of the salt, eight extractions yielding 8·6 g. of pure *d*B,*d*A material; pale yellow needles, m. p. 218°; [α] = + 57·1° in acetone (*c* = 1·12).

The salt was decomposed by adding 4 c.c. of concentrated hydrochloric acid to a suspension in hot water, whereupon the acid separated as a yellow oil, which solidified on cooling with ice The solid was filtered off, dissolved in aqueous ammonia, again filtered, and treated with dilute sulphuric acid. The liberated acid was extracted with ether, dried over anhydrous sodium sulphate and, after removal of the ether, caused to crystallise by heating on the water-bath and scratching; m. p. 135°; [α] = + 89·1° (*c* = 0·8).

The active acid is extremely soluble in benzene and cannot be crystallised from it. The benzene complex was obtained by the evaporation of a benzene solution at room temperature; the viscous oil that remained solidified on scratching; m. p. 134°; " rapid heating " m. p. *ca.* 120° (decomp.) (Found : equiv., 340. Calc. for $2C_{14}H_{10}O_6N_2,C_6H_6$: equiv., 341).

Active Complexes with Benzene.—A number of partly resolved specimens of 2 : 4-dinitro-2′-methyldiphenyl-6-carboxylic acid were crystallised from benzene. The rotations of the benzene complexes (2 mols. acid : 1 mol. benzene) were determined in alcohol, the benzene being then removed by solution in aqueous ammonia, precipitation with hydrochloric acid, and extraction with ether. After drying, the ether was evaporated, the free acid obtained through the ammonium salt as before, and its rotation measured. The results are given below. The rotations in col. 3 are those per g. of *acid* per c.c. per dm., allowance being made for the benzene present in the complexes. The equivalent weights were determined as checks on the compositions of the complexes and acids by titration with standard baryta.

[α] for original acid.	[α] for acid from mother-liquor.	[α] for acid in complex.	*c*, complex.	Equiv. of complex.	Acid from complex.		
					[α].	*c*.	Equiv.
− 13·7°	− 56·8°	− 3·4°	1·6	337	− 3·0°	1·3	302
− 13·5	− 48·9	− 1·9	1·1	337	− 1·6	1·8	304
− 48·9	− 69·3	− 5·0	0·4	339	− 4·9	0·4	300
+ 43·0	+ 70·2	+ 7·0	0·9	338	+ 6·8	1·5	301
+ 43·0	+ 71·0	+ 6·4	1·4	343	+ 6·6	1·7	303
+ 60·9	+ 76·1	+ 17·7	0·9	303	+ 18·2	0·8	303
+ 70·1	+ 72·1	+ 62·3	0·5	339	+ 61·2	0·5	301
+ 73·2	+ 77·7	+ 46·5	0·7	—	+ 48·0	0·6	—
+ 89·8	—	+ 90·2	0·8	340	+ 89·6	0·6	302

Calculated equivalent weight of free acid = 302.
" " " complex = 341.

Comparison of cols. 3 and 6 shows that the optical activities of the partly resolved acids are very nearly the same whether they are measured in the form of complex or not. The data in the bottom line refer to the completely resolved *d*-acid, the benzene complex having been obtained by the evaporation of a benzene solution at room temperature in a vacuum desiccator. Comparison of cols. 1, 2, and 3 shows that the solid benzene complex separating from a benzene solution of partly resolved acid is richer in the less soluble racemate, and that the mother-liquor is richer in active acid. It is thus possible to effect a further resolution by the successive separation of solid complex and evaporation of the mother-liquors.

Further Resolution of Partly Resolved Acids by Crystallisation from Benzene.—Two examples of the procedure and results are given. (1) 1·2 G. of brucine-resolved acid ([α] = − 19·4°, *c* = 1·61) were dissolved by warming in benzene. On cooling, 0·9 g. of complex separated ([α] = − 1·9°, calc. on acid content, *c* = 1·1), and the mother-liquor contained 0·3 g. of acid having [α] = − 48·9° (*c* = 1·23). 0·2 G. of this acid, crystallised from 5 c.c. of benzene, gave 0·12 g. of complex ([α] = − 5·6°, calc. on acid content, *c* = 0·4), and 0·08 g. acid having [α] = − 69·3° (*c* = 0·46) in the mother-liquor.

(2) 1·4 G. of acid ([α] = + 43·0°, *c* = 1·28), crystallised from 25 c.c. of benzene, gave 0·8 g. of complex ([α] = + 6·4°, calc. on acid content, *c* = 1·4), and 0·6 g. of acid ([α] = + 70·5°, *c* = 1·05) from the mother-liquor. 0·5 G. of the latter acid, from 5 c.c. of benzene, gave 0·2 g. of complex and 0·48 g. of acid with [α] = + 73·2° (*c* = 0·97). A further recrystallisation of this acid gave 0·07 g. of complex ([α] = + 46·5°, *c* = 0·7) and 0·41 g. of an active acid with [α] = + 77·7° (*c* = 1·3).

Complex Formation with Water and with Methyl Alcohol.—When the *r*- and the *d*-acid are liberated in water from their salts, they solidify as *monohydrates*. They are obtained in good crystalline form by the addition of water to their ethyl-alcoholic solutions of the acids and allowing them to stand (Found, in air-dried crystals, for *r*-acid; C, 52·57; H, 3·92; for *d*-acid : C, 52·78; H, 3·80. $C_{14}H_{10}O_6N_2,H_2O$ requires C, 52·5; H, 3·7%); m. p.'s : *r*-acid, *ca.* 120° (decomp.) on rapid heating; *d*-acid, 80—85° (decomp.). Rotation of the *d*-acid hydrate : [α] = + 84·6° (*c* = 0·6), which gives [α] = + 90·1° for the acid present in the hydrate; for the original acid, [α] = + 89·8° (*c* = 0·4).

Crystallisation of the *r*- and the *d*-acid from methyl alcohol yields well-defined monoclinic crystals of 1 : 1 *complexes* containing the alcohol; m. p.'s : *r*-acid, 130—135° (decomp.) on rapid heating; *d*-acid, 90—100° (decomp.) on rapid heating (Found, for *r*-acid complex : C, 54·08; H, 4·19; for *d*-acid complex : C, 53·82; H, 4·27. $C_{14}H_{10}O_6N_2,CH_3{\cdot}OH$ requires C, 53·9; H, 4·2%).

A specimen of *d*-acid ([α] = + 89·8°, *c* = 0·6) was converted into hydrate and into the methyl alcohol complex. The rotations per g. of *acid* in the two cases were [α] = + 90·1° (*c* = 0·4) and [α] = + 89·5° (*c* = 0·5) respectively; the rotation of the recovered free acid was [α] = + 89·8° (*c* = 0·4).

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Note by E. E. TURNER.—Mr. Hammick very kindly sent the above paper to me before presenting it for publication. Reference to our original laboratory record showed that our resolution with brucine had all the characteristics of a thoroughly satisfactory resolution, since the two diastereoisomeric brucine salts were crystallised until the rotation was constant, and gave rise to acids having $[\alpha]^{20°}_{5791}$ ± 18·7°. The *d*-acid of this rotation was crystallised from benzene, and both the first crop and *the total solid obtained by evaporation of the mother-liquor* had the same rotation, *viz.*, $[\alpha]^{20°}_{5791}$ + 7·8°. Boiling the first crop with alkali to remove benzene of crystallisation gave an acid which, without any purification, had $[\alpha]^{20°}_{5791}$ + 18·6°. In our hands, therefore, crystallisation of what is now to be regarded as an impure *d*-acid led to no separation.