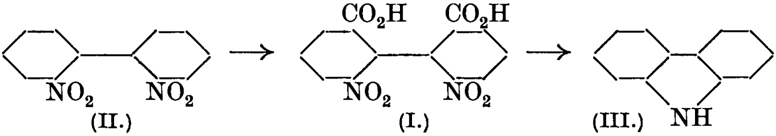
XCIII.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VI. β-Dinitrodiphenic Acid; its Constitution and Resolution into Optically Active Components.*

By George Hallatt Christie, Albert Holderness, and James Kenner.

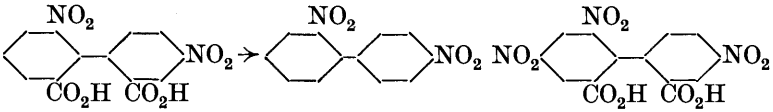
β-Dinitrodiphenic acid, originally obtained by Schultz (*Annalen*, 1880, **203**, 108), is prepared by oxidation of the dinitroquinone produced, with its 2 : 7-isomeride, when phenanthraquinone is dinitrated. This acid has been regarded as a 6 : 6′-dinitrodiphenic acid (I) since it was examined by Schmidt and Kämpf (*Ber.*, 1903, **36**, 3745), who claimed to have converted it by distillation with dry sand into 2 : 2′-dinitrodiphenyl (II). " Wir erhielten dabei sehr wenig eines schwer löslichen Körpers vom Schelzpunkt ca. 240° (wahrscheinlich Dinitrofluorenon) und als Hauptproduct ca. 1 g. einer leichter löslichen Verbindung vom Schmelzpunkt 124—6° Dieselbe wurde genau verglichen mit o-o′-Dinitrodiphenyl, das wir uns nach den Angaben von Ullmann (*Ber.*, 1901, **34**, 3803) bereitet hatten. Beide Präparate zeigten in allen Eigenschaften völlige Uebereinstimmung."



(II.) (I.) (III.)

The conversion of the corresponding diaminodiphenic acid into carbazole (III) recorded at the same time supplied confirmatory, though obviously less conclusive, evidence in support of the very precise statement quoted, so that Kenner and Stubbings (J., 1921, **119**, 593) felt justified in regarding their synthetic 6 : 6′-dinitrodiphenic acid as a stereoisomeride of Schultz's acid when it was found that the two differed in properties.

The observations recorded by Christie and Kenner (this vol., p. 470) rendered it necessary, however, to re-examine Schultz's acid. The outcome of our experiments, carried out under somewhat different conditions from those used by Schmidt and Kämpf, was that in place of 2 : 2′-dinitrodiphenyl, m. p. 124°, 2 : 4′-dinitrodiphenyl (IV), m. p. 93°, was obtained, so that Schultz's acid would be 4 : 6′-dinitrodiphenic acid (V) :



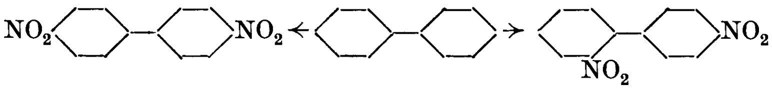
(V.) (IV.) (VI.)

This result in itself is no more definite than that claimed by Schmidt and Kämpf, and perhaps somewhat less so if regard be paid to the considerably lower melting point of our product. Further, we were unable to detect any other product than 2 : 7-dinitrophenanthraquinone when 2-nitrophenanthraquinone was nitrated under the conditions for converting phenanthraquinone into 2 : 7- and what the above result would indicate to be 2 : 5-dinitrophenanthraquinones. The following considerations will, however, probably be held to be decisively in favour of our view rather than that of Schmidt and Kämpf :

(1) The same 2 : 4 : 7-trinitrophenanthraquinone is formed from the dinitroquinone in question and 2 : 7-dinitrophenanthraquinone, and attempts to prepare 2 : 4 : 5 : 7-tetranitrophenanthraquinone by further nitration have been unsuccessful (Christie and Kenner, *loc. cit.*).

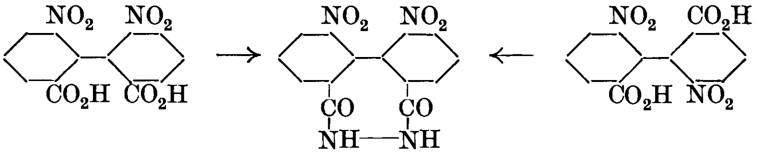
(2) It would be expected that if 4 : 5- and 2 : 7-dinitroquinones are produced from phenanthraquinone by nitration, some of the 2 : 5-isomeride also would be formed. But only two products have been observed.

(3) Dinitration of diphenyl furnishes the 2 : 4′- and 4 : 4′-derivatives as chief, if not sole products (Fittig, *Annalen*, 1862, **124**, 276) :



(4) The amino-group in 6-aminodiphenic acid is not diazotisable, but one of those in the diamino-acid, for which the 4 : 6′-constitution is now advocated, is diazotisable (Schmidt and Schall, *Ber.*, 1905, **38**, 3769). In previous papers, it was shown that such 6-amino-acids readily form phenanthridone derivatives. The accounts in the literature of the acids referred to make it not impossible that they may in reality be phenanthridone derivatives, as has been shown to be the case with other compounds similarly derived (compare Christie and Kenner, *loc. cit.*).

Kenner and Stubbings (*loc. cit.*) converted their synthetic 6 : 6′-dinitrodiphenic acid into a " hydrazide," and suggested that this derivative might furnish a means of converting the new acid into its supposed stereoisomeride :



This idea gained further credence when a "hydrazide" was prepared from the β-acid, and behaved similarly when heated. However, the "hydrazides" from the two sources differed in their behaviour towards acetic anhydride and were readily converted by oxidative hydrolysis with fuming nitric acid according to a procedure very briefly indicated by Curtius and Foersterling (*J. pr. Chem.*, 1895, **51**, 371), into acids melting, respectively, at 300° and 249—253°, as compared with 300° and 258—259° recorded for the original acids. Clearly, then, no interconversion of the acids is to be achieved through the hydrolysis of the "hydrazides" as intermediates.

β-Dinitrodiphenic acid, if it is the 4 : 6′-derivative, is closely related in constitution to 4 : 6 : 4′-trinitrodiphenic acid (VI), of which the resolution into optically active components through the agency of brucine has been described (Christie and Kenner, J., 1923, **123**, 779).

Similar experiments with the β-acid showed that it furnished a uniform brucine salt, but on the other hand two distinct quinine salts were obtained which were easily separable owing to their different solubilities in alcohol. From these salts, solutions of optically active acids and their sodium salts were prepared in the usual manner. A second illustration is therefore provided of an acid capable of existence in an asymmetric form when only three of the four 2, 6, 2′, and 6′-positions are occupied by substituents.

Since the stereoisomerism of β- and 6 : 6′-dinitrodiphenic acids, which originally inspired the experiments on their resolution, would now seem to be non-existent, it is perhaps desirable to record the fact that the resolution of the β-acid has been repeated with freshly prepared materials by Mr. V. M. Trikojus, B.Sc., in the laboratories of the University of Sydney.

EXPERIMENTAL.

β-Dinitrodiphenic acid, prepared by Schmidt and Kämpf's method (*loc. cit.*), was further characterised by the preparation of its *chloride*, colourless, rectangular plates, m. p. 120°, from benzene–light petroleum (Found : N, 7·9. $C_{14}H_6O_6N_2Cl_2$ requires N, 7·6%) ; its *ethyl* ester, colourless, pentagonal prisms, m. p. 114—115° (Found :

N, 7·3. $C_{18}H_{16}O_8N_2$ requires N, 7·2%); and its *amide*, colourless, hexagonal prisms, m. p. 247·5°, from dilute alcohol (Found : N, 17·2. $C_{14}H_{10}O_6N_4$ requires N, 16·9%).

Degradation of β-*Dinitrodiphenic Acid to Dinitrodiphenyl.*—A mixture of β-dinitrodiphenic acid with fine dry sand was distilled under the conditions described by Schmidt and Kämpf (*loc. cit.*); the yellow solid distillate, in agreement with their observation, melted at 240—245° after being extracted with alcohol, but the extract, which would have contained any dinitrodiphenyl which had been distilled, left practically no residue on distillation. The following modified procedure was therefore employed. A finely ground mixture of the acid (1 g.) with Naturkupfer C (0·1 g.) (compare Sabatier and Mailhe, *Compt. rend.*, 1914, **159**, 217) was distributed by stirring over sufficient glass wool to fill an Anschütz flask of 75 c.c. capacity. This flask was connected through a larger one to a filter-pump. When the mixture was very gradually heated in an oil-bath under a pressure of 30 mm., a reaction of explosive violence occurred at 285°. After the dense white vapours had subsided, both the distillate and the blackened residue were extracted with boiling alcohol. The extract was evaporated, diluted with water, and treated with cold dilute ammonia; a small solid residue was obtained. By solution in benzene of the product (0·45 g.) from eight such experiments, dark, insoluble matter was removed, and fairly homogeneous, transparent crystals closely resembling those of 2 : 4′-dinitrodiphenyl were obtained. After further purification by solution in light petroleum–benzene to remove a small quantity of less soluble, granular material, the product melted at 93°. A mixture with authentic 2 : 4′-dinitrodiphenyl melted at the same temperature, even after fusion and resolidification. A mixture with 2 : 2′-dinitrodiphenyl, m. p. 124°, shrank at 68—70°, was largely molten at 90°, but not completely so until 118°. After resolidification, the opaque mass commenced to clear at 90°, was almost all molten at 100—103°, and entirely liquid at 105°. The product was therefore 2 : 4′-dinitrodiphenyl.

For the preparation of the compound from diphenyl, light petroleum (b. p. 70—80°) was much more effective in the late stage of purification than the methyl alcohol recommended by Fittig (*Annalen*, 1862, **124**, 276).

Nitration of 2-*Nitrophenanthraquinone.*—After 2-nitrophenanthraquinone (10 g.) had been boiled under reflux with nitric acid (135 c.c.; *d* 1·5) and sulphuric acid (17 c.c.) for 30 minutes, the mixture was poured into water. From the solution of the precipitate in glacial acetic acid (1200 c.c.), 2 : 7-dinitrophenanthraquinone (8·9 g.), m. p. 301°, was deposited, whilst 0·4 g., m. p. 280—290°, and 0·1 g., m. p. 225—293°, were recovered on concentrating the liquors to 200 c.c. and 50 c.c., respectively.

Hydrolysis of the "Hydrazides" of β- and 6 : 6′-Dinitrodiphenic Acids.—The "hydrazide" of β-dinitrodiphenic acid was prepared from the chloride in the manner already described for the corresponding derivative of 6 : 6′-dinitrodiphenic acid (Kenner and Stubbings, *loc. cit.*). It separates from acetone–light petroleum in small, colourless prisms, m. p. 294—295° (decomp.) (Found : N, 16·7. $C_{14}H_8O_6N_4$ requires N, 17·0%), and does not reduce Fehling's solution. Repeated but unsuccessful attempts were made to prepare a well-defined acetyl derivative of the "hydrazide" corresponding to that previously described as having been obtained from the "hydrazide" of 6 : 6′-dinitrodiphenic acid. The compound (0·25 g.) was heated with nitric acid (4 c.c.; *d* 1·5) for 75 minutes at 100°; the solution then deposited dinitrodiphenic acid, m. p. 300—301°, on dilution with water (15 c.c.).

The "hydrazide" of 6 : 6′-dinitrodiphenic acid was obtained in colourless prisms, m. p. 310° (decomp.), by crystallisation from acetone–light petroleum. The acid formed by hydrolysis with fuming nitric acid at 100° for 40 minutes was isolated by evaporation of the liquors at the ordinary temperature in an exhausted desiccator over sodium hydroxide. Its melting point, 249—253°, was not depressed when the acid was mixed with 6 : 6′-dinitrodiphenic acid.

Resolution of β-Dinitrodiphenic Acid into Optically Active Components.—A solution of the acid (2 g.) and hydrated brucine (5·61 g.) in boiling water (1050 c.c.) deposited, on cooling, fern-shaped sprays of irregular plates (3·9 g.), m. p. 209° (decomp.). By successive concentration to 575 c.c., 200 c.c., and 50 c.c., further crops of 2·2 g., m. p. 206° (decomp.), 0·3 g., m. p. 209° (decomp.), and 0·4 g., m. p. 207° (decomp.), were respectively obtained. The salt was hydrated [Found: H_2O, 4·2. $C_{60}H_{60}O_{16}N_6,2\frac{1}{2}H_2O$ requires H_2O, 3·9%. Found, for the salt dried at 130° : N, 7·8. $C_{12}H_6(NO_2)_2(CO_2H)_2,2C_{23}H_{26}O_4N_2$ requires N, 7·5%]. For 1·5% solutions in 10*N*-acetic acid of the anhydrous salt from each of the first two fractions, $[\alpha]_D = -13{\cdot}29°$ and $-13{\cdot}31°$, respectively. It was therefore not surprising that a solution of the sodium salt of the acid prepared from the brucine salt was inactive.

But when boiling solutions of the acid (4 g.) in alcohol (100 c.c.) and of quinine hydrate (9·2 g.) in alcohol (80 c.c.) were mixed, colourless, rectangular plates (5·7 g.), m. p. 178—179° (decomp.), separated on cooling; no further crystallisation occurred on concentration. On evaporating the alcohol, an oil remained, which was obtained in a solid condition by precipitation with light petroleum from its solution in benzene. The melting point of the plates was unchanged after recrystallisation (Found : C_2H_6O, 2·45. $C_{54}H_{56}O_{12}N_6,\frac{1}{2}C_2H_6O$ requires C_2H_6O, 2·4. Found, for the salt dried at 130° : N, 8·6. $C_{54}H_{56}O_{12}N_6$ requires N, 8·6%). For a 1·43% solution of the dried salt in chloroform, $[\alpha]_D^{16^\circ} = -218{\cdot}1^\circ$.

The more soluble salt melted at first at about 93°, but at 162—163° after being heated to constant weight at 120° (Found : N, 8·55. $C_{54}H_{56}O_{12}N_6$ requires N, 8·6%). For a 1·44% solution of the dried salt in chloroform, $[\alpha]_D^{16^\circ} = -62{\cdot}10^\circ$.

d-β-*Dinitrodiphenic acid*, obtained from the less soluble quinine salt by treatment with hydrochloric acid, melted at 296°, whilst a mixture of the acid with the racemic acid melted over the range 285—293°.

For a 0·96% solution of the acid in ether, $[\alpha]_D^{14^\circ} = +26{\cdot}90^\circ$, whilst for a 0·66% solution of the sodium salt in water, $[\alpha]_D^{15^\circ} = -186{\cdot}4^\circ$.

l-β-*Dinitrodiphenic acid*, obtained from the more soluble quinine salt, also melted at 296°. For a 0·92% solution of the acid in ether, $[\alpha]_D^{15^\circ} = -26{\cdot}46^\circ$, and for a 1·29% solution of the sodium salt in water, $[\alpha]_D^{15^\circ} = +179{\cdot}4^\circ$.

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