

## 11. 1 : 3 : 5 : 7-Tetranitronaphthalene and the Isomeric Tetranitro-derivatives obtained from 2 : 6-Dinitronaphthalene by Nitration.

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An account is given of the preparation of 2 : 6-dinitronaphthalene from 2 : 6-dihydroxynaphthalene and of the production, isolation and properties of the three tetranitronaphthalenes obtained from the former by nitration. Two of these, the 1 : 3 : 5 : 7- and 1 : 2 : 6 : 8-derivatives, furnish 3 : 5-dinitrobenzoic acid on oxidation and, as an aid in ascertaining the orientation of the nitro-groups in the destroyed rings, use is made of a relation between symmetry and melting point which is found to obtain in typical series of naphthalene derivatives containing identical substituents.

ALTHOUGH the dinitronaphthalenes obtained by nitration are the 1 : 8- and 1 : 5-dinitro-, and the trinitronaphthalenes the 1 : 3 : 8- and the 1 : 3 : 5-trinitro-derivatives, the three tetranitronaphthalenes hitherto identified—the 1 : 3 : 5 : 8-; 1 : 3 : 6 : 8-; and 1 : 4 : 5 : 8-isomerides—are exclusively 1 : 8- or *peri*-derivatives. In the second of these, the radicals in each ring occupy respectively the 1 : 3- or *meta*-positions but are so distributed that two of them are also associated in the *peri*-position. It was of interest to ascertain whether the tetranitro-derivative, 1 : 3 : 5 : 7-, in which the *meta*-arrangement holds but the *peri*-association is absent, could be prepared.

Of the methods tried, mention may be made of three. 1 : 3-Dinitronaphthalene (Hodgson and Walker, *J.*, 1933, 1620) was found to be useless as a source, since it furnished 1 : 3 : 8-trinitronaphthalene—a *peri*-derivative—on nitration. And the attempt to prepare the 1 : 3 : 5 : 7-isomeride from diacetyl-1 : 5-diaminonaphthalene failed owing to the sparing solubility of this substance and that of its nitration products in a wide range of solvents, which made isolation and identification impossible. Further, the highly nitrated derivatives were not hydrolysed by acid to give nitro-amines but decomposed, yielding intractable substances.

Thereupon, attention was concentrated on 2 : 6(3 : 7)-dinitronaphthalene, hitherto prepared only from 6-nitro-2-aminonaphthalene in small amount by the diazonium reaction (Vesely and Jakeš, *Bull. Soc. chim.*, 1923, 33, 942), in view of the probability that with the two  $\beta\beta$ -nitro-groups already in place, further substitution would be directed to the more reactive  $\alpha$ -positions. And since no instance had as yet been found among the mono-, di- and tri-nitronaphthalenes of the entry of a nitro-group into a position contiguous with that of one already present in the molecule,\* there was good reason to expect that the dinitration of this  $\beta\beta$ -compound would occur in the desired 4 : 8(1 : 5)-positions which alone were free from that disability.

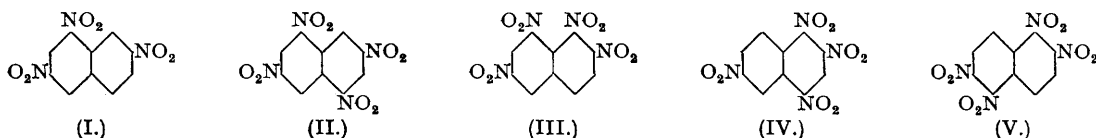
Search for an alternative source of the 2 : 6-dinitro-derivative led to the adoption of 2 : 6-diaminonaphthalene obtained by the amination of 2 : 6-dihydroxynaphthalene by Bucherer's method (*J. pr. Chem.*, 1904, 69, 47). This diamine, by interaction of its tetrazo-compound with nitrite in the presence of cupro-cupric sulphite (cf. Hantzsch and Blagden, *Ber.*, 1900, 33, 2554), furnished 2 : 6-dinitronaphthalene in good yield, the final stage leading to the tetra-derivative being completed by dinitration with nitrosulphuric acid. The solid which

\* Will's [ $\delta$ -] tetranitronaphthalene is not the 1 : 2 : 5 : 8- but the 1 : 4 : 5 : 8-isomeride (Dimroth and Ruck, *Annalen*, 1925, 446, 123) and Dhar's claim to have isolated the 1 : 2 : 6 : 8-isomeride is inadmissible, as no evidence is adduced to show that the product was a definite substance or could have the constitution assigned (*J.*, 1920, 117, 1002).

was removed by filtration from the cold nitration mixture proved to be a single substance (m. p. 260°) and until the precipitate, which separated from the acid filtrate on dilution with much water, was found to contain in addition two isomeric tetranitronaphthalenes (m. p. 138° and 215°) it was regarded as the 1:3:5:7-compound. The total yield of tetranitronaphthalenes obtained from 200 g. of the dinitro-derivative amounted to 149.3 g. or 52.8% of that calculated, the distribution being (i) m. p. 260°, 121.9 g. or 43%; (ii) 138°, 23.8 g. or 8.4%; (iii) m. p. 215°, 3.6 g. or 1.3%. In the final mother-liquors there was also a dark red, highly soluble substance which stained fingers and paper, dissolved with intensification of colour in alkali, and was precipitated from solution in an amorphous condition on acidification: it may have been a polynitronaphthol.

Inasmuch as 1:3:5:7-tetrachloronaphthalene is known (Turner and Wynne, J., 1941, 253), no great difficulty was anticipated in finding out whether, as suggested on p. 33, the tetranitro-derivative, m. p. 260°, has this constitution. But the anticipation proved to be ill-founded, for, although the derived tetramine by octazotisation, followed by interaction of the product with cuprous chloride, gave in the second and third operations, minute yields of a tetrachloronaphthalene which did not depress the m. p., 179°, of the reference compound, yet efforts made some months later failed to repeat these results. Moreover, interaction of the tetranitro-derivative with phosphorus pentachloride—a method applicable to 1:5- and 1:8-dinitronaphthalene—gave inseparable mixtures of tetra- with penta-chloronaphthalene. And oxidation with dilute nitric acid, which yielded 3:5-dinitrobenzoic acid as sole product, ceased to furnish the desired confirmation when it was found that the isomeride, m. p. 138°, under similar conditions gave this acid in addition to its parent, 3:5-dinitrophthalic acid.

Of the four  $\alpha\alpha\beta\beta$ -tetranitro-derivatives obtainable from 2:6-dinitronaphthalene—three of them doubtless arising from 1:3:7-trinitronaphthalene (I) formed as intermediate product—(II) and (III) alone can furnish 3:5-dinitro-phthalic or -benzoic acid as an oxidation product and are therefore assignable to the compounds,



m. p. 260° and 138°. The wide difference between these m. p.'s is thus associated with configurations which differ in respect of symmetry—(II) being centrosymmetrical and (III) asymmetrical.\* That this association is not fortuitous is evident when, for example, the ten members of representative series of naphthalene di-derivatives of the type  $C_{10}H_8R_2$  are grouped with their respective m. p.'s under the three headings (A) those without symmetry, (B) those with a plane of symmetry, (C) those having a centre of symmetry.

With few exceptions, italicised in the table—the most noteworthy of which being those found among the highly polar dihydroxynaphthalenes—it can be seen that none of the m. p.'s in (B) is lower than any of the four

Melting Points of Naphthalene Di-derivatives ( $X = C_{10}H_6$ ).

		$XCl_2$ .	$XBr_2$ .	$XMe_2$ .	$X(NO_2)_2$ .	$X(NH_2)_2$ .	$X(NHAc)_2$ .	$X(OH)_2$ .	$X(OAc)_2$ .	$X(CN)_2$ .	$X(CO_2Me)_2$ .
A	1:2	35°	68°	oil	158°	98°	234°	103°*	105°	190°	85°
	1:3	61	64	oil	145	96	263	124	56	179	—
	1:6	49	61	oil	162	86	257	137	73	211	98
	1:7	64	75	oil	156	118	213	178	108	167	90
B	1:4	68	83	6	132	120	304	176	129	208	67
	1:8	88	109	63	173	67	—	140	148	232	104
	2:3	120	140	104	171	194	247	161	—	251	47
	2:7	114	141	97	234	166	254	190	136	267	135
C	1:5	107	131	80	216	190	360	265	160	263	119
	2:6	135	158	111	279	216	†	222	175	293	186

\* Fieser and Hartwell (*J. Amer. Chem. Soc.*, 1935, **57**, 1485).

† Obtained by Friedländer and Lucht (*Ber.*, 1893, **26**, 3033) but m. p. not recorded.

in (A) and that throughout with only one exception, itself also centrosymmetrical, the 2:6-compound in each series has the highest m. p. If among tetranitro-derivatives a corresponding relationship between symmetry and m. p. may be assumed, the assignment of (II) to the compound of the higher m. p. 260° becomes inevitable.

Support for this view, but again lacking absolute proof, is furnished by the crystallographic examination of the three tetranitronaphthalenes, m. p. 260°, 215° and 138°. For that of the first two we are indebted to Miss M. J. Boyes-Watson and for the third to Miss E. M. Davidson of the Crystallographic Laboratory. From their reports, it is clear that, whereas the molecule of the isomeride, m. p. 260°, is most probably centrosymmetrical, that of each of the others is of the lowest possible symmetry. As this evidence excludes (V), which is centrosymmetrical, from consideration, (IV) may be tentatively assigned to the isomeride, m. p. 215°.

\* The reference here is to the two-dimensional symmetry of the structural formulæ as usually written and not to the symmetry of the molecules represented by those formulæ.

X-Ray data.	M. p. 260°.	M. p. 138°.	M. p. 215°.
Symmetry	Orthorhombic—pseudocubic bipyramids	Monoclinic	Orthorhombic—plate-like crystals
Cell size	$a = 10.3 \text{ \AA}$ . $b = 11 \text{ \AA}$ . $c = 10 \text{ \AA}$ .	$a = 27.50 \text{ \AA}$ . $b = 9.63 \text{ \AA}$ ; $\beta = 93^\circ$ $c = 17.1 \text{ \AA}$ .	$a = 10.3 \text{ \AA}$ . $b = 12.3 \text{ \AA}$ . $c = 18.0 \text{ \AA}$ .
Axial ratio	$a : b : c = 0.934 : 1 : 0.909$	$a : b : c = 2.86 : 1 : 1.78$	$a : b : c = 0.833 : 1 : 1.46$
No. of molecules per unit cell	4	16	8
Space group	P bcm	P $2_1/a$	P cab

M. p. 260°. Since there are 4 molecules per cell, they must occupy special positions in the unit cell and probably lie on centres of symmetry. The molecule seems to be centrosymmetrical.

M. p. 138°. There is every indication from X-ray and optical data that the molecules lie in the  $ac$  plane, giving a layer lattice. There is no sign whatever that the molecules possess any symmetry.

M. p. 215°. Since there are 8 molecules per cell, they must occupy general positions in the unit cell. The molecule seems to be asymmetrical.

In the light of these relationships and of such chemical evidence as has been forthcoming, we see no reason to doubt that the tetranitronaphthalene, m. p. 260°, is the 1 : 3 : 5 : 7-derivative we set out to prepare.

The directive influence of the  $\beta\beta$ -radicals on the positions assumed by the entering  $\alpha$ -nitro-groups in the production of (II) would seem to be exerted in accordance with the first of two well-defined "laws" of substitution in the naphthalene series, *viz.*, inhibition of entry into any position contiguous with one already occupied by an  $\alpha$ - or  $\beta$ -nitro-group already present. But in that of (III), the second "law" would seem to be operative, *viz.*, predilection for entry into the *peri*-position relatively to an  $\alpha$ -nitro-group already present. If the yields of (II) and (III) afford evidence of the relative strength of these directive influences, that of "inhibition" is predominant in the dinitration of 2 : 6-dinitronaphthalene.

#### EXPERIMENTAL.

1 : 3-Dinitronaphthalene, when oxidised with dilute nitric acid ( $d$  1.16) at 200°, gave as sole product 3 : 5-dinitrobenzoic acid, m. p. 203°, which did not depress the m. p. of an authentic specimen (Found : C, 39.7; H, 2.1; N, 13.7. Calc. for  $C_7H_4O_6N_2$  : C, 39.6; H, 1.9; N, 13.2%). Its isolation in place of the expected 3 : 5-dinitrophthalic acid is to be ascribed to the well-known loosening effect of *ortho-para*-nitro-groups, which in this case led to the elimination of the 2-carboxyl radical. Nitration with a 67% excess of nitrosulphuric acid converted 1 : 3-dinitronaphthalene (3 g.), suspended in sulphuric acid (30 g.), into the 1 : 3 : 8-trinitro-derivative (1.5 g.), which, crystallised from acetone, had m. p. 216—220°.

2 : 6-Dihydroxynaphthalene was obtained in the first instance from Schäffer acid (2-naphthol-6-sulphonic acid) by fusion with caustic potash. Later, we were indebted to Messrs. Imperial Chemical Industries (Dyestuffs) Ltd. for a generous supply of the substance which greatly facilitated the progress of the investigation. Before use, the pale brown powder, m. p. 208—210°, was converted into the diacetyl derivative, m. p. 173°, and this in turn hydrolysed by dilute alkali in a nitrogen atmosphere, a colourless product being obtained which crystallised from water in large, thin scales, m. p. 222° (in a vacuum). For conversion into the diamino-compound, 20 g. were heated in a rotating autoclave at 140° during 6 hours, with 400 c.c. of 40% ammonium sulphite solution mixed with 260 c.c. of 20% aqueous ammonia, the solid product being washed first with water, then with 100 c.c. of 5% caustic soda solution, and again with water. Next, suspended in hot water, it was dissolved by adding hydrochloric acid, the solution being made acid to brilliant-green as indicator, then decolourised by animal charcoal, and the base precipitated by the minimum of caustic soda solution. It crystallised from a 50% aqueous pyridine solution in microscopic needles, m. p. (in a vacuum) 217—219°. The yield amounted to 16 g. Addition of hydrochloric acid in excess (40 c.c.) to the decolourised solution precipitated the dihydrochloride in beautiful needles (Found : N, 12.1. Calc. for  $C_{10}H_{10}N_2 \cdot 2HCl$  : N, 12.1%).

From the diamionaphthalene, the 2 : 6-dinitro-compound was prepared by a method based on that by which Hantzsch and Blagden obtained 2-nitro- from 2-amino-naphthalene (*loc. cit.*). First, the diamine (20 g.) in fine powder was dusted into concentrated sulphuric acid (100 g.) and vigorously stirred until all was dissolved at 20—30°. Solid nitrosylsulphuric acid (40 g.), previously washed free from liquid by acetic acid, was then added in one quantity at 15° and, when it had dissolved, acetic acid (140 c.c.) was added slowly at 25—30°, stirring being continued during  $\frac{1}{2}$  hour at this temperature. A test sample when added to a little ice should then give a clear solution and show excess of nitrous acid with starch-iodide paper. From the solution, cooled at 5° and vigorously stirred, the tetrazonium compound was precipitated by alcohol (600 c.c.), added very slowly, particularly at first, to prevent the temperature from rising above 20°. Left in the ice-bath until precipitation was complete, the product collected on a filter and washed with alcohol was light brown, but in water rapidly became dark. Its conversion into the dinitro-derivative was effected by suspending finely ground cuprocupric sulphite (80 g.) in a solution of sodium nitrite (400 g.) in water (2 l.) and adding with vigorous stirring the tetrazonium compound freshly dissolved in water. After the rapid evolution of nitrogen had ceased, the whole was warmed on the steam-bath, filtered, washed, and the residue warmed with 2% sulphuric acid until nitrous fumes were no longer observed. Collected on a filter, the red residue, washed finally with alcohol and dried in a desiccator, was ground to a fine powder and sublimed at 230° rising to 270° under 15 mm. The yellow sublimate was crystallised from acetic anhydride; it formed long yellow needles, m. p. 279°, the yield amounting to 10—12 g., whereas Veselý and Jakeš describe it as forming orange-red serrated scales, m. p. 268° (Found : C, 55.5; H, 3.0; N, 13.1. Calc. for  $C_{10}H_6O_4N_2$  : C, 55.0; H, 3.0; N, 12.9%).

(i) 1 : 3 : 5 : 7-Tetranitronaphthalene was obtained by stirring finely powdered 2 : 6-dinitronaphthalene (20 g.) into concentrated sulphuric acid (300 c.c.) at 10°, then adding to the suspension fuming nitric acid (100 c.c.) at such a rate that this temperature was not exceeded, and leaving the mixture overnight. Gradually warmed to 80° in the course of  $\frac{1}{2}$  hour and maintained at that temperature for a similar period, the product, rendered ice-cold, was collected on a sintered funnel, washed with concentrated sulphuric acid, then with water and finally with alcohol. From acetic anhydride, it formed orange-yellow, orthorhombic, pseudocubic bi-pyramids, sparingly soluble in the usual solvents, m. p. 260° with decomposition at 263—265° in sealed or open capillary tube (Found : C, 39.1; H, 1.5; N, 13.7. Calc. for  $C_{10}H_4O_8N_4$  : C, 39.0; H, 1.3; N, 13.2%). The yield amounted to 9.6 g. On oxidation with dilute nitric acid ( $d$  1.16) at 200°, it gave a product from which 3 : 5-dinitrobenzoic acid, m. p. 203°, which did not depress the m. p. of an authentic specimen, was the only substance isolated (Found : C, 39.6; H, 2.2; N, 13.4%).

The product obtained by heating it (1.2 g.) with phosphorus pentachloride (4 g.) and oxychloride (4 c.c.) at 180—200° during 15—30 minutes gave on distillation with steam a chloro-derivative (0.23 g.) crystallising from alcohol in slender needles, m. p. 133—134°, which on analysis proved to be a mixture of tetra- with penta-chloronaphthalene in varying proportion—in one case the Cl found was as high as 57.2%—but inseparable either by fractional crystallisation or fractional distillation with steam.\*

1 : 3 : 5 : 7-Tetra-aminonaphthalene.—When the finely ground tetranitro-compound (5 g.) was washed by alcoholic hydrogen chloride (10 c.c.) into a warm solution of stannous chloride (60 g.) in the same solvent (60 c.c.), vigorous action occurred, which was completed by heating the mixture on a steam-bath for  $\frac{1}{2}$  hour. After the solid product, dissolved in hot water (100 c.c.), had been freed from tin by means of an excess of 30% caustic soda solution, the precipitated amine (2.8 g.) forming yellow crystals was washed with water and dried in a vacuum desiccator. It was only sparingly soluble in most solvents, best in hot aqueous pyridine, and in solution rapidly became black owing to oxidation. The tetrahydrochloride formed colourless needles (Found: C, 36.1; H, 5.1; N, 16.6; Cl, 42.2. Calc. for  $C_{10}H_{12}N_4 \cdot 4HCl$ : C, 35.9; H, 4.8; N, 16.8; Cl, 42.5%).

For conversion of the tetramine into tetrachloronaphthalene, Schoutissen's method (*J. Amer. Chem. Soc.*, 1933, **55**, 4535) was followed in the main, the octazotisation being effected by dissolving the hydrochloride (2 g.) in syrupy ortho-phosphoric acid ( $d$  1.75; 70 c.c.), adding concentrated sulphuric acid (6 c.c.) to the solution cooled in a freezing mixture, and then, slowly, at  $-5^\circ$  a solution of sodium nitrite (2.5 g.) in concentrated sulphuric acid (14 c.c.) with continuous stirring. On completion of the addition, the temperature was allowed to rise to 15—20° and  $\frac{1}{2}$  hour later the reddish mixture was tested for excess of nitrite, which should be present in small amount. Urea (2.5 g.), finely powdered, was then dusted in and, when all effervescence had ceased, the solution was slowly added to a well-stirred solution of cuprous chloride (5.2 g.) in concentrated hydrochloric acid (90 c.c.) cooled in ice, the reaction being completed by raising the temperature slowly to 30° and later to the boiling point. After filtration, the residue, rendered alkaline with caustic soda and distilled with steam, furnished a product (*ca.* 3 mg.) which crystallised from aqueous alcohol in very slender needles, m. p. 178—181°, and when ground with an authentic specimen of 1 : 3 : 5 : 7-tetrachloronaphthalene, gave a mixture which fused at 177—180°, solidified at 177° and then melted at 177—180°.

On repetition of the process, a slightly larger yield of the product was obtained (*ca.* 5.5 mg.) which on analysis gave Cl, 54.1% (Calc. for  $C_{10}H_4Cl_4$ : Cl, 53.4%). But five attempts to confirm these results, made some months later when corroboration of the constitution had been sought in vain by other methods (p. 34), furnished products (3—5, but in one case 10 mg.) the m. p.'s of which were successively 146°, 138°, 148°, 141°, and 145°, raised by 10—15° after admixture with equal weights of 1 : 3 : 5 : 7-tetrachloronaphthalene. It would therefore seem that the earlier results must have depended on some small manipulative detail which later was overlooked.

The precipitate obtained by pouring the acid filtrates and washings collected from the dinitration of 2 : 6-dinitronaphthalene (200 g.) was pale yellow when dry (81 g.). On extraction with boiling acetone (700 c.c.), a grey residue was left (11.6 g.) sparingly soluble in the ordinary solvents but easily in boiling nitrobenzene, from which almost the whole (10.1 g.) separated on cooling in crystals (m. p. 259°) characteristic of 1 : 3 : 5 : 7-tetranitronaphthalene.

From the hot acetone solution, on the addition of sufficient hot water to induce faint opalescence, a separation in very small scales, m. p. 141—180°, was obtained (17.9 g.) which except for a small amount, m. p. *ca.* 207°, was soluble in benzene and crystallised therefrom in short brittle needles (m. p. 116—120°). Further addition of water to the acetone filtrate gave an ill-defined, pale red separation, m. p. 155—168° (31.5 g.), the red filtrate from which, after removal of the acetone by distillation, deposited an oil solidifying over-night to a red, microcrystalline solid (6.8 g.). By fractional crystallisation of these separations, mainly by the aid of acetic anhydride, acetic acid, benzene-ligroin or nitrobenzene, it proved possible to isolate a further amount of the 1 : 3 : 5 : 7-isomeride (15.8 g., making 25.9 g. in all); a second tetranitronaphthalene, m. p. 138° (23.8 g.), more soluble in most solvents than the foregoing; and a third (3.6 g.), the most soluble of all, which crystallised from alcohol in very pale yellow, four-sided tablets, m. p. 215°. Unexpectedly, the 1 : 3 : 5 : 7-isomeride was found in each of the main fractions and its complete separation from the third, m. p. 215°, proved particularly troublesome.

(ii) 1 : 2 : 6 : 8-Tetranitronaphthalene, m. p. 138°, is more soluble in benzene than its isomerides and crystallises therefrom or from benzene-ligroin with 1 mol. of "benzene of crystallisation" in clusters of needles, m. p. 92°, which is lost on exposure to the air (Found:  $C_8H_6$ , 20.5. Calc. for  $C_{10}H_4O_8N_4 \cdot C_6H_6$ :  $C_8H_6$ , 20.2%). It is moderately soluble in the ordinary solvents, crystallises from acetic anhydride in pale brown, monoclinic needles, frequently twinned, and dissolves only very sparingly in petrol or chloroform (Found: C, 39.2; H, 1.4; N, 18.2. Calc. for  $C_{10}H_4O_8N_4$ : C, 39.0; H, 1.3; N, 18.2%). When cooled below its m. p., it solidifies as a clear glass, unless while still fused it is sown at *ca.* 90—100° with a crystal, and it does not begin to decompose below 230°.

On oxidation with dilute nitric acid ( $d$  1.16) at 190—200°, it gave a product from which both 3 : 5-dinitrophenthalic acid, m. p. 226° (Found: C, 37.9; H, 1.9; N, 10.9. Calc. for  $C_8H_4O_8N_2$ : C, 37.5; H, 1.6; N, 10.9%), and 3 : 5-dinitrobenzoic acid, m. p. 201—202° (Found: N, 13.7. Calc. for  $C_7H_4O_8N_2$ : N, 13.2%), were isolated, the latter of which did not depress the m. p. of an authentic specimen. When heated with phosphorus pentachloride (4 g.) and some oxychloride (4 c.c.) at 180° during 20 minutes, it gave a product (1.2 g.) which on distillation with steam yielded a chloro-derivative, m. p. 125—127° (Found: Cl, 50.6. Calc. for  $C_{10}H_4Cl_4$ : Cl, 53.4%), too small in amount to be recrystallised for comparison with 1 : 2 : 8 : (?)-tetrachloronaphthalene, m. p. 131° (Turner and Wynne, *loc. cit.*).

(iii) Tetranitronaphthalene (m. p. 215°) is the most soluble of the isomerides in the ordinary solvents. It crystallises from acetic anhydride in pale yellow, orthorhombic plates and in either an open or a sealed capillary tube decomposes vigorously at the moment of fusion (Found: C, 39.2; H, 1.8; N, 18.2. Calc. for  $C_{10}H_4O_8N_4$ : C, 39.0; H, 1.3; N, 18.2%). Mixed with an equal amount of the 1 : 3 : 5 : 7-isomeride, it begins to decompose rapidly at 202°, about one half undergoing fusion at this temperature and the remainder below 230°, and on refusion after solidification has m. p. 230—232°, accompanied by decomposition. The small amount available made further investigation impossible.

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\* Fractional sulphonation could not be employed, since 1 : 3 : 5 : 7-tetrachloronaphthalene does not undergo sulphonation when shaken in light petroleum solution (b. p. 80—100°) at 100° during 3 hours with chlorosulphonic acid or with 10 or 20% oleum. With the oleum much charring occurred.