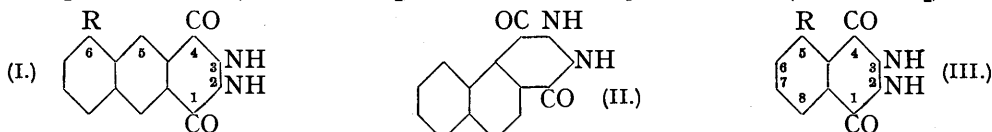


### 177. Chemiluminescent Organic Compounds. Part VII. Substituted Phthalaz-1 : 4-diones. Effect of Substituents on the Luminescent Power.

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Several naphthalazdiones have been prepared, and their luminescent powers compared with those of corresponding phthalazdiones. The effects of substituents are in a similar sense in the two series; but the latter series is the more luminescent, except as regards the parent compounds. 5-Methylphthalazdione and some halogenated phthalazdiones have also been prepared and examined. The first presents an anomaly in luminescent power.

OBSERVATIONS on a number of new diones tend to confirm the conclusion of Drew and Pearman (J., 1937, 586) that substitution of negative groups (*e.g.*, NH<sub>2</sub>, OH, Cl) in the phenyl group of phthalaz-1 : 4-dione, especially in the positions near to the hydrazide ring, increases the luminescent power, whereas that of positive groups (*e.g.*, NO<sub>2</sub>) has an opposite or at least a much weaker effect. For instance, with hæmoglobin as catalyst, the following substances are arranged in order of decreasing luminescent power at laboratory temperature: 5-aminophthalazdione (III, R = NH<sub>2</sub>), 6-amino- $\beta\beta$ -naphthalazdione (I, R = NH<sub>2</sub>),  $\alpha\beta$ -naphthalazdione (II),  $\beta\beta$ -naphthalazdione (I, R = H), phthalazdione (III, R = H), 5-nitrophthalazdione (III, R = NO<sub>2</sub>), and 6-nitro- $\beta\beta$ -naphthalazdione (I, R = NO<sub>2</sub>).



It is seen that substitution of a benzo-group for two hydrogen atoms of phthalazdione increases the luminescent power, especially when the 5 : 6-hydrogen atoms are those substituted; and that the further substitution of an amino-group in the benzo-group increases, whereas that of a nitro-group decreases, the luminescent power. The substituted naphthalene derivatives, so far as they have been studied, appear to be inferior to the benzene derivatives from the point of view of luminescence. Since the reverse is true of the parent compounds, it is clear that the enhancing effect of a 6-amino-group in the naphthalene series is less than that of a 5-amino-group in the benzene series; though the depressant effect of a nitro-group (similarly situated) appears to be greater in the naphthalene than in the benzene series.

5-Methylphthalazdione (III, R = CH<sub>3</sub>) has, however, a lower luminescent power than phthalazdione itself, and, since the methyl group is more negative than hydrogen, this effect is anomalous. The explanation must await the collection of fresh data on the effect of alkyl substituents.

Three new halogenated diones were compared with phthalazdione, the luminescent power being found in the following order of decreasing magnitude: 5-bromophthalazdione (III, R = Br), 6-bromophthalazdione, 6-iodophthalazdione, and phthalazdione. Here there is no exception to the rules previously deduced (*loc. cit.*), the halogens acting as negative groups. The additional information tends to show that the lighter the halogen, the more its presence enhances the luminescent power. The results with the 6-bromo- and -iodo-diones, when compared with that with 6 : 7-dichlorophthalazdione (which has a lower luminescent power than phthalazdione itself), suggest that the introduction of a second halogen in the 7-position probably depresses the luminescent power of a 6-halogenophthalazdione.

So far, no exception has been found to the rule that all compounds containing an unsubstituted cyclohydrazide ring attached to a benzene ring are chemiluminescent.

#### EXPERIMENTAL.

**3-Bromophthalimide.**—To an ice-cold mixture of water (20 c.c.) and concentrated sulphuric acid (3 c.c.) was gradually added a solution of 3-aminophthalimide (3.36 g.) in 5% aqueous sodium hydroxide (12 c.c.) which had been mixed with a solution of sodium nitrite (1.4 g.) in water (10 c.c.) and cooled in ice. The diazo-solution was filtered and added to a solution of cuprous bromide in hydrobromic acid, the mixture heated at 100°, and the 3-bromophthalimide

filtered off, sublimed, and recrystallised from glacial acetic acid. It formed colourless plates, m. p. 260°, very sparingly soluble in hot water (Found : N, 6.4.  $C_8H_4O_2NBr$  requires N, 6.2%).

The above method of diazotisation was applied also to 4-aminophthalimide, for the preparation of 4-bromo- and 4-iodophthalimide.

*5-Bromophthalaz-1 : 4-dione*.—3-Bromophthalimide (1 g.) was heated under reflux with hydrazine hydrate (4 c.c.) for  $\frac{1}{2}$  hour, the solution diluted with water, and the *dione* precipitated by addition of acetic acid. It formed a very sparingly soluble, nearly colourless, crystalline powder, m. p. 322°, soluble in alkali solution (Found : N, 12.0.  $C_8H_5O_2N_2Br$  requires N, 11.6%).

*6-Bromophthalaz-1 : 4-dione*, prepared from 4-bromophthalimide as above, formed a similar powder, m. p. 343° (Found : N, 11.9%).

*6-Iodophthalaz-1 : 4-dione*, similarly prepared from 4-iodophthalimide (almost colourless plates, m. p. 233°; Edinger, *J. pr. Chem.*, 1896, **53**, 383, gives m. p. 222—224°), was a cream-yellow powder, m. p. 345°, very sparingly soluble in organic solvents but soluble in alkali solution (Found : N, 9.65.  $C_8H_5O_2N_2I$  requires N, 9.7%).

*5-Methylphthalaz-1 : 4-dione*.—3-Methylphthalonitrile (Gabriel and Thieme, *Ber.*, 1919, **52**, 1083) was hydrolysed to 3-methylphthalic acid, and this acid or its anhydride condensed with hydrazine. (a) A solution of 3-methylphthalic acid (1 g.) in hydrazine hydrate (5 c.c.) was evaporated on a water-bath, and the residue heated gradually to 250° ( $\frac{1}{4}$  hour), cooled, and extracted with 5% aqueous sodium hydroxide; the filtered extract, acidified with 25% aqueous acetic acid, gave the *dione* as a precipitate. (b) 3-Methylphthalic anhydride (1 g., obtained by sublimation of the acid) was heated under reflux with hydrazine hydrate (1 c.c.) and glacial acetic acid (10 c.c.) for 2 hours; the solid was filtered off and dissolved in 5% aqueous sodium hydroxide, and the *dione* obtained as before. It was a white powder, m. p. 340°, insoluble except in alkali solution (Found : N, 16.1.  $C_9H_9O_2N_2$  requires N, 15.9%).

*$\beta\beta$ -Naphthalaz-1 : 4-dione*.—Naphthalene-2 : 3-dicarboxylic anhydride (0.2 g.), prepared by sublimation of the acid, was heated under reflux with hydrazine hydrate (0.3 c.c.) and glacial acetic acid (10 c.c.) for 1 hour, needles of the *dione* separating. The mixture was diluted with water (10 c.c.), the precipitate collected and dissolved in 5% aqueous sodium hydroxide, and the *dione* obtained as in the foregoing preparation. It formed colourless needles, m. p. 345° (Found : C, 68.1; H, 4.2.  $C_{12}H_8O_2N_2$  requires C, 67.95; H, 3.8%). The *monosodium* salt was obtained in pale yellow needles by precipitating a hot solution of the *dione* in 5% aqueous sodium hydroxide with alcohol (Found for air-dried material: Na, 9.3.  $C_{12}H_7O_2N_2Na, H_2O$  requires Na, 9.15%).

*6-Nitro- $\beta\beta$ -naphthalaz-1 : 4-dione*.—5-Nitronaphthalene-2 : 3-dicarboxylic anhydride (Baker, *J.*, 1934, 1413) (0.2 g.) was heated under reflux with hydrazine hydrate (0.3 c.c.) and glacial acetic acid (10 c.c.), and the product worked up as in the last preparation. The *dione* was a golden-yellow powder, unmelted at 350°; it was soluble only in alkalis (orange-red solutions) (Found : N, 16.5.  $C_{12}H_7O_4N_3$  requires N, 16.35%). The *monosodium* salt was obtained, by cooling a solution of the *dione* in hot 0.2% aqueous sodium hydroxide, as brick-red plates, sparingly soluble in hot water (Found : Na, 7.9.  $C_{12}H_6O_4N_3Na, H_2O$  requires Na, 7.75%).

*6-Amino- $\beta\beta$ -naphthalaz-1 : 4-dione* was obtained only in the crude state, but it was sufficiently pure to show a bright chemiluminescence. It was prepared by reducing ammonium 5-nitronaphthalene-2 : 3-dicarboxylate to the 5-amino-acid by means of ferrous sulphate, transforming the acid into 5-acetamidonaphthalene-2 : 3-dicarboxylic anhydride by means of acetic anhydride, and heating the anhydride with hydrazine hydrate and acetic acid, followed by hydrolysis of the acetyl group with 5% aqueous sodium hydroxide at 100°. It formed a pale brownish powder, m. p. 320° (decomp.), very sparingly soluble in organic solvents but soluble in alkali solution (Found : N, 16.9.  $C_{12}H_9O_2N_3, H_2O$  requires N, 17.15%). The amount of material was too small, however, to allow it to be shown whether this substance was in reality a monohydrate.

*$\alpha\beta$ -Naphthalaz-1 : 4-dione*.—Naphthalene-1 : 2-dicarboxylic acid (Bradbrook and Linstead, *J.*, 1936, 1739) was converted into the anhydride by sublimation. The anhydride (1 g.) was boiled under reflux ( $\frac{1}{2}$  hour) with hydrazine hydrate (0.6 c.c.) and glacial acetic acid (20 c.c.). The precipitated *dione* was filtered off and purified as in the previous cases. It was a colourless powder, unmelted at 360°, and insoluble except in alkalis (yellow solutions) (Found : N, 13.2.  $C_{12}H_8O_2N_2$  requires N, 13.2%). The sodium salt formed pale yellow plates.

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