132. *Chemiluminescent Organic Compounds. Part IV. Amino- and Hydrazino-*cyclo*phthalhydrazides and their Relative Luminescent Power.*

By H. D. K. Drew and F. H. Pearman.

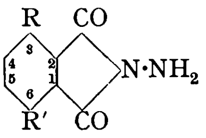
THE amino-substituted phthalaz-1 : 4-diones (particularly the 5-amino-derivative) luminesce more strongly than the other known members of the series. A number of amino- and hydrazino-substituted diones, and their derivatives containing acetyl and methyl groups, are now described, together with some of their 5-ring isomerides (*N*-amino-imides). The last are non-luminescent, but several of the new diones are comparable, as regards luminescent power, with the 5-amino-dione at laboratory temperature and somewhat superior to it at 100°.

Methylation of 3-aminophthalimide with methyl sulphate gave 3-*methylaminophthalimide*, but with methyl iodide the chief product was the *methiodide* of N-*methyl*-3-*dimethylaminophthalimide*, from which the molecule of methyl iodide could not be eliminated. 3-Methylaminophthalimide gave N-*amino*-3-*methylaminophthalimide* (I; $R = CH_3{\cdot}NH$, $R' = H$) with 1 mol. of aqueous hydrazine hydrate, and 5-methylaminophthalaz-1 : 4-dione (II; $R = CH_3{\cdot}NH$, $R' = H$) with 3 mols. of hydrazine hydrate; (I) is transformed above its melting point into (II).

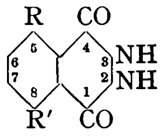
3 : 6-*Diaminophthalimide*, which occurs in a red and a golden-brown form, was obtained by heating 3 : 6-dichlorophthalimide or 3 : 6-dichlorophthalic anhydride with ammonia under pressure in presence of cuprous iodide. This phthalimide is changed into red 3 : 6-*diamino*-N-*aminophthalimide* (I; $R = R' = NH_2$) with excess of aqueous hydrazine at 90°, but into yellow 5 : 8-*diaminophthalaz*-1 : 4-*dione* (II; $R = R' = NH_2$) with hydrazine

hydrate at 120°. 3 : 6-Diamino-*N*-aminophthalimide does not react with hydrazine hydrate at room temperature, although N-*amino*-3 : 6-*diacetamidophthalimide* reacts at once. 3 : 6-Dichloro-*N*-aminophthalimide in these circumstances forms the open-chain dihydrazide, which re-forms the 5-ring compound at room temperature in water or when acidified but closes to the 6-ring *cyclo*-hydrazide at 120° (this vol., p. 26). These cases illustrate the effect of temperature on the ring closure of the open-chain hydrazides. 3 : 6-Diaminophthalic acid was not obtained pure, but 3 : 6-*diacetamidophthalic anhydride* was prepared.

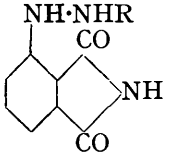
4 : 5-*Dichlorophthalimide* could not be converted into 4 : 5-diaminophthalimide with ammonia and cuprous iodide, but 6 : 7-dichlorophthalaz-1 : 4-dione was changed by these reagents into the required 6 : 7-*diaminophthalaz*-1 : 4-*dione*, which crystallised as a *dihydrate.*



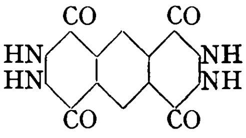
(I.)



(II.)



(III.)



(IV.)

Diazotisation and reduction of 3-aminophthalimide gave *sodium phthalimide*-3-*hydrazine*-β-*sulphonate* (III, R = SO_3Na) and this was changed by mineral acid into 3-*hydrazinophthalimide* (III, R = H), which occurs in a yellow and an orange form having identical chemical properties but differing in melting point. Similar pairs of forms occur among other substituted phthalimides (Pratt and Perkins, *J. Amer. Chem. Soc.*, 1918, **40**, 203; Chattaway, J., 1911, 1915); they are not accountable by reference to lactam-lactim tautomerism, since they arise also in cases where the hydrogen of the imino-group is substituted. Alcoholic hydrazine hydrate converted 3-hydrazinophthalimide and the above sulphonate into orange N-*amino*-3-*hydrazinophthalimide* (I; R = $NH·NH_2$, R′ = H) and *sodium* N-*aminophthalimide*-3-*hydrazine*-β-*sulphonate* (I; R = $NH·NH·SO_3Na$, R′ = H) respectively, and excess of aqueous hydrazine hydrate converted them into white 5-*hydrazinophthalaz*-1 : 4-*dione* (II; R = $NH·NH_2$, R′ = H) and *sodium phthalaz*-1 : 4-*dione*-5-*hydrazine*-β-*sulphonate* (II; R = $NH·NH·SO_3Na$, R′ = H) respectively.

Pyromellitaz-1 : 4 : 6 : 9-*tetraone* (IV), a bis*cyclo*phthalhydrazide of novel type, was prepared from pyromellitic anhydride and hydrazine. It shows a powerful yellow chemiluminescence with alkaline oxidising agents. Its amino-derivatives and others are being examined.

It was noticed throughout that fluorescence occurred in the phthalimides and *cyclo*-hydrazides containing an amino-group in an *o*-position to the junction of the rings, but not in those containing an amino-group in the *m*-position. The *N*-aminophthalimides derived from fluorescent phthalimides were non-fluorescent; this is not due to the removal of the imide hydrogen, but is an effect of the *N*-amino-group itself, since fluorescence persists in the *N*-methyl- and *N*-phenyl-phthalimides.

Luminescent Power.—The substances described in this and in our previous paper (J., 1937, 26) were tested for chemiluminescence by oxidation, in presence of aqueous sodium hydroxide or ammonia, with hydrogen peroxide and other oxidising agents, both alone and with hæmoglobin or a copper salt as catalyst. Only the phthalaz-1 : 4-diones showed chemiluminescence, the 5-ring compounds giving no visible light in any instance. The open-chain hydrazides glow only when transformation into 6-ring hydrazides has taken place.

By means of a Karrer–Poritsky low-brightness optical photometer the chemiluminescence of the diones was compared at 18° and at 100°. The optimum conditions for 5-aminophthalaz-1 : 4-dione were first found and the other diones were tested with the same molecular proportions of reagents. The table shows the qualitative order of brightness observed under the two sets of conditions, the ascending numbers indicating the places of the substances in decreasing order of brightness.

		Order of brightness.	
Phthalaz-1 : 4-dione.	Colour of light emitted.	At 18° (in presence of hæmoglobin).	At 100° (without catalyst).
5-Amino-	blue	1	4
5-Methylamino-	greenish-blue	2	2
5 : 8-Diacetamido-	greenish	3	1
5-Hydroxy-	bluish-violet	4	3
5-Hydrazino-	blue	5	7
5-Acetamido-	greenish-blue	7	6
6-Amino-	blue	8	8
5 : 8-Dichloro-	bluish-violet	9	9
5-Chloro-	,,	10	11
6-Acetamido-	blue	11	13
†5 : 8-Diamino-	whitish-blue	12	12
5-Benzamido-	blue	13	14
5-Hydrazine-β-sulphonate	whitish-blue	14	18
Phthalaz-1 : 4-dione	,,	15	10
†6 : 7-Diamino-	bluish-violet	16	16
†5-Nitro-	whitish-yellow	17	15
6 : 7-Dichloro-	bluish-violet	18	17
†6-Nitro-	whitish-yellow	19	19
Pyromellitaz-1 : 4 : 6 : 9-tetraone	yellow	6	5

† indicates that the observed brightness was too low owing to internal absorption (coloured solution).

The observations at 18° were made on 1 c.c. of 0·04*M*-solution of the dione containing 12 molecular proportions of sodium hydroxide, to which were added 4 drops of aqueous hydrogen peroxide (6%) and 6 drops of hæmoglobin solution (1%) in 0·1*N*-sodium hydroxide; those at 100° were made in the same manner, but the hæmoglobin was omitted.

The points which emerge from the comparisons are: (1) Negative (*op*-directing) groups (NH_2, NH·Me, OH, $NH\cdot NH_2$, and, to a lesser extent, Cl) cause increased light emission in the visible region; whereas positive (*m*-directing) groups (NO_2, and such groups as $CO\cdot CH_3$, COPh, and SO_3Na substituted in side chains) tend to have the opposite or at least a much weaker effect.

(2) Substitution of favourable groups in the 5- and 8-positions has a much greater effect than substitution in the 6- and 7-positions.

(3) Substitution in the 5- and 8-positions of two favourable groups usually produces a greater effect than substitution of one such group only (5 : 8-diaminophthalaz-1 : 4-dione appears to be an exception, but its red solution is strongly absorbent and it should probably be placed near the top of the list).

(4) The emitted visible light is changed in colour and greatly increased in intensity when phthalaz-1 : 4-dione is converted into pyromellitaz-1 : 4 : 6 : 9-tetraone, which contains two hydrazide rings.

(5) The order of brightness is changed with increase of temperature.

Preliminary measurements with seven of the diones indicated that maximum luminescence was obtained with 10—16 mols. of sodium hydroxide per mol. of dione, the quantity varying with the nature of the dione but being usually about 12 mols.; 4—5 mols. of hydrogen peroxide were required for maximum brightness, further increase producing no effect. With these proportions of dione and sodium hydroxide, the effect of dilution over the range 0·02 to 0·08*M* was small, equal volumes of the solutions containing the same amounts of hydrogen peroxide and hæmoglobin being employed for the comparison.

EXPERIMENTAL.

N-*Methyl*-3-*dimethylaminophthalimide Methiodide*.—3-Aminophthalimide (1 g.), methyl iodide (4 g.; 4 mols.), and 96% methyl alcohol (15 c.c.) were heated in a sealed tube at 120—130° for 8 hours; the crystals deposited were filtered off (a further crop was obtained from the filtrate; total yield, 0·9 g.) and recrystallised from methyl alcohol. The *methiodide* formed colourless tetragonal plates, m. p. 204° (decomp.), very soluble in water and alcohol (Found: C, 42·0; H, 4·5. $C_{12}H_{15}O_2N_2I$ requires C, 41·8; H, 4·35%). Silver nitrate precipitated silver iodide, and aqueous silver oxide gave also deliquescent colourless needles of the base. Sublimation, boiling with quinoline or with sodium ethoxide in ethyl alcohol, or heating with ammonia under pressure failed to remove methyl iodide. When 1, 2, or 3 mols. of methyl iodide were employed in the preparation, mixtures of 3-methylaminophthalimide (below), the above methiodide, and unchanged material were obtained, indicating that the imide ring becomes methylated only after dimethylation of the amino-group and formation of the methiodide.

3-*Methylaminophthalimide.*—3-Aminophthalimide (2 g.) and methyl sulphate (3 c.c.) were heated at 120—130° for ½ hour under reflux; the brown fluid was stirred into water (200 c.c.), and the yellow powder obtained recrystallised from boiling water (500 c.c.). The *substance* (1 g.) formed long, deep yellow needles, m. p. 218° (Found: C, 61·1; H, 4·5; N, 16·0. $C_9H_8O_2N_2$ requires C, 61·3; H, 4·5; N, 15·9%). Solutions in boiling water or alcohol had a deep green fluorescence, but in benzene or acetone the fluorescence was bluish. A nitroso-derivative was obtained, in colourless needles, by the action of nitrous acid on a solution in hydrochloric acid. The compound is soluble in cold alkalis. The 3-N-*acetyl* derivative was obtained, by boiling it with excess of acetic anhydride in presence of a trace of concentrated sulphuric acid, in pale buff prisms (from glacial acetic acid), m. p. 285° (decomp.); its solutions were only weakly fluorescent (Found: C, 60·4; H, 4·9. $C_{11}H_{10}O_3N_2$ requires C, 60·55; H, 4·6%).

N-*Amino*-3-*methylaminophthalimide.*—A mixture of 3-methylaminophthalimide (1·2 g.) and hydrazine hydrate (0·36 g.; 1 mol.) in water (20 c.c.) was refluxed for 1 hour; the crystals produced were freed from traces of the isomeric *cyclo*-phthalhydrazide by washing with 2% sodium hydroxide solution. The *amino-phthalimide* (1·1 g.) formed yellow prismatic needles (Found: C, 56·6; H, 4·95. $C_9H_9O_2N_3$ requires C, 56·55; H, 4·7%); it melted at 194°, but at higher temperatures transformation into the *cyclo*hydrazide occurred; its solutions were not fluorescent.

5-*Methylaminophthalaz*-1 : 4-*dione.*—3-Methylaminophthalimide (1·2 g.) and hydrazine hydrate (1·1 g.; 3 mols.) were refluxed for 1 hour; the product was present partly as its hydrazine salt, which was hydrolysed by water. The phthalazdione formed cream-coloured microcrystals, m. p. 331° (decomp.); Gleu and Pfannstiel (*J. pr. Chem.*, 1936, **146**, 137) gave m. p. 310—325° (decomp.). It was little soluble in ordinary solvents but dissolved in alkalis (violet fluorescence) or in concentrated hydrochloric acid (Found: C, 56·7; H, 4·9. Calc. for $C_9H_9O_2N_3$: C, 56·55; H, 4·7%). Its sodium salt was decomposed by carbon dioxide, and it readily yielded a nitroso-compound (buff needles). The 5-N-*acetyl* derivative, prepared by heating the 3-*N*-acetyl derivative of 3-*N*-methylaminophthalimide and hydrazine hydrate (1 mol.) in water, formed small, pointed, buff needles (from water), m. p. 329° (decomp.), not fluorescent in neutral solutions (Found: N, 18·2. $C_{11}H_{11}O_3N_3$ requires N, 18·0%).

3 : 6-*Diaminophthalimide.*—(a) A mixture of 3 : 6-dichlorophthalic anhydride (2·5 g.), aqueous ammonia (25 c.c.; *d* 0·88), and cuprous iodide (0·5 g.) was heated in a sealed tube at 120—130° (8 hours); deep red needles (0·8 g.) separated on cooling and were rapidly filtered off and washed with water; the filtrate soon became black on exposure to air; the needles were freed from an insoluble black impurity by extraction with alcohol (Soxhlet). (b) The foregoing procedure was more satisfactory when 3 : 6-dichlorophthalimide was used instead of the anhydride; the yield was greater (1·2 g.) and there was less amorphous by-product. Modifications of these processes failed to give improvement. 3 : 6-*Diaminophthalimide* formed bright red, acicular needles when separating from alcohol at room temperature but golden-brown plates when crystallised at 100°; the red form slowly changed into the brown when kept. Crystallisation from aniline and nitrobenzene gave the red and the brown form respectively; both forms melted at 298° (decomp.); the brown form appeared more soluble in alcohol (Found: C, 54·35; H, 4·2; N, 23·6. $C_8H_7O_2N_3$ requires C, 54·25; H, 3·95; N, 23·7%). It was readily soluble in glacial acetic acid but sparingly in water; it dissolved without chemical change to a red solution in cold 5% aqueous sodium hydroxide and to a colourless solution in concentrated hydrochloric acid (the hydrochloride formed colourless needles, not hydrolysed in cold water); these solutions were not fluorescent, but the orange or yellow solutions in alcohol, ether, or benzene exhibited green fluorescence. The phthalimide could be diazotised and then coupled with β-naphthol. When boiled (10 mins.) with a mixture of acetic anhydride (4 mols.; 1 vol.) and glacial acetic acid (2 vols.), the phthalimide gave 3 : 6-*diacetamidophthalimide*, in yellow pointed needles (from alcohol) or rhombic plates (from acetic acid), m. p. 321° (decomp.), insoluble in water but soluble to yellow solutions (blue fluorescence) in organic solvents (Found: N, 16·2. $C_{12}H_{11}O_4N_3$ requires N, 16·1%).

3 : 6-*Diamino*-N-*aminophthalimide.*—A mixture of 3 : 6-diaminophthalimide (3·4 g.), hydrazine hydrate (2 g.; 2 mols.), and water (100 c.c.) was refluxed; 3 : 6-*diamino*-N-*amino-phthalimide*, which separated during the reaction, crystallised from water (yield, 3·5 g.) in deep scarlet needles of a *monohydrate* (Found: C, 45·7; H, 4·9. $C_8H_8O_2N_4,H_2O$ requires C, 45·7; H, 4·75%), which lost the water at 100° but regained it when exposed to air. The anhydrous substance melted at 282° (Found: C, 49·9; H, 4·3; N, 29·25. $C_8H_8O_2N_4$ requires C, 50·0;

H, 4·2; N, 29·15%); it was moderately readily soluble in water or alcohol and readily soluble in acetic acid; the orange solutions were only faintly fluorescent (yellow). It was insoluble in cold dilute sodium hydroxide, but was partly hydrolysed on boiling.

N-*Amino*-3 : 6-*diacetamidophthalimide*, prepared by heating 3 : 6-diacetamidophthalimide with hydrazine hydrate (1 mol.) in aqueous alcohol (96%), formed long yellow needles, m. p. 304° (decomp.), from water (Found: N, 20·6. $C_{12}H_{12}O_4N_4$ requires N, 20·3%); the benzylidene derivative crystallised in pale yellow needles, m. p. 319° (decomp.). The action of nitrous acid in acetic acid converted it into 3 : 6-diacetamidophthalimide. Both of the above *N*-aminophthalimide derivatives reduced Fehling's solution. 3 : 6-*Diacetamido*-N-*acetamidophthalimide* was prepared, by heating anhydrous 3 : 6-diamino-*N*-aminophthalimide with acetic anhydride (3 mols.), in lemon-yellow prismatic rods (from acetic acid; the solution had a strong light blue fluorescence); it was insoluble in water and melted at 248° (Found: C, 52·3; H, 4·7. $C_{14}H_{14}O_5N_4$ requires C, 52·6; H, 4·7%).

5 : 8-*Diaminophthalaz*-1 : 4-*dione*.—This was prepared in nearly quantitative yield (a) by refluxing 3 : 6-diaminophthalimide with hydrazine hydrate (3 mols.) for 1 hour, the residue being extracted with cold aqueous ammonia (20%), and the filtered extract acidified with acetic acid to precipitate the *dione*; or (b) by similarly treating 3 : 6-diamino-*N*-aminophthalimide with hydrazine hydrate (2 mols.). It formed deep yellow rhombic needles of a *monohydrate* from water (Found: H_2O, 8·4. $C_8H_8O_2N_4,H_2O$ requires H_2O, 8·6%), and was moderately soluble in water or alcohol. Its aqueous solutions, which were acid to litmus and had a very strong green fluorescence, were slowly oxidised in air, rapidly if sodium hydroxide was present. The dione, m. p. 329° (decomp.), was soluble in acetic acid but decomposed on boiling; it did not reduce Fehling's solution (Found, in anhydrous substance: C, 50·1; H, 4·3; N, 29·3. $C_8H_8O_2N_4$ requires C, 50·0; H, 4·2; N, 29·15%). The hydrochloride was hydrolysed by water, but could be diazotised and coupled with β-naphthol. Owing to oxidation, the sodium salt could not be isolated. 5 : 8-*Diacetamidophthalaz*-1 : 4-*dione*, prepared by heating 3 : 6-diacetamidophthalimide or 3 : 6-diacetamido-*N*-acetamidophthalimide with hydrazine hydrate (3 mols.) on a water-bath (½ hour), formed colourless hair-like needles (from water), m. p. 279° (decomp.), and was not fluorescent (Found: C, 52·4; H, 4·5. $C_{12}H_{12}O_4N_4$ requires C, 52·2; H, 4·35%); it dissolved at once in dilute alkalis to colourless solutions, and lost the acetyl groups only on boiling; with acetic anhydride, it was acetylated in the hydrazide ring, giving a *triacetyl* derivative of 5 : 8-diaminophthalaz-1 : 4-dione in small white plates, m. p. 306° (decomp.) (Found: C, 52·5; H, 4·5. $C_{14}H_{14}O_5N_4$ requires C, 52·6; H, 4·7%), which lost the new acetyl group on treatment with alkali in the cold.

3 : 6-*Diacetamidophthalic Anhydride*.—3 : 6-Diamino-*N*-aminophthalimide was warmed on a water-bath with 5% aqueous caustic soda (15 mins.), the resulting solution cooled, and a large excess of concentrated hydrochloric acid added; the hydrochloride of 3 : 6-diaminophthalic acid then crystallised. It was converted, by hydrolysis with a little water, into the acid (white needles, not melted at 340°), and this was dissolved in 5% caustic soda solution and reprecipitated with acetic acid. The crude acid, which still contained a sodium salt, was boiled (10 mins.) with acetic anhydride (4 mols.); the reddish solution crystallised on cooling. 3 : 6-*Diacetamidophthalic anhydride* formed long, pale yellow needles from acetic acid, m. p. 279°; it was insoluble in water but soluble in cold alkalis; its solution in acetic acid had a strong sky-blue fluorescence (Found: C, 54·9; H, 4·05. $C_{12}H_{10}O_5N_2$ requires C, 54·9; H, 3·8%). Hydrazine hydrate (1 mol.) converted it almost completely into *N*-amino-3 : 6-diacetamidophthalimide (m. p. and mixed m. p. 302—304°).

4 : 5-*Dichlorophthalimide* was prepared by heating 4 : 5-dichlorophthalic anhydride (10 g.) with ammonium carbonate (5 g.) at 250° (½ hour). The product was extracted with boiling water, and the residue crystallised from alcohol, the phthalimide separating in colourless rhomboidal plates, m. p. 221° (Found: N, 6·65. $C_8H_3O_2NCl_2$ requires N, 6·45%). Attempts to convert it into 4 : 5-diaminophthalimide by means of ammonia in presence of cuprous iodide led only to a black product insoluble in alcohol.

6 : 7-*Diaminophthalaz*-1 : 4-*dione*.—6 : 7-Dichlorophthalaz-1 : 4-dione (2·5 g.), cuprous iodide (0·5 g.), and aqueous ammonia (50 c.c., *d* 0·88) were heated in a sealed tube at 160—170° (16 hours); the pale yellow solution obtained was filtered and treated with dilute acetic acid; the *dione* (1·8 g.) then separated in small, buff, hexagonal plates, m. p. above 340°; it formed a *dihydrate* from water (Found: C, 42·2; H, 5·3; H_2O, 15·4. $C_8H_8O_2N_4,2H_2O$ requires C, 42·1; H, 5·3; H_2O, 15·8%). The dione, which formed a white sodium salt, was sparingly soluble in water or alcohol and was not fluorescent; it could be diazotised and coupled with phenols; it condensed with phenanthraquinone in glacial acetic acid, giving a *phenanthrazine*

derivative in orange microcrystals, m. p. above 340°, apparently also a dihydrate (Found: C, 66·2; H, 4·1. $C_{22}H_{12}O_2N_4,2H_2O$ requires C, 66·0; H, 4·0%).

Sodium Phthalimide-3-*hydrazine*-β-*sulphonate*.—3-Aminophthalimide hydrochloride (2·4 g.), suspended in 16% hydrochloric acid (25 c.c.), was treated with sodium nitrite (1·1 g.) in a little water at 0—5°, and the diazo-solution at once run into an ice-cold solution of sodium sulphite (11 g., heptahydrate) and sodium carbonate (20 g., monohydrate) in water (80 c.c.); after 10 minutes, the orange solution was treated with concentrated hydrochloric acid (30 c.c.) and heated at 100° (½ hour). Crystals separated at 0° overnight, and were recrystallised from boiling water (20 c.c.) and dried at 100° (yield, 2·1 g.). The *sulphonate* formed pale yellow, tetragonal plates, becoming deep yellow when moistened; it reduced Fehling's solution (Found: C, 34·1; H, 2·4; Na, 8·15. $C_8H_6O_5N_3SNa$ requires C, 34·4; H, 2·2; N, 8·25%).

3-*Hydrazinophthalimide*, prepared by warming the above sulphonate and concentrated hydrochloric acid on a water-bath for a few minutes, and treating the resulting white needles of the hydrochloride of 3-hydrazinophthalimide with aqueous ammonia (10%), formed deep yellow needles, m. p. 216° (dried at 100°). Crystallisation from water at 90° converted the substance into a second form, orange-pink rhombic plates, m. p. 208° (Found: in yellow form, C, 54·2; H, 4·2; in orange form, C, 54·1; H, 4·1. $C_8H_7O_2N_3$ requires C, 54·2; H, 4·0%), but rapid crystallisation at a lower temperature gave a mixture of both forms; the mixed m. p. of the two forms was intermediate. Both forms reduced Fehling's solution. They were at once soluble in dilute sodium hydroxide solution, and were precipitated as the yellow form by acetic acid. Crystallisation from cold water gave a mixture of both forms, but with benzene there was no interconversion. The substance is not fluorescent.

N-*Amino*-3-*hydrazinophthalimide*.—3-Hydrazinophthalimide (1·7 g.), hydrazine hydrate (0·5 g.; 1 mol.), and alcohol (50 c.c.; 96%) were boiled under reflux (2 hours); the crystals which remained were washed with dilute sodium hydroxide solution to remove a little unchanged hydrazinophthalimide. N-*Amino*-3-*hydrazinophthalimide* formed orange-red prisms (from alcohol), m. p. 202°, only slightly soluble in water (Found: C, 50·2; H, 4·3. $C_8H_8O_2N_4$ requires C, 50·0; H, 4·15%), which reduced Fehling's solution.

Sodium N-*Aminophthalimide*-3-*hydrazine*-β-*sulphonate*.—A mixture of sodium phthalimide-3-hydrazine-β-sulphonate and hydrazine hydrate (1 mol. or 3 mols.) in alcohol (96%) was heated under reflux (2 hours); ammonia was evolved and the yellow plates of the initial salt were gradually replaced by pale orange rods of the desired *compound*. This was sparingly soluble in alcohol, from which it separated unchanged (Found: C, 32·8; H, 2·7; Na, 7·8. $C_8H_7O_5N_4SNa$ requires C, 32·7; H, 2·4; Na, 7·8%); it was very soluble in hot water, in which it changed rapidly into the following salt, which separated in white hairy needles.

Sodium Phthalaz-1 : 4-*dione*-5-*hydrazine*-β-*sulphonate*.—Sodium phthalimide-3-hydrazine-β-sulphonate (1·2 g.), hydrazine hydrate (1 mol. or 3 mols.), and water (10 c.c.) were heated at 100° (½ hour), ammonia being evolved. Acidification of the solution with dilute acetic acid precipitated the dione *salt* in white hairy needles, readily soluble in water (Found: C, 32·6; H, 2·6; Na, 7·9. $C_8H_7O_5N_4SNa$ requires C, 32·7; H, 2·4; Na, 7·8%). Warm hydrochloric acid converted it into 5-hydrazinophthalaz-1 : 4-dione (below).

5-*Hydrazinophthalaz*-1 : 4-*dione*.—(a) 3-Hydrazinophthalimide or *N*-amino-3-hydrazinophthalimide was heated with an excess of hydrazine hydrate and water; (b) sodium phthalaz-1 : 4-dione-5-hydrazinesulphonate was warmed with concentrated hydrochloric acid. A solution of the resulting colourless needles of the hydrochloride of the required dione in warm aqueous caustic soda (2%) was acidified with acetic acid; the *dione* separated in white rhombic platelets, m. p. 312° (decomp.), which reduced Fehling's solution (Found: C, 49·9; H, 4·3. $C_8H_8O_2N_4$ requires C, 50·0; H, 4·15). It was non-fluorescent, and darkened slowly when kept, as did also its colourless *sodium* salt (Found: Na, 10·45. $C_8H_7O_2N_4Na$ requires Na, 10·75%), but its hydrochloride was stable.

Pyromellitaz-1 : 4 : 6 : 9-*tetraone*.—Pyromellitic acid, m. p. 265°, was converted into its dianhydride by boiling with acetic anhydride. The dianhydride (1·2 g.), dissolved in hot glacial acetic acid (50 c.c.), was mixed with hydrazine hydrate (0·6 g.) in acetic acid (10 c.c.) and boiled under reflux (1 hour); the yellow plates which separated initially were converted into a buff powder (1·26 g.). This was dissolved in hot dilute sodium hydroxide solution; acidification with acetic acid precipitated the *tetraone* as a white powder, insoluble in all ordinary solvents and devoid of reducing properties (Found: C, 48·5; H, 2·7; N, 23·0. $C_{10}H_6O_4N_4$ requires C, 48·8; H, 2·4; N, 22·8%). Its *sodium* salt, sulphur-yellow rods, readily soluble in hot water, appeared to be a tetrahydrate of the disodium compound, but there was no loss of water at 150° (Found: Na, 12·6, 12·9. $C_{10}H_4O_4N_4Na_2,4H_2O$ requires Na, 12·7%).

We thank the Department of Scientific and Industrial Research, the Chemical Society, and the Dixon Fund of the University of London for grants, and Imperial Chemical Industries Ltd. for supplying us with chlorophthalic anhydrides.

QUEEN MARY COLLEGE (UNIVERSITY OF LONDON). [*Received, February 27th*, 1937.]

(*Addendum, April 9th*) Rowe and Peters have repeated the preparation of the acetyl derivatives of phthalaz-1 : 4-dione (this vol., p. 25) and are in agreement with the constitutions (p. 19) attributed to the diacetyl and the two monoacetyl derivatives (private communication).