481. *Conjugated Macrocycles. Part XXIX.* Tribenzotetrazaporphin Metal Derivatives and Dibromotribenzotetrazaporphin.*

By J. A. Elvidge, J. H. Golden, and R. P. Linstead.

The preparation and purification of tribenzotetrazaporphin have been considerably improved. A contaminant is tentatively identified as monobenzotetrazaporphin.

Tribenzotetrazaporphin has been converted into the copper, nickel, and cobalt derivatives, and brominated to dibromotribenzotetrazaporphin (III). Oxidation of the last yields phthalimide and dibromomaleimide.

Light absorptions are given and commented upon.

Discussion of the ways in which imidines might interact, with elimination of ammonia, to give tetrazaporphins, led two of us [1] to condense di-imino*iso*indoline with succinimidine. This reaction gave tribenzotetrazaporphin (I), the first unsymmetrically substituted tetrazaporphin to be isolated and characterised. Further studies have made the pure pigment more accessible, and we have converted it into metal derivatives (II) and the dibromo-derivative (III). The formation of these derivatives, and degradation of the dibromo-compound to phthalimide and dibromomaleimide, provide additional support for the macrocyclic structure (I) deduced earlier for the royal-blue pigment.

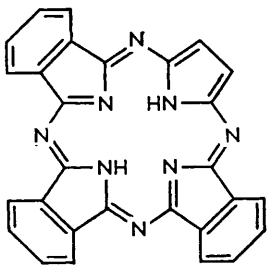
The disadvantage of the preparation of tribenzotetrazaporphin from imidines was the concomitant formation of three times the amount of phthalocyanine. Because of the similiarity of the two pigments, the isolation was lengthy, involving systematic extraction (to afford initial enrichment) and three stages of chromatography. Attempts to separate

* Part XXVIII, *J.*, 1957, 700.

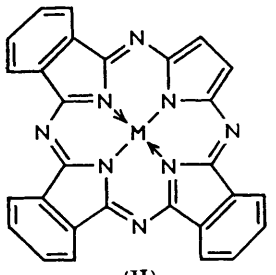
[1] Elvidge and Linstead, *J.*, 1955, 3536.

the pigments by other methods, and to prepare tribenzotetrazaporphin from other starting materials, gave no useful results.

A major improvement came from a reconsideration of our earlier generalisations.[1] Evidently some component of the di-imino*iso*indoline–succinimidine reaction mixture was acting as a hydrogen donor for the conversion of di-imino*iso*indoline into phthalocyanine;



(I)

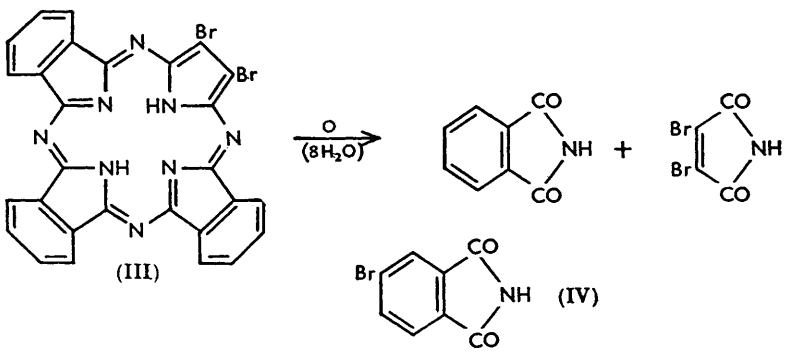


(II)

this was probably the succinimidine; it was not the solvent, ethanol, because its replacement by *tert.*-butanol had no effect. As competitors for the available hydrogen in the system, sodium chlorate and maleic acid were most effective. The tribenzotetrazaporphin was then obtained (in undiminished yield) contaminated with less than two-thirds of its weight of phthalocyanine. After an extractive crystallisation, the contamination was sufficiently small for the chromatography [1] to be modified and much larger throughputs were attained. Most of the phthalocyanine was adsorbed on tartaric acid (at higher proportions it is washed through the column) and the last traces were removed by chromatography on deactivated alumina in exceptionally short columns, the method obviating irreversible adsorption of tribenzotetrazaporphin.[1] It was then possible for one worker to obtain 200 mg. of the pigment in 3 weeks, compared with the 7—8 weeks previously needed for accumulation of 10—20 mg.

Metal Derivatives (II).—In boiling *o*-dichlorobenzene with copper bronze, anhydrous cobalt acetate, and Raney nickel, the pigment was converted into the copper, cobalt, and nickel derivatives, $C_{28}H_{14}N_8M$. Thus there are two replaceable hydrogen atoms in the molecule, $C_{28}H_{16}N_8$. The evidence [1] for the structure (I) was then complete.

Dibromo-compound (III).—The molecule of tribenzotetrazaporphin contains one pyrrole ring in which the two β-positions are free. Consequently it was expected that the pigment



(III) (IV)

would undergo electrophilic substitution: in fact bromination occurred readily in chlorobenzene at room temperature, a contrast to the behaviour of phthalocyanine,[2] and a stable dibromotribenzotetrazaporphin, $C_{28}H_{14}N_8Br_2$, was obtained, whose structure (III) was confirmed by degradation. Oxidation in concentrated sulphuric acid provided a mixture

[2] Barrett, Bradbrook, Dent, and Linstead, *J.*, 1939, 1820.

containing imides, separated by paper chromatography and identified as phthalimide and dibromomaleimide. No other imide was detected, and in particular the absence of 4-bromophthalimide (IV) was proved. These results are compatible only with the structure (III) and so with (I) for the parent pigment.

The 4-bromophthalimide, required as a marker in the paper chromatography, was prepared by an unambiguous route from 4-nitrophthalimide rather than by Waldmann's method.[3] Dunlap's method [4] for dibromomaleimide required modification.

Light Absorptions.—These have been determined for the metal derivatives (II) and the dibromo-pigment (III), in *o*-dichlorobenzene over the range 320—1000 mμ (see Table and

Light absorption characteristics.

(The full curves make certain peaks appear as minor ones : these are given in parentheses.)

	$\lambda_{max.}$ (mμ)				$\log_{10}\varepsilon$				Solvent
Tribenzotetrazaporphin ...	349	(566)	594	675	4·77	4·36	4·84	4·89 [1]	A
Cu ,, ...	349	(574)	630	663	4·83	4·38	4·94	4·94	B
Ni ,, ...	343	(566)	623	655	4·64	4·31	4·90	4·84	B
Co ,, ...	319	(567)	625	658	4·64	4·26	4·67	4·61	B
Dibromo- ,, ...	347	597	656	682	4·80	4·62	4·65	4·82	B
Phthalocyanine	350	(602, 638)	665	698	4·74	4·43 4·62	5·18	5·21	C *
Cu ,, ...	350	(611, 648)	679		4·76	4·56 4·51	5·34		C †
Ni ,, ...	(327) 350	(604, 643)	670		4·29 4·57	4·51 4·54	5·32		C †
Co ,, ...	348	(606)	672		4·65	4·53	5·19		C †
Tetrazaporphin	333		545	617	4·70		4·60	4·75 [6]	A
Cu ,, ...	334	(531)	578		4·57	4·13	4·98 [6]		B
Ni ,, ...	314 345	(530)	577		4·44 4·57	4·20	4·85 [6]		B

Solvents : A, chlorobenzene; B, *o*-dichlorobenzene; C, 1-chloronaphthalene.
* Dr. M. Whalley } Recent determinations on pure samples in these laboratories.
† Dr. G. E. Ficken }

Fig. 1). The general form of the absorption curve for tribenzotetrazaporphin (I) is similar to that of tetra*cyclo*hexenotetrazaporphin [5] or tetrazaporphin itself [6] (see ref. 1), but the spacing between the two main bands in the visible is rather larger (81 mμ) than that for all the other tetrazaporphins so far prepared, which show an interval of about 70 mμ.

The metallic derivatives of tribenzotetrazaporphin show two bands in the visible region, of similar intensity to one another and to those for the metal-free pigment, but 33 mμ apart. The spectra are thus unusual because in the other tetrazaporphins metallation results in replacement of the two main bands in the visible by an intense absorption peak, almost midway between them (see Table; also refs. 5, 7), which is accompanied by one or two subsidiary peaks at shorter wave-lengths. Another difference is that nickel tribenzotetrazaporphin shows a single maximum in the near-ultraviolet region, whereas previously examined nickel derivatives of (symmetrically) substituted tetrazaporphins show a double peak in that region. Presumably these effects are related to the dissymmetry of the molecule (I).

Substitution of the nucleus of tribenzotetrazaporphin to give dibromotribenzotetrazaporphin (III) gives rise to a third sharp peak in the visible region (see Fig. 1). No close comparisons for this are available, but a complication in the spectrum is to be expected, judging from the difference between the spectra of tribenzotetrazaporphin and phthalocyanine.

Monobenzotetrazaporphin.—In our previous work on tribenzotetrazaporphin we encountered a persistent contaminant, characterised by absorption bands at *ca.* 640 and 590 mμ, which was separated on a kieselguhr column as a mauve band.[1] Solutions of this

[3] Waldmann, *J. prakt. Chem.*, 1930, **126**, 65.
[4] Dunlap, *Amer. Chem. J.*, 1896, **18**, 332.
[5] Ficken and Linstead, *J.*, 1952, 4846.
[6] Linstead and Whalley, *J.*, 1952, 4839.
[7] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521.

pigment were reddish-blue and showed a red fluorescence which became bright pink in ultraviolet light. The same pigment was present in small amount in the mother-liquors from tribenzotetrazaporphin in our present work.

FIG. 1. *Absorption of (A) nickel tribenzotetrazaporphin (in o-*$C_6H_4Cl_2$*), (B) dibromotribenzotetrazaporphin (in o-*$C_6H_4Cl_2$*), and (C) tribenzotetrazaporphin (in* PhCl).

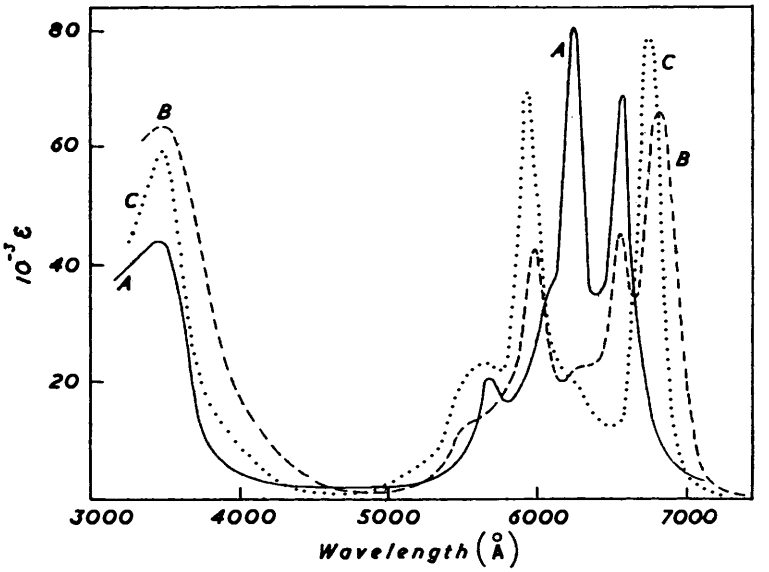
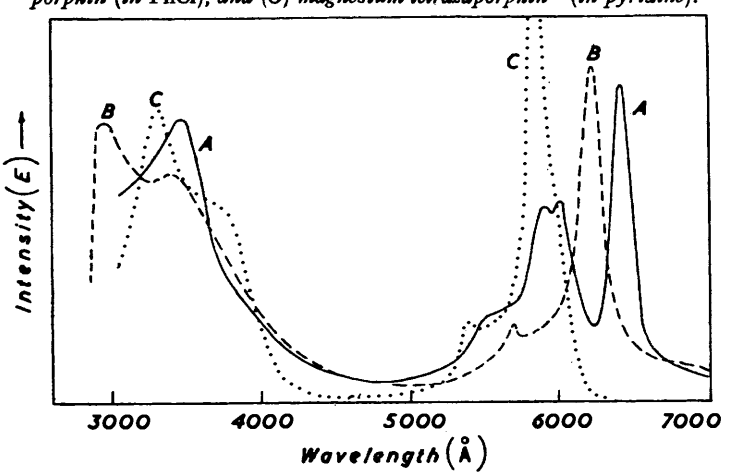


FIG. 2. *Absorption of (A) monobenzotetrazaporphin (in* PhCl), *(B) metal (?* Mg) *monobenzotetrazaporphin (in* PhCl), *and (C) magnesium tetrazaporphin* [6] *(in pyridine).*



The material from the accumulated solutions was chromatographed in chlorobenzene on kieselguhr, as before, and the tribenzotetrazaporphin removed as a fast-running blue band (1). This was followed by a mauve band of the new pigment (2). On continued elution, a small light blue band (3) and then a green band (4) passed down. Spectroscopic examination and acid treatment indicated that the traces of material were (3) a mixture of the new pigment with a heavy-metal tribenzotetrazaporphin, and (4) an alkaline-earth metal derivative of the new pigment. The light-absorption curve for the last was undoubtedly that of a new, pure, metallic tetrazaporphin (see Fig. 2). On acid treatment the absorption spectrum changed to that of fraction (2). Hence this solution was that of

a new metal-free tetrazaporphin, and the unusual doublet at 590—600 mμ was therefore authentic and not caused by a contaminant. A plot of $\lambda_{max.}$ of the longest-wavelength band against the number of benzene rings, for tetrazaporphin, tribenzotetrazaporphin, and phthalocyanine, indicated that the new pigment ($\lambda_{max.}$ 641 mμ) was *mono*benzotetrazaporphin. The fluorescence, which is reminiscent of that of tetrazaporphin, suggested the same.

This spectroscopic identification of monobenzotetrazaporphin has been made certain by recent work of Brown, Linstead, and Whalley [8] on the tetrazaporphins with methyl and fused-benzene-ring substituents.

Experimental

Microanalyses were by Mr. F. H. Oliver and Miss J. Cuckney of this Department.

Attempts to separate Tribenzotetrazaporphin from Phthalocyanine.—(i) Interaction of di-imino-*iso*indoline, succinimide, and lithium butoxide in butanol gave a mixture of lithium pigments, easily soluble in many organic liquids, but chromatography failed because of demetallation on the columns. (ii) The magnesium pigments, likewise easily soluble, were formed only in traces. (iii) Satisfactory separation of the metal-free mixture of pigments [1] was not effected by extractive crystallisation, vacuum-sublimation, or fractional precipitation from 80—100% phosphoric acid or concentrated sulphuric acid.

Estimation of the Pigment Mixtures.—The crude pigment [1] (*ca.* 0·6 g. sample) was stirred with 75% acetic acid for 5 hr. and the mixture centrifuged. The solid was washed by centrifugation with 75% acetic acid, methanol, and then ether, and dried. The loss in weight represented non-pigment material (*ca.* 73%). The crude pigment (0·6 g.) was dusted into stirred concentrated sulphuric acid (30 c.c.) during 15 min. After 2 hr., the solution was poured on crushed ice (from distilled water), and the mixture (*ca.* 75 c.c.) centrifuged. The solid was washed with water by centrifugation and dried: it was pure phthalocyanine (yield, *ca.* 20%) (Found: C, 74·7; H, 3·8; N, 21·7. Calc. for $C_{32}H_{18}N_8$: C, 74·7; H, 3·5; N, 21·8%). By difference the tribenzotetrazaporphin content was *ca.* 7%. The spectroscopic method—measurement of extinctions at 594 and 698 mμ (in PhCl solution)—confirmed the result.

*Condensation of Di-imino*iso*indoline with Succinimidine* (cf. ref. 1).—Dilution of the reaction mixture decreased the yield of crude pigment. Passage of nitrogen to facilitate the removal of ammonia increased the yield. Increase in b. p. of the alcohol solvent increased somewhat the yield of crude pigment but decreased the relative content of tribenzotetrazaporphin. Basic solvents offered no advantage, whilst in acetic acid pigment was not formed.

Attempts to prepare Tribenzotetrazaporphin from Alternative Compounds.—No useful results came from interaction of (i) succinic and phthalic anhydrides or nitriles in molten urea in the presence of ammonium molybdate, (ii) succinimidine and phthalonitrile in boiling ethanol, (iii) succinimidine and 1-imino-3-morpholino*iso*indolenine,[9] and (iv) di-imino*iso*indoline and diethyl succindi-imidoate and its hydrochloride.[10]

*Effect of Hydrogen-acceptors and Oxidising Agents on the Condensation of Di-imino*iso*indoline with Succinimidine.*—(i) Di-imino*iso*indoline (3·14 g.), succinimidine (0·7 g.), and maleic acid (0·25 g.) were boiled together in ethanol (20 c.c.) for 15 hr., during which dry nitrogen was passed through the solution. The composition of the product (1·7 g.) was estimated by the method given above (Found: Non-pigment material, 87·7; Phthalocyanine, 4·6; Tribenzotetrazaporphin, 7·7%). (ii) Condensation, without the maleic acid, afforded 1·63 g. of product (Found: Non-pigment material, 72·5; Phthalocyanine, 20·7; Tribenzotetrazaporphin, 6·8%). (iii) Sodium chlorate (0·3 g.) was as effective as maleic acid. Less effective were *m*-dinitrobenzene > sodium perchlorate, nitrobenzene, triethylamine *N*-oxide > chloranil. Di-*tert.*-butyl peroxide was ineffective. With benzoyl peroxide and lead tetra-acetate, no pigment was formed.

Tribenzotetrazaporphin (cf. ref. 1).—(a) *Formation.* Di-imino*iso*indoline (9·42 g.), succinimidine (2·1 g.), and sodium chlorate (0·9 g.) were boiled together in dry ethanol (50 c.c.) for 24 hr., whilst dry nitrogen was passed through the solution. The product (4·07 g.) was washed thoroughly with 75% acetic acid and then ethanol, and the residue was dried, powdered, and extracted continuously with benzene to yield crude tribenzotetrazaporphin (0·95 g.).

[8] Brown, Linstead, and Whalley, unpublished work.
[9] Clark, Elvidge, and Golden, *J.*, 1956, 4135.
[10] Pinner, *Ber.*, 1883, **16**, 352.

(b) *Chromatography.* (i) A filtered chlorobenzene solution of a portion of the crude pigment (15 mg./l.) was run continuously on to a column (8 × 40 cm.) of tartaric acid hydrate (B.P.; Hopkin & Williams, Ltd.). Some phthalocyanine washed through (in *ca.* 3 l.), followed by tribenzotetrazaporphin (at about the original concentration) contaminated with a trace of phthalocyanine. Most of the phthalocyanine was adsorbed as a green band, and the column was run until this extended nearly to the bottom (after 50 l.). The column was then washed with chlorobenzene (3 l.). (ii) 4-L. batches of the tribenzotetrazaporphin eluate (11·4 mg./l.; 53 l.) were run on to separate columns (6 cm. diam. × 1 cm.) of alumina (Spence, type H, deactivated to Brockmann grade IV [11] with 10% of water [12]). [Each alumina column, packed dry, was supported in a chromatogram tube on a filter-paper disc resting on silver sand. A paper disc protected the upper surface of the alumina.] Tribenzotetrazaporphin was retained on the alumina whilst the phthalocyanine passed through. *Without delay*, each column was washed with chlorobenzene (0·5—1·5 l.) and then eluted with chlorobenzene (1·5—3 l.) containing 5% of ethanol. 12-L. batches of the ethanolic eluates were filtered and distilled to 50 c.c., and the concentrates kept overnight. The small dark blue needles (total yield, 430 mg.) were free from phthalocyanine but contained a trace of a related pigment ($\lambda_{max.}$ *ca.* 640, 590 mμ). Extractive crystallisation of 50—100 mg. portions gave tribenzotetrazaporphin (average recovery, 87%) (Found: C, 72·6; H, 4·0; N, 24·2. Calc. for $C_{28}H_{16}N_8$: C, 72·4; H, 3·5; N, 24·1%).

Before conversion into derivatives, the pigment was chromatographed on kieselguhr,[1] but was found to be pure.

Chlorobenzene which contained unwanted pigment was recovered by filtration through a column (6 cm. diam × 3 cm.) of alumina–charcoal (5 : 1 by vol.) supported on alumina (6 cm.). Ethanolic chlorobenzene was washed continuously with water for 24 hr., and then run through a similar column surmounted by calcium chloride (3—8 mesh; 10 cm.).

Metal Derivatives of Tribenzotetrazaporphin.—Tribenzotetrazaporphin (67 mg.), copper bronze (1·5 g.), and *o*-dichlorobenzene (30 c.c.) were heated together under reflux for 5 hr. Next day, the solid was collected and extracted (Soxhlet) with chlorobenzene, to yield *copper tribenzotetrazaporphin* (51 mg.), which formed fine dark blue needles after extractive recrystallisation from chlorobenzene (Found: C, 64·0; H, 3·1; N, 21·4; Cu, 12·1. $C_{28}H_{14}N_8Cu$ requires C, 63·9; H, 2·7; N, 21·3; Cu, 12·1%).

Tribenzotetrazaporphin (42·7 mg.) was extracted into a suspension of anhydrous cobalt acetate (1·5 g.) in boiling *o*-dichlorobenzene (50 c.c.), and after 5 hr. the mixture was allowed to cool. Next day, the solid was washed well with 10% acetic acid, ethanol, and ether, and the residue extractively crystallised from chlorobenzene, to give *cobalt tribenzotetrazaporphin* (41·3 mg.) as dark blue needles (Found: C, 64·6; H, 3·0; N, 20·9; Co, 11·1. $C_{28}H_{14}N_8Co$ requires C, 64·5; H, 2·7; N, 21·5; Co, 11·3%).

o-Dichlorobenzene (35 c.c.), containing Raney nickel (1 g.), was boiled for 5 hr. in an extractor, the thimble of which contained tribenzotetrazaporphin (50 mg.). The extract mixture was kept overnight and then the solid was extracted with chlorobenzene for 30 hr., and the *nickel tribenzotetrazaporphin* (20·6 mg.) was extractively recrystallised from chlorobenzene to give dark blue needles with a lavender reflex (Found: C, 64·7; H, 3·2; N, 22·0; Ni, 10·2. $C_{28}H_{14}N_8Ni$ requires C, 64·5; H, 2·7; N, 21·5; Ni, 11·3%).

Dibromotribenzotetrazaporphin.—(a) *Preparation.* A solution of tribenzotetrazaporphin (57 mg.) in chlorobenzene (12 l.) was divided into 2-l. portions. Each was stirred and treated with bromine (0·5 c.c.), and 10 min. later was washed with 2N-sodium carbonate (2 × 200 c.c.) and with water (2 × 200 c.c.) and filtered through cotton wool. Concentration of the combined solutions to 25 c.c., and cooling, yielded *dibromotribenzotetrazaporphin* (60·6 mg., 79%), which, on extractive crystallisation from chlorobenzene, formed dark blue needles with a purple reflex (Found: C, 54·1; H, 2·7; N, 18·3; Br, 25·7. $C_{28}H_{14}N_8Br_2$ requires C, 54·0; H, 2·3; N, 18·0; Br, 25·7%).

(b) *Oxidative degradation.* A solution of the pigment (86·2 mg.) in concentrated sulphuric acid (4 c.c.) at 0° was treated rapidly with 0·01N-potassium dichromate (20 c.c.) and then kept at 70° for 5 min. Ferrous sulphate (0·5 g.) was added and the solution extracted with benzene for 48 hr. The extract was treated with charcoal, dried (Na_2SO_4), and evaporated, and the residue was taken up in ether, and the solution filtered and evaporated, but inorganic

[11] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.
[12] B.P. 565,405/1944; Kaplan and Meller, *J. Gen. Chem.* (*U.S.S.R.*) (U.S. trans.), 1949, **19**, 507.

contaminants had not been removed. Attempts to separate the mixture of imides by fractional sublimation, adsorption chromatography in chloroform on alumina, and partition chromatography between ether or ethyl acetate and water on silica gel were abortive. However, paper chromatography was successful.

Dibromomaleimide (5 mg.), phthalimide (5 mg.), 4-bromophthalimide (5 mg.), a 1 : 3 : 1 mixture of these three imides (10 mg.), and the degradation product (10 mg.) were dissolved separately in butanol (1-c.c. portions). The solutions (2 drops of each) were applied to a sheet (12 × 12 in.) of Whatman no. 1 filter paper to form a row of 5 spots near to the lower edge, and the paper was developed upwards with butanol saturated with aqueous ammonia (*d* 0·88), in a glass tank, until the solvent front had advanced 20—30 cm. (*ca.* 9 hr.). The paper was dried in the air for 4 hr., dipped in 1 : 1 acetone–ethanol, blotted, and when almost dry, exposed to chlorine gas (in a tank) for 10 min. The paper was dipped for 2 min. into a 1 : 1 mixture of saturated *o*-tolidine in 2% acetic acid and 0·05N-potassium iodide in 2% acetic acid. The paper was washed with 2% acetic acid, blotted, and dried in the air. The chromatogram appeared as blue spots, which faded to a permanent pale brown (cf. ref. 13). R_F values were :

Dibromomaleimide	0·25		
Phthalimide		0·56	
4-Bromophthalimide			0·70
1 : 3 : 1 Mixture of imides	0·26	0·54	0·71
Degradation product	0·26	0·53	

Dibromomaleimide.—Dunlap's method [4] was modified in that dibromomaleic anhydride [14] (1 g.) was fused with urea (0·35 g.) at 85—90° for 2 hr. (We found his original conditions led to decomposition and polymerisation.) Treatment of the cold, red-brown melt with water (100 c.c.) left dibromomaleimide (146 mg., 15%), m. p. 220° undepressed by a sample (m. p. 225—227°) obtained in 7% yield *via* the bromination of succinimide.[15] Ciamician and Silber [15] give m. p. 225°.

4-Bromophthalimide.—4-Nitrophthalimide [16] was reduced to 4-aminophthalimide.[17] A solution of the amine (5·4 g.) in concentrated sulphuric acid (15 c.c.) was cooled in an ice-salt mixture, and stirred with powdered sodium nitrite (2·6 g.). Subsequently, potassium bromide (13 g.) was added to the greenish solution (frothing), which was cooled again, and then copper powder (8 g.) was added in portions (frothing). After 15 min., the mixture was poured into ice-water (200 c.c.) (frothing), and the filtrate was extracted with benzene overnight. Concentration of the extract afforded 4-bromophthalimide (1·24 g.), m. p. 213—218°, which after recrystallisation from acetic acid had m. p. 229° (Found : N, 6·5. Calc. for $C_8H_4O_2NBr$: N, 6·2%). Waldmann's bromophthalimide [3] had m. p. 225—229°.

Monobenzotetrazaporphin.—Material from the mauve band in the kieselguhr chromatograms [1] and from the mother-liquors from the crystallisation of tribenzotetrazaporphin (above) was bulked. A solution in chlorobenzene (2 l.; 10 mg.) was run on to a column (4 × 90 cm.) of kieselguhr (acid-washed, British Drug Houses, Ltd.) and the chromatogram developed with chlorobenzene. Coloured zones separated, and were eluted, and the constituents identified, as follows : (1) Blue, eluted in *ca.* 30 l., $\lambda_{max.}$ 675, 594, 566, 349 mμ, tribenzotetrazaporphin. (2) Mauve, eluted in *ca.* 15 l., $\lambda_{max.}$ 641, 599, 589, 345 mμ, monobenzotetrazaporphin (Fig. 2). (3) Pale blue, eluted in *ca.* 3 l., $\lambda_{max.}$ (visible) 661, 641, 629, 599, 589, 565 mμ, unaffected by hydrochloric acid : a mixture of monobenzotetrazaporphin and a (? heavy)metal tribenzotetrazaporphin. (4) Green, eluted by 3 : 97 ethanol–chlorobenzene (1 l.), $\lambda_{max.}$ 622, 569, 340, 295 mμ, demetallated by cold hydrochloric acid [solution then had $\lambda_{max.}$ identical with fraction (2)], ? magnesium monobenzotetrazaporphin (see Fig. 2).

We gratefully acknowledge a grant (to J. H. G.) from the Department of Scientific and Industrial Research, and generous gifts of chlorobenzene from Imperial Chemical Industries Limited, Dyestuffs Division.

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[13] Rydon and Smith, *Nature*, 1952, **169**, 922; Reindel and Hoppe, *Chem. Ber.*, 1954, **87**, 1103.
[14] Diels and Reinbeck, *Ber.*, 1910, **43**, 1274.
[15] Ciamician and Silber, *Ber.*, 1884, **17**, 556.
[16] *Org. Synth.*, Coll. Vol. II, p. 459.
[17] Rodionov and Fedorova, *Bull. Soc. chim. France*, 1939, **6**, 478.