Tetrapyrroles. Part 2.† Synthesis and Electronic Spectra of Some Quinone-porphyrins

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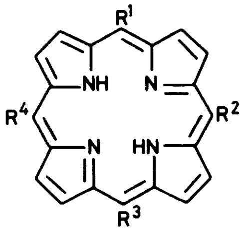
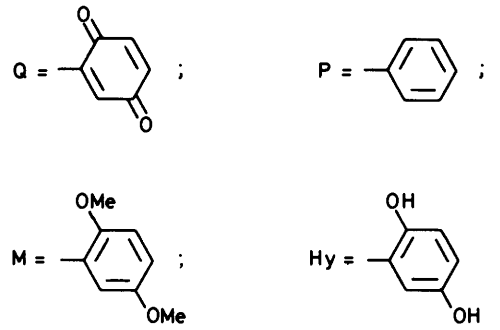
Four quinone-porphyrins have been synthesised. Their electronic spectra show several unusual features consistent with light-induced intramolecular charge-transfer.

SEVERAL studies[1-3] have shown that quinones quench the fluorescence of porphyrins and metalloporphyrins. This quenching occurs dynamically at diffusion-controlled rates and probably *via* an electron-transfer intermediate, which may be written (porphyrin)$^{+\bullet}\cdots$(quinone)$^{-\bullet}$. In this respect the fluorescence-quenching reaction resembles the primary light-induced charge-separation of photosynthesis.[4] In bacterial photosynthesis,[5] for example, an intermediate of this type (although the porphyrin was dimeric) has been proposed as a primary electron-transfer product.



	R^1	R^2	R^3	R^4
(1)	Q	Q	Q	Q
(2)	P	Q	Q	Q
(3)	P	P	Q	Q
	P	Q	P	Q
(4)	P	P	P	Q
(5)	P	P	P	P
(6)	M	M	M	M
(7)*	Hy	Hy	Hy	Hy



* Satisfactory microanalytical results were not obtained

Attempts at the chemical modelling of this process have led recently to the synthesis of a new class of porphyrin,[6-9] quinone-porphyrins, in which a quinone moiety is covalently linked to a porphyrin. Depending upon the exact nature of this linkage, the porphyrin–quinone distances and orientations are more or less constrained. This should allow a more detailed interpretation of their interaction.

We report below further details of our synthesis[7] of the quinone–porphyrin (1) and of its extension to the unsymmetrically substituted porphyrins (2)—(4). In general we have followed the synthetic procedures of Adler[10] (for the symmetrically substituted porphyrins) and of Anton and Loach[11] (for the unsymmetrically substituted ones). The electronic emission and absorption spectra of the products are unusual in several respects.

EXPERIMENTAL

Synthesis of meso-*Tetrakis-*(2,5-*dimethoxyphenyl*)*porphyrin* (6).—2,5-Dimethoxybenzaldehyde (0.05 mol) in propionic acid (500 ml) was brought to reflux. Pyrrole (0.05 mol) was then added. After refluxing for 2.5 h the propionic acid was distilled off. The residue was chromatographed on alumina (grade III) in CH_2Cl_2. The purple band was collected, evaporated to dryness and recrystallised from CH_2Cl_2–CH_3OH to yield the *product* (1.0 g, 9%), m.p. >300 °C (Found: C, 73.35; H, 5.6; N, 6.45. $C_{52}H_{46}N_4O_8$ requires C, 73.05; H, 5.4; N, 6.55%).

Synthesis of meso-*Tetrakis-*(2,5-*dihydroxyphenyl*)*porphyrin* (7).—All glassware was dried (100 °C, *in vacuo*) before use and CH_2Cl_2 was freshly distilled from phosphorus pentaoxide. Compound (6) (0.4 mmol), dissolved in the minimum volume of CH_2Cl_2, was dropped from a closed funnel into BBr_3 (2 ml) in CH_2Cl_2 (20 ml) at −80 °C in an apparatus with a $CaCl_2$ drying tube. After stirring at −80 °C (1 h) the mixture warmed slowly to room temperature. After standing (24 h) the mixture was cooled to 0 °C and excess of water added slowly to hydrolyse unchanged BBr_3. The mixture was shaken with triethylamine to neutralise the green porphyrin dication in the aqueous phase. The purple precipitate was filtered from the mixed solvents, washed well with water, and dissolved in acetone, discarding some acetone-insoluble material. The precipitate was chromatographed on silica (Kieselgel 60) in acetone–petroleum (1 : 1) and recrystallised from methanol–petroleum. The product (90%) had unsatisfactory microanalytical figures. R_F Values for t.l.c. on silica in $CHCl_3$ were for (6) 0.2 and (7) 0.0 and in ethyl acetate (6) 0.95 and (7) 0.75.

Synthesis of meso-*Tetrakis-*(p-*benzoquinonyl*)*porphyrin* (1).—Compound (7) (0.06 mmol) was dissolved in the minimum of CH_3OH and heated to reflux. Dichlorodicyanoquinone (DDQ) (0.36 mmol) in CH_3OH was added and the mixture refluxed for 0.5 h. The purple-black precipitate was filtered from the cooled solution, washed with CH_3OH, and dried to yield the *product* (0.05 mmol, 80%), m.p. >300 °C (Found: C, 71.85; H, 3.05; N, 7.8. $C_{44}H_{22}N_4O_8$ requires C, 71.95; H, 3.0; N, 7.65%).

Synthesis of Compounds (2)—(4).—Pyrrole (50 mmol),

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† Part 1, ref. 14.

benzaldehyde (25 mmol), and 2,5-dimethoxybenzaldehyde (25 mmol) were refluxed in propionic acid (500 ml) for 1.5 h. Propionic acid was then distilled off, the residue extracted into CH_2Cl_2 and chromatographed on alumina to give a single broad purple band which was collected and evaporated to a purple-black solid. T.l.c. in benzene on silica revealed six components; the most mobile was (5) and the least mobile (6). This mixture was separated on a larger scale by short-column chromatography (s.c.c.).[12] T.l.c.-grade silica (Kieselgel 60; 200 g) as a slurry in CH_2Cl_2 was poured into a wide (7 cm diameter) glass column whose upper end could be connected to a source of N_2 at *ca.* 1 atmosphere excess of pressure. The mixed solid porphyrins (700 mg) were transferred to the column in saturated CH_2Cl_2 solution and eluted by solvents of progressively increasing polarity. Fraction 1 (benzene–petroleum 1 : 1) was identified as (5) and discarded. Fraction 2 (benzene) was collected and evaporated to dryness. The resulting solid was treated as described above to yield *compound* (4) (yield * 68%), m.p. >300 °C (Found: C, 81.85; H, 4.25; N, 8.95. $C_{44}H_{28}N_4O_2$ requires C, 82.6; H, 4.35; N, 8.7%). Fraction 3 (eluted by benzene) was isolated and treated as before to yield *compound* (3) (yield * 75%), m.p. >300 °C (Found: C, 78.45; H, 3.75; N, 8.4. $C_{44}H_{26}N_4O_4$ requires C, 78.35; H, 3.85; N, 8.3%). Fraction 4 (eluted by CH_2Cl_2) was isolated and treated as before to yield compound (2) (yield * 91%), m.p. >300 °C (Found: C, 75.3; H, 3.35; N, 7.7. $C_{44}H_{24}N_4O_6$ requires C, 75.0; H, 3.4; N, 7.95%). Fraction 5 (CH_2Cl_2) was identified spectroscopically and by t.l.c. as the symmetrical porphyrin (5). The extra component detected by t.l.c. in the solid mixture before chromatography was presumably one of the two geometrical isomers of (3), which were not resolved on the column.

U.v.–visible spectra were recorded on a Unicam SP 1800 whose output was digitised to 8-bit precision and recorded on paper tape for computer processing. Holmium and praesodymium filters were used for calibration. The computer programs were written in DEC 10 FORTRAN, incorporating calls to Hewlett–Packard 7200-series plotting routines. Listings are available. Fluorescence spectra were investigated with an Aminco-Bowman spectrofluorimeter with 150 W xenon source and an EMI 9785 red-sensitive photomultiplier.

RESULTS

U.v.–visible absorption spectra of the quinone–porphyrins (1)—(4) resemble broadly that of the archetypal *meso*-substituted porphyrin (5). That is, absorption bandwidths increase progressively along the series (5)—(1) while the general appearance of the spectrum (an intense Soret or B band at 420 nm and a system of weaker Q bands in the range 500—650 nm) [13] alters little. In fact the spectra of (4)—(1) are well reproduced by convoluting the spectrum of (5) with broadening functions of appropriate half-widths (Table). Results of a typical computation are shown in the Figure. Positions of the absorption band maxima of the quinone-porphyrins (Table) suggest [14] that the electron-withdrawing power of the *para*-quinone moiety (as transmitted across the point of union to the macrocycle) is rather greater than that of phenyl and comparable with that of *para*-fluorophenyl.

None of the quinone-porphyrins showed detectable fluorescence (*i.e.* $\phi_f < 10^{-3}$) in degassed toluene. Such low levels of fluorescence are unprecedented [13] in light-atom porphyrins. Radiative lifetimes were estimated [15] from the Q_x(0–0) band areas to be *ca.* 10^{-7} s, so that the fluorescent (or prefluorescent) states must be deactivated by processes with $k_1 > 10^{10}$ s^{-1}.

Ultraviolet–visible absorption data for porphyrins (1)—(6) in benzene at 21 °C

Porphyrin	(1)	(2)	(3)	(4)	(5)	(6)
B (nm)	410	414	418	418	419	420
Q_y(0—1) (nm)	504	504	513	512	514	512
Q_y(0—0) (nm)				544	549	545
Q_x(0—0) (nm)	596	600	598	594	592	590
Q_x(0—0) (nm)	660	660	658	654	648	652
* γ/cm^{-1}	400	200	130	50		0

* In the Lorenzian broadening function $L(\nu) = \gamma^2/(\nu^2 + \gamma^2)$: the tabulated value of γ is that which best fits the observed B-band profile of the quinone-porphyrin when convoluted with the observed B-band profile of (5) [B(ν)] according to $A(\nu) = N\int_{w=0}^{\infty} B(w)L(\nu - w)\mathrm{d}w$ where N is an arbitrary normalising factor and the integration is evaluated as a sum over, in practice, rather more modest limits.

The deactivation processes were further studied, for (1), (4), and (5) (which was included for comparison) by picosecond flash spectroscopy. The first-formed singlet states of (1) and (4) had sub-picosecond lifetimes in contrast to that of (5), which survived for several nanoseconds. A major product of all three singlets was the porphyrin-like triplet. In the cases of (1) and (4), this triplet further decayed to yield a long-lived (*ca.* 10^{-8} s) electron-transfer state.[16]

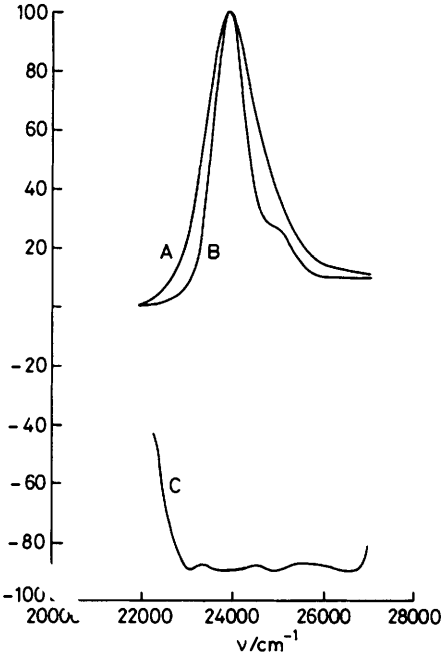

FIGURE A, Observed absorption band profile of (1) in benzene solution at 25 °C. B, Observed absorption band profile of (5) in benzene at 25 °C. C, Weighted least-squares difference between A and B convoluted with a Lorenzian of half-width 400 cm^{-1}

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* Yields based on statistical proportions of the mass of mixed porphyrins added to column for s.c.c separation

DISCUSSION

Replacing even one of the *meso*-phenyl substituents on (5) by a quinone moiety causes at least three major changes in its spectroscopic behaviour. First, it broadens all the absorption bands, secondly, it greatly decreases the fluorescence quantum yield and thirdly, it introduces a sub-picosecond deactivation process for the optical singlet state. When considering the origin of these effects, it is of interest to note that they can all be more or less duplicated intermolecularly by adding quinones to solutions of (5). Thus DDQ broadens [17,18] the *Q* bands of (5) in benzene solutions, DDQ and benzoquinone quench the fluorescence of (5) in toluene solution by both static [18] and dynamic [3] routes, and solutions of (5) in the presence of high concentrations of benzoquinone show picosecond flash spectroscopic behaviour resembling that of the quinone-porphyrins.[16] Additionally, the intermolecularly induced broadening of the absorption bands of (5) is apparently symmetrical and does not shift the band maximum.[17,18]

Substituent-induced u.v.–visible absorption band broadening of this type may arise in two different ways. First, the substituent may modulate the energies of the porphyrin electronically excited states by coupling them to its own rotational, vibrational, or electronic states. Alternatively, the substituent may shorten the excited-state lifetime, leading to uncertainty-broadening, by promoting an extremely rapid reaction from the optical state.

In the quinone-porphyrins, substituent rotation is of course confined to the axis of the porphyrin–quinone bond while in the bimolecular quinone-porphyrin complex the complexed quinone should rotate freely. Despite this difference of rotational freedom, the porphyrin absorption bands are similarly broadened in both cases. Moreover in *meso*-tetrakis(*o*-hydroxyphenyl)porphyrin, substituent rotation is slow enough to allow isolation [19] of geometrical isomers. And yet its absorption spectrum does not show broadening of the present type.[20]

Vibrational modulation of the porphyrin excited states by adjacent quinones seems more probable. Their carbonyl groups have an intense i.r. absorption. This means that the local electric dipole moment varies rapidly with changes in the CO bond length. Thus the electric field from the proximal CO dipoles will vary over a wide range during each vibrational period. And this in turn will couple the porphyrin electronic energy states to the instantaneous value of the CO bond length at the moment of porphyrin electronic absorption. This mechanism resembles that widely accepted [21] for the *d–d* absorption bands of transition metal complexes, and its effects should be detectable by resonance–Raman spectroscopy.[22]

Direct coupling of quinone electronic states to those of the porphyrin system is a less convincing explanation of the broadening. It is true that the tail of the benzoquinone $\pi^*\leftarrow n$ transition overlaps the porphyrin Soret (B-band) region, so that, given an adequate interaction integral, this would be a plausible source of B-band broadening. However the quinone-porphyrin visible (Q) bands, which occur in a region completely devoid of quinone optical states, are even more broadened than the Soret bands. And, moreover, such coupling is unlikely to produce *symmetrical* broadening of the porphyrin bands over so wide a region of the spectrum.

Lifetime-broadening of metalloporphyrin absorption bands has been observed under high-resolution conditions, and in one case (ferrocytochrome) this has been attributed [23] to porphyrin–metal charge transfer in the excited state. An analogous process of porphyrin–quinone charge transfer thus seems a possible source of the band-broadening observed in the quinone-porphyrins. Such an explanation would have the philosophical attraction of explaining the band-broadening, the very low fluorescence yields, and the sub-picosecond processes implied by the picosecond photolysis results in terms of a single process, very rapid porphyrin–quinone electron transfer in the optical state. But there are at present no other grounds for preferring it to vibrational modulation as an explanation of the broadening. Since the former explanation implies that the broadening is homogeneous, while the latter that it is heterogeneous, they should be experimentally distinguishable by laser hole-burning experiments on the broadened and unbroadened Soret (B) absorption bands of (1) and (5).

In conclusion, the present quinone-porphyrins may be considered as possible bases for models of photosynthetic charge-transfer. On illumination in fluid solution at room temperature a charge-transfer state $P^{+\bullet}$–$Q^{-\bullet}$ is stabilised for *ca.* 10 ns [16] before decaying to regenerate the ground electronic state. Chemical modifications of (1)—(4), with a view to coupling this state to reversible metal-ion-based redox reactions, are in progress.

The synthesis of (2)—(4) was initiated by D. Vailhen, Ecole Nationale Superieure de Chimie de Paris, while visiting our laboratories. We thank Dr. T. L. Netzel, Brookhaven National Laboratories, for making available to us the results of his picosecond spectroscopic measurements.

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REFERENCES

[1] P. A. Shakhverdov, *Doklady Akad. Nauk SSSR*, 1967, **174**, 1141.

[2] A. Harriman, G. Porter, and N. Searle, *J. Chem. Soc., Faraday Trans. 1*, 1979, 1515.

[3] S. M. Pemberton, Ph.D. Thesis, University of London, 1978.

[4] G. Porter, *Proc. R. Soc. London., Sect. A*, 1978, **362**, 281.

[5] J. Jortner, *J. Am. Chem. Soc.*, 1980, **102**, 6676.

[6] I. Tabushi, N. Koga, and M. Yanagita, *Tetrahedron Lett.*, 1979, 257.

[7] J. Dalton and L. R. Milgrom, *J. Chem. Soc., Chem. Commun.*, 1979, 609.

[8] T.-F. Ho, A. R. McIntosh, and J. R. Bolton, *Nature (London)*, 1980, **286**, 254.

[9] K. N. Ganesh and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, 1980, 1129.

[10] A. D. Adler, R. F. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

[11] J. A. Anton and P. A. Loach, *J. Heterocycl. Chem.*, 1975, **12**, 573.

[12] B. J. Hunt and W. Rigby, *Chem. Ind.* (*London*), 1967, 1868.

[13] M. Gouterman in ' The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, vol. IIIA, p. 1.

[14] J. Dalton, L. R. Milgrom, and S. M. Pemberton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1980, 370.

[15] S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 1962, **37**, 814; J. B. Birks and D. J. Dyson, *Proc. R. Soc. London*, *Sect. A*, 1963, **275**, 135.

[16] M. A. Bergkamp, J. Dalton, and T. L. Netzel, *J. Am. Chem. Soc.*, 1982, **104**, 253.

[17] H. A. O. Hill, A. J. McFarlane, and R. J. P. Williams, *J. Chem. Soc. A*, 1969, 1704.

[18] A. C. Chan, J. Dalton, L. R. Milgrom, and D. J. Walland, 28th IUPAC Congress, Vancouver, 1981.

[19] L. K. Gottwald and E. F. Ullman, *Tetrahedron Lett.*, 1969, 3031.

[20] J. Dalton and L. R. Milgrom, unpublished data.

[21] F. A. Cotton and G. Wilkinson, ' Advanced Inorganic Chemistry,' Wiley, New York, 1980, 4th edn., p. 666.

[22] W. H. Fuchsman, Q. R. Smith, and M. M. Stein, *J. Am. Chem. Soc.*, 1977, **99**, 4190.

[23] Y. J. Aronowitz and M. Gonterman, *J. Mol. Spectrosc.*, 1977, **64**, 267, and references therein.