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Porphyrin–quinone compounds as synthetic models of the reaction centre in photosynthesis

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ABSTRACT. **Data on the synthesis, steric structure, and photochemical properties of porphyrin–quinone compounds as synthetic models of the reaction centre in photosynthesis are examined and described systematically.**

The bibliography includes 113 references.

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I. Introduction

The electron transfer from the electronically excited chlorophyll molecule or its dimer via intermediate acceptors to the primary quinone-type acceptor is a key step in photosynthesis.[1–4] The efficiency of charge separation in photosynthesis is close to unity. One of the factors ensuring such efficiency is the high degree of the structural organisation of the photosynthetic apparatus. However, the complex structure of the reaction centres of photosynthesising organisms makes it difficult to understand the mechanisms of charge separation in photosynthesis. This and also the attempts to create, by analogy with photosynthesis, artificial systems for the utilisation of solar energy have stimulated the synthesis and study of various compounds which are models of the reaction centres in photosynthesis, such as covalently bound porphyrins with different structures: porphyrin–polymer complexes,[5–7] porphyrin dimers,[8,9] porphyrin–quinone compounds,[10,11] etc.

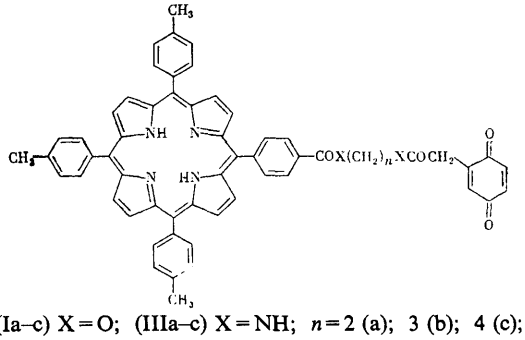
The electron transfer from the porphyrin, whose molecular structure is similar to that of chlorophyll, to a covalently bound quinone models the primary charge separation stage in photosynthesis. The high electron-accepting capacity of quinones has been demonstrated in a number of studies on the flash photolysis of solutions containing electron-donating additives and quinones.[12–22] However, attempts to model charge separation processes in photosynthesis with the aid of homogeneous solutions have encountered considerable problems. The most important of these is the extremely low, compared with photosynthesis, efficiency of the separation of the oxidised and reduced forms of the reactants in solutions. Despite the fact that effective quenching of the fluorescence of chlorophyll and its analogues by quinones has been observed in solutions, the attempts to detect radical-ions have been unsuccessful.[12,13] This is apparently due to the rapid recombination of the radical-ions as a result of the collisions between the radical-cation of the porphyrin (P^+) and the radical-anion of the quinone (Q^-) in solutions.

The attempts to use micelles,[23,24] liposomes,[25,26] and cyclodextran compounds[27] to stabilise the radical-ions and to elucidate the detailed mechanism of the photoseparation of charges have also failed to yield the desired result. This has in fact stimulated the synthesis and study of porphyrin–quinone compounds (P–Q), in which the porphyrin and the quinone are separated by a system of covalent bonds.

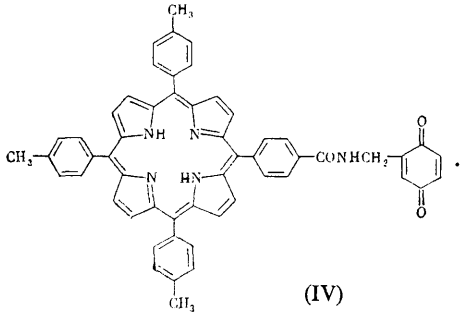
In terms of the character of the bond between the porphyrin and the quinone, all the P–Q compounds synthesised hitherto since 1978 can be divided into two main groups: (1) P–Q compounds with a flexible covalent bond and (2) P–Q compounds with a rigid bond between the porphyrin and the quinone. In addition, covalently bound triads, containing an electron-donating fragment together with P and Q, can be differentiated as an independent group.

II. Porphyrin–quinone compounds with a flexible covalent bond between the porphyrin and the quinone

P–Q derivatives with a flexible bond are the simplest and most readily available. There exist different ways of linking P and Q:



(Ia–c) X = O; (IIIa–c) X = NH; n = 2 (a); 3 (b); 4 (c);



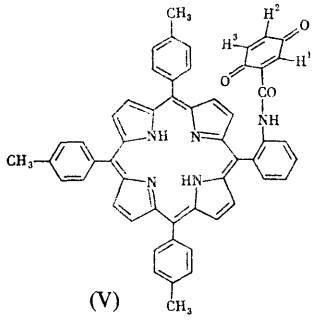
(IV)

Compounds (I) in which the porphyrin and quinone components are linked by a diol chain of different lengths were some of the first to be synthesised.[28,29] 5-(4-Chlorocarboxyphenyl)-10,15-20-tri(4-tolyl)porphyrin (II), obtained by the Rothemund reaction from pyrrole and a mixture of 4-toluic aldehyde and 4-carboxybenzaldehyde[30] and subsequent treatment with thionyl chloride, was condensed in the presence of pyridine with an excess of the alcoholic component obtained by esterifying 2,5-dimethoxyphenylacetic acid with ethane-1,2-diol (derivative a), propane-1,3-diol (derivative b), and butane-1,4-diol (derivative c) with formation of a porphyrin-dimethoxybenzene derivative. The yield of the product was ~60%. After removing the methyl protecting group with BBr_3 and oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), compound (I) was purified chromatographically on silica gel.

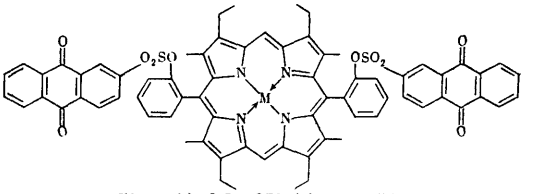
The replacement of the ester linkage by the hydrolytically more stable amide linkage leads to compound (III). It has been suggested[31] that the amide linkage makes the structure more rigid because of its greater similarity to the double bond. The conditions in the synthesis and purification of the derivative (III) are almost identical to those for compound (I), but the hydroquinone adduct was oxidised with PbO_2, which greatly simplified the isolation of the product (III). The yields in the stage involving the condensation of the porphyrin (II) with the amino-component were 40–50%.

In order to obtain the porphyrin-quinone (IV) with a shortened chain, the acid chloride (II) was treated with 2,5-dimethoxybenzylamine.[32] After removing the protecting group and oxidising the hydroquinone component, the product (IV) was obtained similarly to compound (III).

On formation of the amide bond between the two chromophores in the *ortho*-position in the benzene ring of the porphyrin, compound (V) is obtained with a still more rigid structure than compound (IV):[33]



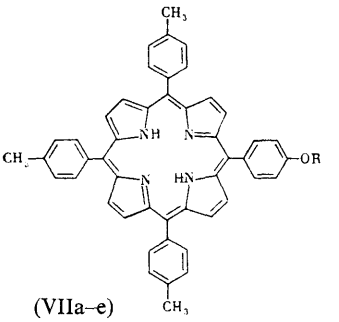
(V)



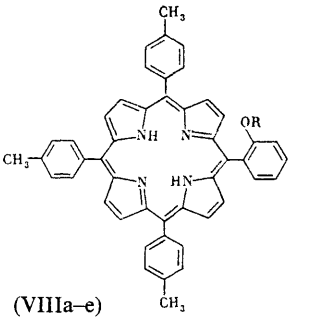
(VI a, b), M = 2H (a); Zn (b).

One equivalent of 5-(2-aminophenyl)-10,15,20-triphenylporphyrin, obtained by the Rothemund reaction from pyrrole and a mixture of benzaldehyde and 2-nitrobenzaldehyde and subsequent reduction with $SnCl_4$ in concentrated hydrochloric acid,[34] was treated with 10 equivalents of 1,4-diacetoxy-2-chlorocarbonylbenzene. The yield of the protected hydroquinone derivative was 76%. Selective hydrolysis with HCl in methanol (pH ~1) followed by oxidation with PbO_2 led to the product (V) in 75% yield.

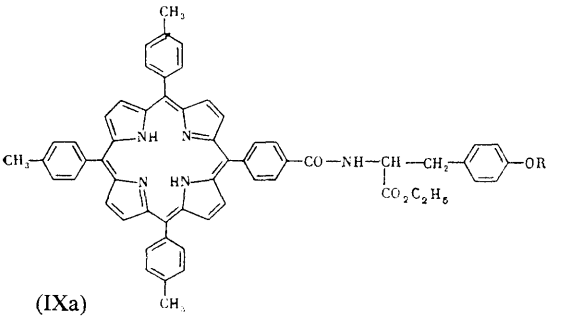
The fact that the sulphonyloxy-derivative involving the *ortho*-position of the phenyl residue in porphyrins has a rigorously defined "folded" conformation[35] led to the idea of synthesising the diquinone compound (VIa).[36] The structure (VIa) was synthesised by condensing 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolylmethane with the corresponding aldehyde in the presence of toluene-*p*-sulphonic acid and subsequent oxidation with DDQ and isolation of the product by column chromatography on silica. The zinc complex (VIb) was obtained by treating the free base (VIa) with zinc acetate:



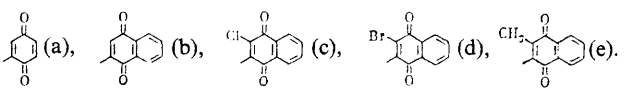
(VIIa–e)



(VIIIa–e)

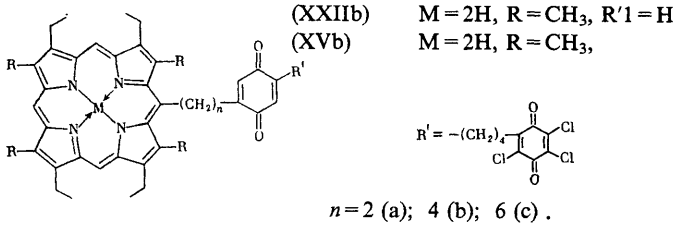


(IXa)

R =  (a), (b), (c), (d), (e).

A convenient method of synthesis of a large number of derivatives (VII)–(IX) has been developed on the basis of the photoinduced cross-condensation reaction between a phenol-containing porphyrin and a quinone.[37,38] 5-(4-Hydroxyphenyl)-10,15,20-tri(4-tolyl)-porphyrin was irradiated at a wavelength > 590 nm in the presence of a tenfold excess of 1,4-benzoquinone with formation of the condensation product (VIIa). No side products were then detected

by thin-layer chromatography (TLC) and ^{1}H NMR spectroscopy. Other P–Q derivatives (VIIb–e), (VIIIa–e), and (IXa) were obtained similarly. The yields were 90–94% for a relatively low degree of conversion (6–41%). The condensation took place via a stage involving the formation of the hydroquinone adduct and the subsequent oxidation to the P–Q compound by the excess of the initial quinone:



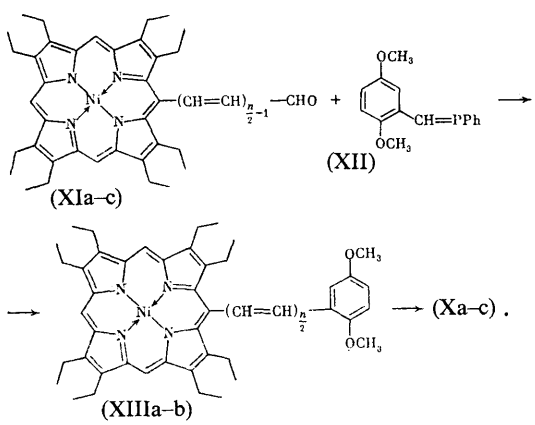
(D)(Xa–c) M = 2H, R = C_2H_5, R′ = H
(XIVa–c) M = Zn, R = C_2H_5, R′ = H
(XXIIb) M = 2H, R = CH_3, R′1 = H
(XVb) M = 2H, R = CH_3,

R′ = $-(CH_2)_4-$

n = 2 (a); 4 (b); 6 (c).

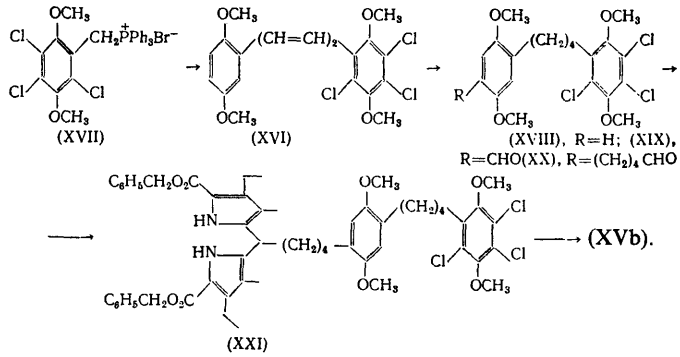
In order to avoid the possible influence of the heteroatom in the chain between the donor and the acceptor on the interaction between the chromophores and on the photoinduced intramolecular charge transfer and also the influence of the phenyl residues on the porphyrin ring, compounds (Xa–c) were synthesised. The chromophores were linked by polymethylene chains of different lengths (n = 2–6).[39] The synthesis was carried out as follows. The nickel complexes of octaethylporphyrins (XIa–c),[40,41] containing the formyl group in the *meso*-position, were condensed by the Wittig reaction with the triphenylphosphorane (XII), producing the dimethoxyphenyl complexes (XIIIa–c) in 82–95% yield (the Scheme 1). After removing the protecting group BBr_3, hydrogenation over Pd/C, and oxidation with DDQ, the yields of compounds (Xa–c) were 20–36%. The zinc complexes (XIVa–c) were obtained by treating the porphyrins (Xa–c) with zinc acetate.

Scheme 1



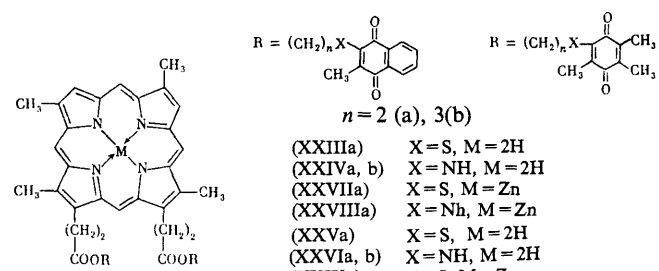
In natural photosynthesis, electron transfer takes place via many stages, which apparently promotes the stabilisation of the state with separated charges. The porphyrin (XVb), containing two series-connected acceptors with a corresponding oxidation-reduction potential (ORP) models such transfer.[42] The presence of two different quinones in this compound ensures a potential gradient in the molecule. The diquinone precursor (XVI) was obtained by the Wittig reaction from 2,5-dimethoxycinnamaldehyde and phosphonium bromide (XVII) (Scheme 2):

Scheme 2



After hydrogenation to compound (XVIII) over Pd/C, formylation by dichloromethyl methyl ether with formation of compound (XIX), and the lengthening of the chain by means of the Wittig reaction with the corresponding phosphonium salt, the aldehyde (XX) was condensed with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole. The yield of the bipyrrole (XXI) was 85%. After removal of the benzyl protecting group from compound (XXI), the condensation of the product with 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-methylenebis(pyrrole) led to the corresponding aetioporphyrin derivative in 24% yield. Demethylation of the latter with BBr_3 and oxidation with DDQ afforded the diquinone derivative (XVb) (yield 24%).

In order to elucidate more accurately the influence of the second acceptor on the charge separation process, the aetioporphyrin (XXIIb), containing only one quinone residue, was synthesised[43] by a procedure similar to that used for compound (XVb):

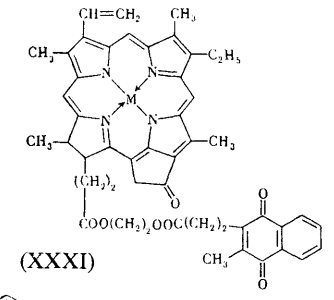


n = 2 (a), 3(b)

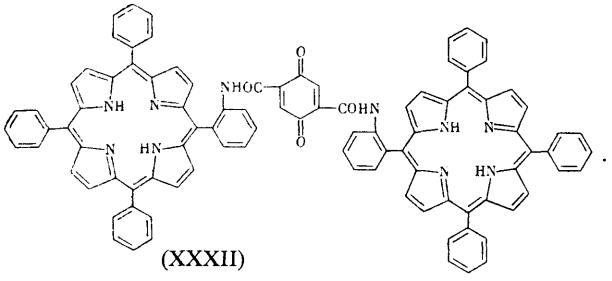
(XXIIIa) X = S, M = 2H
(XXIVa, b) X = NH, M = 2H
(XXVIIa) X = S, M = Zn
(XXVIIIa) X = Nh, M = Zn
(XXVa) X = S, M = 2H
(XXVIa, b) X = NH, M = 2H
(XXIXa) X = S, M = Zn
(XXXa) X = NH, M = Zn.

The present authors[44,45] synthesised P–Q compounds using for the first time deuterioporphyrin IX—a natural porphyrin. The hydroxyquinone derivatives were obtained by adding 2-mercaptoethanol, 2-aminoethanol, and 3-aminopropanol to 2-methylnaphthoquinone and 2,3,5-trimethylbenzoquinone. After purification, the yields were 55–91% for the sulphur containing quinones and 8–25% for the nitrogen-containing quinones. Compounds (XXIII)–(XXX) made it possible to investigate the influence of the nature of the heteroatom linked directly to the quinone fragment on the charge separation process. The condensation of hydroxyquinones with deuterioporphyrin IX using di-t-butyl pyrocarbonate and 4-dimethylaminopyridine led to the diquinone derivatives (XXIII)–(XXVI) in 76–89% yields. After compounds (XXIII)–(XXVI) had been treated

with zinc acetate, the corresponding zinc complexes (XXVII)–(XXX) were obtained:



(XXXI)



(XXXII)

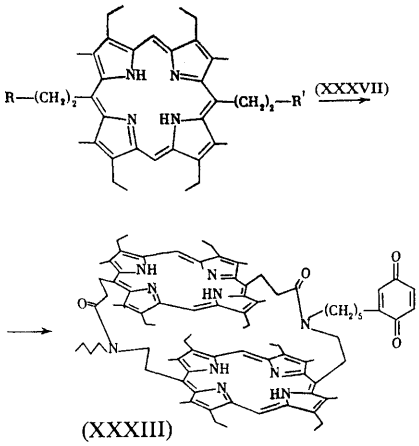
Compound (XXXI) has been synthesised[46] by a method in which carboxy-derivatives of pyrochlorophyll *a* and 2-methylnaphthoquinone were condensed via an ethylene glycol bridge.

It is known that one of the primary donors in bacterial photosynthesis is a chlorophyll "special pair".[47] The model compound (XXXII), in which two 5-(2-aminophenyl)-10,15,20-triphenylporphyrin derivatives are joined together by a bridge containing the benzoquinone structure, was therefore synthesised.[48] However, steric factors hinder the formation of the steric structure of the diporphyrin (XXXII) analogous to the structure of the natural chlorophyll dimer.

A more adequate model of the "special pair" is a rigid dimeric structure of the "surface to surface" type containing two porphyrin macrocycles connected by two covalent bonds.[49–52]

Compound (XXXIII),[53] in which two aetioporphyrin derivatives are linked covalently in the *meso*-position in the "surface to surface" orientation and benzoquinone is joined to the side chain, may make it possible to elucidate the role of the dimeric porphyrins in the stabilisation of the photoinduced state with separated charges. The synthesis was carried out in accordance with Scheme 3: Successive treatment of the di(methanesulphonate) (XXXIV), obtained by the method of Collman et al.,[54] with butylamine [involving the formation of compound (XXXV)] and with 1-(5-aminopentyl)-2,5-dimethoxybenzene led to the diamine (XXXVI) [the yields in the stages involving the formation of compounds (XXXV) and (XXXVI) were 38 and 67% respectively after chromatographic purification]. After the condensation of the amino-derivative (XXXVI) with the acid chloride (XXXVII) by the method of Collman et al.[54] (the yield in the condensation stage was 42%) and the removal of the methyl protecting group with BBr_3 followed by oxidation with DDQ (yield 28%), the P–Q dimer (XXXIII) was obtained. Compound (XXXIII) was purified by preparative TLC.

Scheme 3



(XXXIII)

(XXXIV), R = R' = OSO_2CH_3, (XXXV), R = OSO_2CH_3, R' = NHC_4H_9

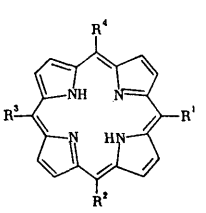
(XXXVI), R = NHC_4H_9, R' = $NH(CH_2)_5$–, (XXXVII), R = R' = COCl.

III. Porphyrin–quinone compounds with a rigid bond between the porphyrin and the quinone

1. Polymer-based models

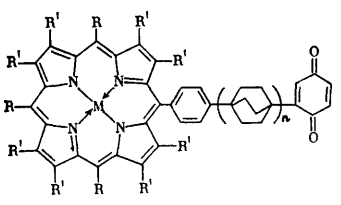
In P–Q compounds with a flexible linkage, there is an appreciable conformational mobility determined by external factors such as solvent polarity, the presence of external ligands, etc. This hinders the interpretation of the experimental results for the electron phototransfer in such systems. It therefore became necessary to create model structures in which the orientations of the donor and acceptor are known beforehand. One of the aspects of studies in this field involved the construction of a model of the photoreaction centre on a polymer base.[55] In this model, the porphyrin and quinone groups are distributed along a polymer chain and are separated by a known distance. The average distance between the chromophores can be regulated by altering the pH and the ionic strength of the solution. The copolymerisation of acrylic acid with 5-(10,15,20-tritolylporphyrinyl)phenyl methacrylate and 2-isopropenylanthraquinone led to the corresponding porphyrin-quinone polymer containing on average one porphyrin and three anthraquinone groups in the polymer chain.

2. Models with a rigid covalent bridge



(XXXVIII) $R^1 = R^2 = R^3 = R^4 = C_6H_3O_2$;
(XXXIX) $R^1 = C_6H_5$; $R^2 = R^3 = R^4 = C_6H_3O_2$;
(XL) $R^1 = R^2 = C_6H_5$; $R^3 = R^4 = C_6H_3O_2$;
(XLI) $R^1 = R^3 = C_6H_5$; $R^2 = R^4 = C_6H_3O_2$;
(XLII) $R^1 = R^2 = R^3 = C_6H_5$; $R^4 = C_6H_3O_2$;
(XLIII) $R^1 = R^2 = R^3 = C_6H_5$; $R^4 = C_6H_3O_2$;
(XLIV) $R^1 = R^2 = C_6H_5$; $R^3 = R^4 = C_6H_3O_2$;
(XLV) $R^1 = R^3 = C_{15}H_{21}$; $R^2 = R^4 = C_6H_3O_2$.

Another way of ensuring the rigidity of the structure is the formation of a C–C bond directly between the porphyrin and quinone components. The first models of this type (XXXIII)–(XLV) were obtained by the Rothemund condensation of pyrrole with an equimolecular amount of either 2,5-dimethyoxybenzaldehyde [in the case of compound (XXXVIII)] or with a mixture of the corresponding aldehydes [in the case of compounds (XXXIX)–(XLV)][56–58] and subsequent treatment with BBr_3 and DDQ. However, in contrast to natural systems, the distance between P and Q in compounds (XXXVIII)–(XLV) is small.

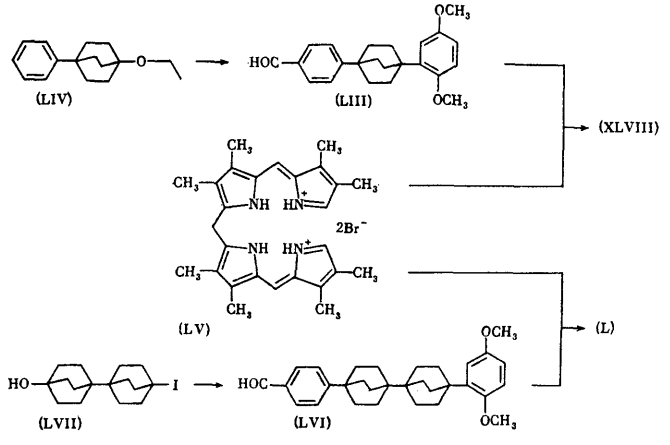


(XLVI) M = 2H, R = H, R' = CH_3, n = 0;
(XLVII) M = Zn, R = H, R' = CH_3, n = 0;
(XLVIII) M = 2H, R = H, R' = CH_3, n = 1;
(XLIX) M = Zn, R = H, R' = CH_3, n = 1;
(L) M = 2H, R = H, R' = CH_3, n = 2;
(LI) M = Zn, R = H, R' = CH_3, n = 2;
(LII) M = 2H, R = n-$CH_3C_6H_4$, R' = H, n = 1.

The structures (XLVI)–(LII), in which the P and Q fragments are linked by a rigid covalent bridge of variable length, are more suitable models of the reaction centres in photosynthesis.[59,60] In such compounds, there is a possibility of rotation only relative to the C–C bond. The models (XLVI)–(LII) are suitable for the investigation of the dependence of the efficiency of the charge separation on the distance between the donor and the acceptor.

The synthesis of these compounds is based on the method involving the condensation of linear tetrapyrroles and the corresponding aldehydes with formation of *meso*-substituted porphyrins (Scheme 4).[59]

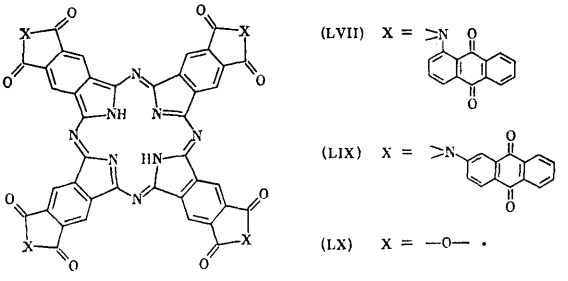
Scheme 4



Arylbicyclo[2.2.2]octylbenzaldehyde (LIII), obtained from the ethyl ether of 4-phenylbicyclo[2.2.2]octanol (LIV), was condensed with *ac*-biladiene (LV) in 40% yield. Arylbibicyclo[2.2.2]octylbenzaldehyde (LVI), obtained from 4'-iodo-1,1'-bibicyclo[2.2.2]octan-4-ol (LVII), reacted similarly with *ac*-biladiene (LV) affording a yield of 30%. After the removal of the protecting group with BBr_3, oxidation with PbO_2, and chromatographic purification, the derivatives (XLVIII) and (L) respectively were obtained. Compound (XLVI) was synthesised similarly. Zinc was introduced by treating compounds (XLVI), (XLVIII), and (L) with zinc acetate to form the complexes (XLVII), (XLIX), and (LI) respectively.

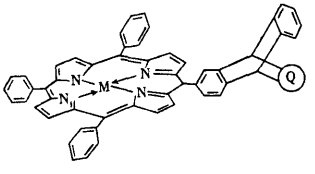
Compound (LII)[60] with the same type of bond but based on a tetraarylporphyrin was obtained by the Rothemund condensation of pyrrole with the appropriate amount of a mixture of 4-methylbenzaldehyde and 1-(4-formylphenyl)-4-(1,4-benzoquinonyl)-bicyclo[2.2.0]octane synthesised from 1-hydroxy-4-iodobicyclo-[2.2.2]octane in three stages.

Phthalocyanines, which are structural analogues of porphyrins, can also behave as electron donors in photochemical processes. The phthalocyanine-quinone compounds (LVIII) and (LIX), which possess only a rotational degree of freedom relative to the C–N bond, were obtained for the first time[61] by condensing the tetraanhydride (LX) with 1- or 2-aminoanthraquinone and subsequent purification by three reprecipitations from dimethylformamide with benzene. The yields of compounds (LVIII) and (LIX) were 38 and 77% respectively:

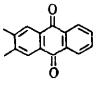


(LVII) X =
(LIX) X =
(LX) X = —O— .

In order to increase the rigidity of the linkage and to prevent the rotation of the chromophores relative to one another, the model compounds (LXI)–(LXIII), in which the porphyrin and quinone components are separated by a triptycene bridge, were synthesised:[62]



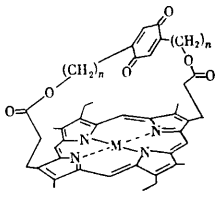
M = 2H (a); Zn (b)

(LXIa, b) Q = 
(LXIIa, b) Q = 
(LXIIIa, b) Q =  .

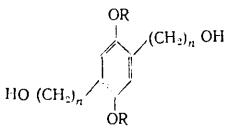
5-(2-Anthryl)-10,15,20-triphenylporphyrin, obtained in 25% yield by condensing a mixture of 2-anthraldehyde, benzaldehyde, and pyrrole, was refluxed in xylene with a fivefold excess of benzoquinone, which led to compound (LXIa) in 40% yield. For the synthesis of compound (LXIIa), the corresponding bicyclic naphthoquinone was obtained by the Diels–Alder addition of naphthoquinone to anthracene with subsequent oxidation *in situ*. After alkylation with dichloromethyl methyl ether and hydrolysis to the aldehyde (yield 30%), the product was condensed with benzaldehyde and pyrrole to form compound (LXIIa) in 15% yield. The derivative (LXIIIa) was obtained similarly by the Rothemund method in 18% yield. The bicyclic anthraquinone necessary for the synthesis of compound (LXIIIa) was obtained from triptycene acylated by phthalic anhydride and treated with polyphosphoric acid.

3. "Capped" porphyrin-quinones

P–Q derivatives, in which the quinone is rigorously oriented over the centre of the porphyrin ring, the so called "capped" porphyrin-quinones, are of considerable interest for the modelling of the charge separation process in photosynthesis. The linkage between the fragments is achieved by means of two or four covalent bridges located opposite one another. The advantages of such model systems consist in the possibility of controlling during synthesis the relative oxidation-reduction potentials of the fragments, the distances between them, and their mutual orientation:



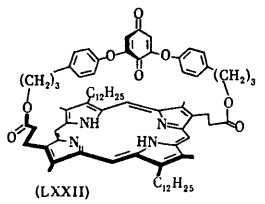
(LXVI) M=2H, n=2;
(LXVII) M=2H, n=3;
(LXX) M=Mg, n=2;
(LXXI) M=Mg, n=3.



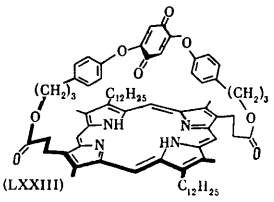
(LXVIII) R=CH_3, n = 2;
(LXIV) R=CH_2OCH_3, n = 2;
(LXIX) R=CH_3, n=3;
(LXV) R=CH_2OCH_3, n = 3.

The synthesis of such P–Q compounds is based on porphyrins with a symmetrical structure. The condensation of the acid chloride of mesoporphyrin II with the corresponding hydroquinone derivatives (LXIV) and (LXV) at high dilution in CH_2Cl_2 in the presence of Et_3N afforded "capped" porphyrins in 7 and 15% yields respectively. The subsequent removal of the protecting groups with BCl_3 and oxidation by PbO_2 led to compounds (LXVI) and (LXVII).[63,64] The quinone component was modified as follows: after the Friedel–Crafts chloromethylation in the 2- and 5-positions, 1,4-dimethoxybenzene was converted into the nitrile and the subsequent hydrolysis and esterification with ethanol gave rise to the diester which was reduced to the alcohol (LXVIII). In order to increase the chain length (to n = 3), 2,5-bis(dichloromethyl)-1,4-dimethoxybenzene was treated with diethyl malonate to form the tetraester, from which the ethoxycarbonyl groups were then removed under mild conditions by refluxing in dimethyl sulphoxide and the product was reduced to the diol derivative (LXIX). However, the methyl protecting group cannot be removed by known methods, without decomposing the structure, from the "capped" porphyrins obtained by condensing the acid chloride of mesoporphyrin II with the alcohols (LXVIII) and (LXIX). This problem was solved by replacing the methyl protecting group by the more labile methoxymethyl protecting group. After acylation and demethylation of the alcohol (LXVIII), the resulting hydroquinone was protected by methoxymethyl ether which was followed by deacylation to give the diol derivative (LXIV). The alcohol (LXIX) was modified analogously to give compound (LXV). Magnesium was introduced into the "capped" porphyrins (LXVI) and (LXVII) by Eschenmoser's method[65] with formation of the magnesium complexes (LXX) and (LXXI).

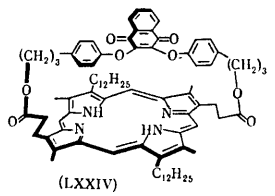
As for the linear P–Q compounds (VII) and (IX),[37,38] the method of photoinduced cross-condensation has been used to synthesise the "capped" porphyrins (LXXII)–(LXXIV) from the modified mesoporphyrin II.[66] The porphyrin component was obtained by condensing 1,5-di(2-chlorocarbonylethyl)-3,7-didodecyl-2,4,6,8-tetramethylporphyrin with 3-(4-hydroxyphenyl)-1-propanol, which led to the formation of the "capped" porphyrins (LXXII)–(LXXIV) on irradiation in the presence of the corresponding quinone derivatives:



(LXXII)



(LXXIII)



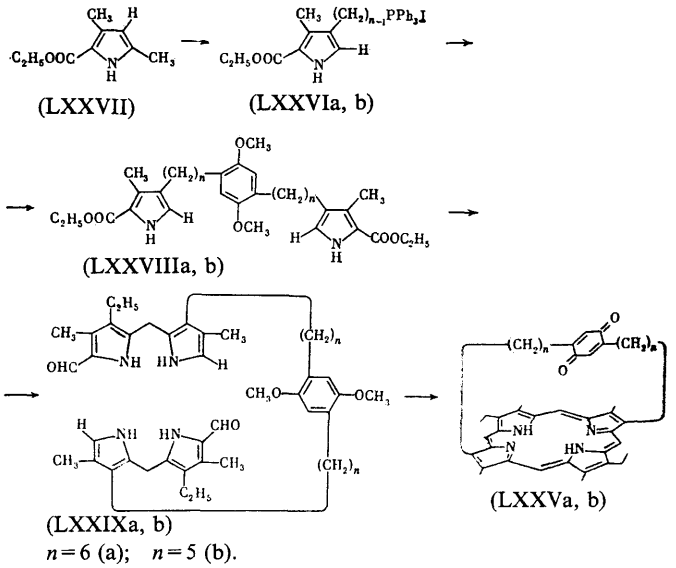
(LXXIV)

In order to achieve different spatial orientations of the donor and acceptor in the molecule relative to one another with the aim of elucidating the dependence of the rate of electron transfer on the relative disposition of the chromophores, the following quinones were selected: 2,6-dichloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, and 2,3-dichloro-1,4-naphthoquinone. The yields obtained in the photoreaction were 34, 42, and 8% of compounds (LXXII), (LXXIII), and (LXXIV) respectively. The low degree of conversion in these reactions was due to the formation of intermediate linear monoquinone derivatives, which cyclise after additional irradiation into the "capped" porphyrins (LXXII) and (LXXIII). In the synthesis of compound (LXXIV), the diquinone derivative was obtained as a side product in 10% yield.

The replacement of the ester linkage by an oligomethylene chain made it possible to create a more stable "capped" P–Q system (LXXVa,b).[67] The key stage of the synthesis (Scheme 5) is the double Wittig reaction of the pyrrole-substituted phosphonium salt (LXXVI), obtained from the pyrrole (LXXII) with a free β-position and 1,4-diformyl-2,5-dimethoxybenzene. The subsequent reduction of the corresponding alkenes leads to the oligomethylene-bridged bis(pyrroles) (LXXVIIIa,b) in 83% (for compound a) and 42% (for compound b) yields (after two stages). The condensation of the bis(pyrroles) (LXXVIIIa,b) having free α-positions with two equivalents of 5-chloromethyl-2-(2,2-dicyanoethylene)-4-ethyl-3-methylpyrrole afforded, after hydrolysis and decarboxylation, the substituted bis(dipyrrolylmethane) (LXXIX). The yield obtained in catalysed cyclisation at high dilution, which promotes the intramolecular reaction, was 20–60% after chromatographic purification, depending on the length of the oligomethylene chain. The demethylation BBr_3, which is allowed by the more stable C–C bond than the ester linkage in compounds (LXXVI) and (LXX), and

oxidation by PbO_2 lead to the porphyrins (LXXXa,b) (in 60 and 70% yields respectively):

Scheme 5



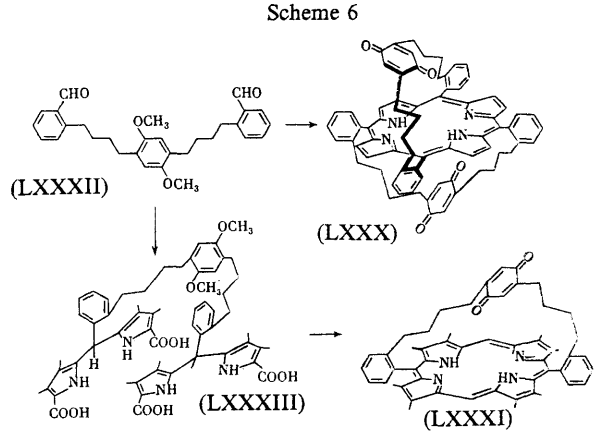
(LXXVII) (LXXVIa, b) (LXXVIIIa, b) (LXXIXa, b) (LXXVa, b)

$n=6$ (a); $n=5$ (b).

According to the strategy of the synthesis, the porphyrin cyclisation is carried out in the last stages, which ensures appreciable yields of the products even for a relatively short chain (n = 5). We may note that Scheme 5 permits the synthesis of "capped" model systems with different chain lengths ($n \geqslant 4$).

The wide variety of ways in which the porphyrin and quinone structures are linked together makes it possible to select the most suitable mutual orientation of the chromophores in the model system. Thus, apart from the compounds described above, the synthesis of the "capped" P–Q derivatives (LXXX) and (LXXXI), containing an oligomethylene chain in the *meso*-position in the porphyrin ring, has been achieved.[68,69] The starting material in the synthesis of compounds (LXXX) and (LXXXI) was the dialdehyde (LXXXII), obtained by the successive modification of 3,3′-(2,5-dimethoxybenzyl-1,4-phenylenedi)-1-propanol (Scheme 6):

Scheme 6

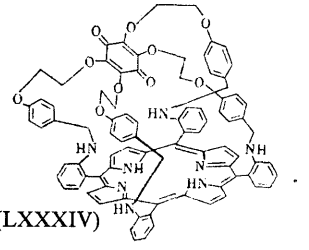


(LXXXII) (LXXX) (LXXXIII) (LXXXI)

The Rothemund condensation of the dialdehyde (LXXXII) with a twofold excess of pyrrole afforded the corresponding porphyrin derivative in 0.1% yield. Its subsequent demethylation with BBr_3 and oxidation with DDQ lead to the diquinone derivative (LXXX) in 41% yield.[68] The extremely low yield of the condensation reaction is due to the lack of specificity in its occurrence, which leads to a large number of cyclisation side products: oligomers and polymers.

Apart from the procedure described above, the dialdehyde (LXXXII) has been condensed with 2-ethoxycarbonyl-3,4-dimethylpyrrole (yield 78%). After subsequent transesterification with benzyl alcohol and catalytic hydrogenation, the corresponding bis(dipyrrolylmethane) (LXXIII) was obtained. The decarboxylation and subsequent condensation were carried out in dichloromethane in the presence of trichloroacetic acid and triethoxymethane (yield 11%). Demethylation with BBr_3 and oxidation with DDQ of the porphyrin fraction, freed chromatographically from oligomers and decomposition products, led to the "capped" P–Q compound (LXXXI) in 54% yield.

In order to synthesise a rigid structure in which the porphyrin and quinone planes are rigorously parallel, compound (LXXXIV) with four covalent bonds between the P and Q fragments has been synthesised:[70]



(LXXXIV)

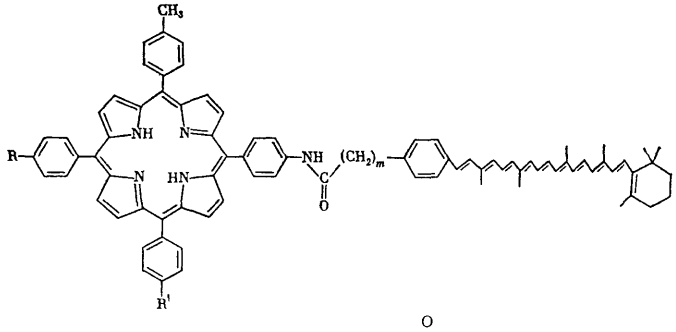
The introduction of an alkoxy-group into fluoranil by treatment with five equivalents of 4-(2-hydroxyethoxy)benzaldehyde in the presence of an excess of CsF led to 2,3,5,6-tetra[2-(4-formylphenoxy)ethoxy]benzoquinone (LXXXV) in 47% yield. The entropically favourable macrocyclisation of the tetraaldehyde (LXXXV) with the αααα-atropisomer of 5,10,15,20-tetra(2-aminophenyl)porphyrin, obtained by the isomerisation of the corresponding atropisomer in the presence of silica gel,[71] occurred with a yield of 85% and the reaction was catalysed by trifluoroacetic acid. The formation of the Schiff base was followed spectroscopically at 330 nm and the kinetic analysis of the reaction mixture was carried out with the aid of high performance liquid chromatography (HPLC). After chromatographic purification and reduction with $NaBH_4$, the "capped" P–Q compound (LXXXIV) was obtained.

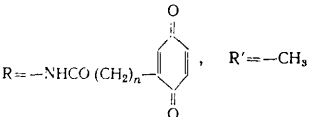
IV. Models with an additional donor (triads)

A new stage in the construction of model systems for the investigation of photosynthesis has been the synthesis of compounds containing a donor fragment together with the porphyrin and the quinone. During photosynthesis, the primary charge separation is accompanied by electron transfer from the primary donor to the oxidised chlorophyll-type photosensitiser.[1–4] The introduction of a donor into the P–Q compound made it possible to slow down the recombination of the light-separated charges by means of the dark reduction of the porphyrin radical-cation. Thus the triads make it possible to model more adequately the charge separation processes in photosynthesis.

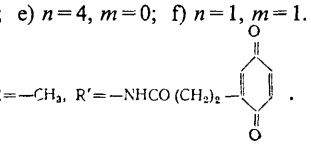
The carotenoid structure with a system of conjugated double bonds, which participate directly in photosynthesis,[3,4] may serve as a suitable donor. The synthesis of the triads (LXXXVIa–f) and (LXXXVIIc), consisting of a tetraarylporphyrin linked covalently to

the carotenoid and quinone structures by a chain of atoms of different length (n = 0–4, m = 0, 1), has been described:[72,73]



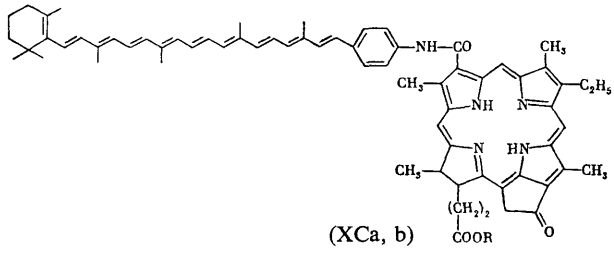
(LXXXVIa–e)  , $R' = -CH_3$

a) $n=0$, $m=0$; b) $n=1$, $m=0$; c) $n=2$, $m=0$;
d) $n=3$, $m=0$; e) $n=4$, $m=0$; f) $n=1$, $m=1$.

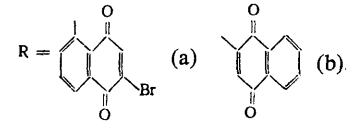
(LXXXVIIc)  .

4-(β-apo-7′-carotenyl)benzoic acid (LXXXVIII), obtained by the Wittig reaction from β-apo-8′-carotenal and the corresponding phosphonium salt, was condensed with 5,15-di(4-aminophenyl)-10,20-di(4-methylphenyl)porphyrin (LXXXIX) (obtained by the Rothemund reaction) using dicyclohexylcarbodiimide and 4-dimethylaminopyridine. The same reagents were used in the condensation of carotenoporphyrin with 2,5-diacetoxyphenylacetic acid, while subsequent deacylation with KBH_4 and oxidation with PbO_2 led to the final structure (LXXXVIb). The triads (LXXXVIa,f) were obtained similarly from the corresponding modified hydroquinone derivatives.

However this synthetic scheme was unsuitable for the preparation of compounds (LXXXVIc–e) and (LXXXVIIc), because the corresponding hydroquinone derivatives readily formed lactones with the carboxy-group of the chain in the stage involving the synthesis of the quinone component. Another method of synthesis of the triads was as follows: 2,5-dibenzyloxybenzoic acid was methylated with CH_2N_2, reduced with $LiAlH_4$, and brominated with PBr_3. After malonate synthesis and the removal of the ethoxycarbonyl group, the acid chloride was obtained by treatment with $SOCl_2$ and condensed with the porphyrin (LXXXIX). After the removal of the benzyl protecting group by $(CH_3)_3SiI$ and oxidation by PbO_2, the P–Q obtained was condensed with the acid chloride (LXXXVIII) to form the triad (LXXXVIc). The derivatives (LXXXVId,e) and (LXXXVIIc) were synthesised similarly. By altering the length of the connecting unit between the porphyrin and quinone structures, it is possible to select a distance ensuring effective charge separation:



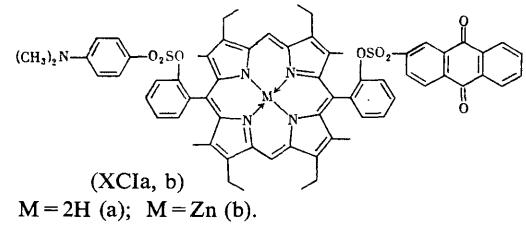
(XCa, b)



Similar triads (XCa,b), based on chlorophyll and naphthoquinone structures, were synthesised by the stepwise condensation of fragments of the system by a procedure similar to that used for compounds (LXXXVI a,b,f). The carboxy-derivative of methyl-pyrophaeophorbide *a* was condensed with aminocarotenoid by the acid chloride method. After the hydrolysis of the methyl ester by K_2CO_3 and esterification with 2-bromojuglone or lawsone, the corresponding products (XCa, b) were obtained.[74]

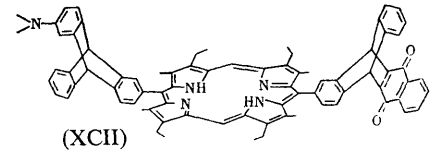
We may note that the (LXXXVI), (LXXXVII), and (XC) systems suffer from the same disadvantages as the models with a flexible covalent linkage between the donor and the acceptor.

The triad (XCIa), in which the secondary donor is a dimethylaniline derivative, was obtained by a procedure similar to that for the diquinone structure (VIa).[36] The zinc complex (XCIb) was obtained by treating the free base (XCIa) with zinc acetate.



(XCIa, b)
M = 2H (a); M = Zn (b).

In order to generate the three-component systems (XCII)[75] with a rigorously specified spatial orientation, a rigid triptycene bridge was used, as in compounds (LXI)–(LXIII). *NN*-Dimethylaniline was also chosen as the secondary donor in the triad (XCII). The condensation (catalysed by toluene-*p*-sulphonic acid) of a 1 : 1 mixture of the aldehyde of triptycenonaphthoquinone, obtained by the method of Wasielewski and Niemczyk,[62] and 2-formyl-6-nitrotriptycene, obtained in 95% yield by the Friedel–Crafts formulation of 2-nitrotriptycene with dichloromethyl methyl ether in the presence of $AlCl_3$, with two equivalents of di(3-ethyl-4-methylpyrrolyl)ethane led to a mixture of tetrahydroporphyrins, from which the final product (XCII) was obtained after oxidation with DDQ (overall yield of porphyrin 80%), reduction of the nitro-group with $SnCl_2$/HCl, chromatographic separation (yield 63%), and methylation of the amino-group with $CH_2O/NaBH_3CN$:



(XCII)

The methods of synthesis of all the model compounds examined are extremely varied. However, among them it is possible to distinguish two principal schemes for the construction of the covalent bond between the molecular fragments. The first involves the condensation of the system components with the simultaneous formation of the porphyrin ring.[36,42,56–60,62,67–69,75] The second involves the synthesis of porphyrin-quinones from synthetic[28,29,31–33,37–39,48,53,61,63,64,70,72,73] or natural[44–46,74] porphyrins and chlorins. An extremely large set of different porphyrin and

quinone structures of the model systems is necessary for the optimum selection of the corresponding donors and acceptors in photoinduced electron transfer reactions. The wide variety of the different forms of linkage between the chromophores has arisen because of the search for the most suitable conformations of the model systems and the optimum spatial orientation of their components for a high efficiency of the charge separation process.

V. Spatial disposition and mutual orientation of the fragments in model systems

The efficiency of electron transfer is known to depend significantly on the mutual orientation of the donor and acceptor. A study of the spatial organisation of P–Q compounds is therefore of considerable interest for the elucidation of the mechanism of electron transfer in such molecules.

The following methods are used to investigate the steric structure of P–Q derivatives: NMR spectroscopy, three-dimensional modelling, and X-ray diffraction analysis. The use of three-dimensional modelling is limited because of the presence of a large number of conformations for compounds with a flexible linkage. This method is used most effectively to determine the intramolecular distances between the fragments in structures with a rigid bond where the displacement of the chromophores relative to one another is difficult or almost impossible. Such data make it possible to calculate the probability and degree of overlap of the π-electron systems of the components, which determines the efficiency of the intramolecular electron transfer. Thus the distances between the donor and acceptor fragments have been determined with the aid of three-dimensional models in the porphyrin-quinones (XLVI)–(LII), (LXI)–(LXIII), and (XCII) with a rigid bond. For the three rigidly linked P–Q compounds (XLVI), (XLVIII), and (L), the distances between the chromophores are 6, 10, and 14 Å,[59] while the centres in the similar structure (LII) are at a distance of 16 Å.[60] The donor and acceptor in compounds (LXI), (LXII), and (LXIII) with a triptycene bridge are separated by 10, 10.5, and 11 Å, while the distance between the boundaries of the π-electron systems of the porphyrin and the quinone is > 6–7 Å, which weakens significantly the direct overlap of the electron wave functions.[62] For the triad (XCII), the distance between the centres of the porphyrin and the quinone is 10.5 Å, that between dimethylaniline and the porphyrin is 10 Å, and that between dimethylaniline and the quinone is 25 Å.[75] For the "capped" porphyrin (LXXXIV), the distance between the parallel planes of the chromophores has been found to be ~10 Å.[70]

However, for the "capped" structures, this method is rarely used, because it does not permit an accurate determination of the distance between the chromophores. The reason for this is that the possibility of the vibration of the molecular fragments along the bonding axis and the presence of different conformational forms are not ruled out in systems of this kind. In order to investigate the intramolecular orientation of the chromophores and the spatial organisation of such model systems, ^{1}H NMR spectroscopy is employed. Appreciable upfield shifts of the signals due to the protons of the quinone ring [up to 4 p.p.m. for compounds (LXVI)–(LXXI) and (LXXV), up to 2.8 p.p.m. for compound (LXXII), and up to 2 p.p.m. for compounds (LXXX) and (LXXXI) in the ^{1}H NMR spectra relative to the unbound quinones are characteristic of the "capped" P–Q compounds (LXVI)–(LXXI), (LXXII), (LXXV), (LXXX), and (LXXXI)]. This is due to the influence of the ring current of the porphyrin.[63,66–69,76,77] The shifts of the signals for the P–Q compounds with a longer chain [compounds (LXVII) and (LXXVa)] compared with their analogues with a shortened bond [compounds (LXVI) and (LXXVb)] are greater by 0.2–0.65 p.p.m. This effect can be accounted for by the fact that the longer and flexible chain enables the quinone structure to approach the porphyrin more closely and to experience a greater influence of its π-electron system.[67,76,77] This hypothesis is confirmed by three-dimensional modelling[67] and the results obtained for other "capped" porphyrins.[76,78] Similar changes in the ^{1}H NMR spectrum are also characteristic of the proton signals of the methylene chain located above the plane of the porphyrin ring. The influence of the ring current on the chemical shift of these protons diminishes as the porphyrin is approached.[67,76] Thus the signals of the corresponding protons of the propionic residues in compounds (LXVI) and (LXVII) are located in the usual region, but, as a consequence of the rigidity of the structure, all four protons of the propionyl chain are non-equivalent and their signals are distributed in the form of four complex multiplets, each due to 2H, and not a simple AA'BB' system.[63,76]

Further studies on the conformational flexibility of the linkage in compounds (LXVI) and (LXVII) led to the observation of a linear temperature variation of the chemical shifts of the protons of the quinones and the nearest methylene groups. When the temperature is raised, the signals of the protons of the quinone and of its environment undergo a downfield shift [the shift constant is 4.5×10^{-3} p.p.m. K^{-1} for the quione proton and 5.1×10^{-3} p.p.m. K^{-1} for the nearest methylene group in compound (LXVII)]. Thus the distance between the fragments of the molecule increases with increase in temperature and diminishes on cooling.[76]

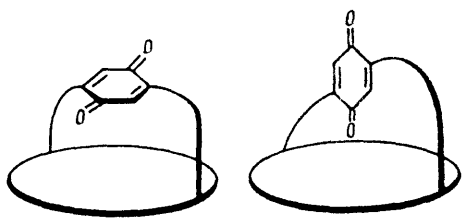


Figure 1. Schematic illustration of two extreme conformations of P and Q in "capped" porphyrin-quinones.[76]

The planes of the porphyrin and the quinone in the "capped" P–Q compounds (LXVI)–(LXXI), (LXXV), (LXXX), and (LXXXI) can be parallel or perpendicular to one another or they can occupy intermediate positions (Fig. 1). The necessary conformation of the fragments can be established in the course of specific synthesis.[66] Thus, when different substituted quinones were employed, "capped" P–Q structures with perpendicular (LXXII), parallel (LXXIII), and orthogonal (LXXIV) spatial orientations of the donor and acceptor were obtained. The molecular structure of the "sandwich" porphyrin (LXXX) has been determined by X-ray diffraction.[79] In compound (LXXX), having the S_4 symmetry, the two quinone rings are rigorously parallel to one another and to the plane of the porphyrin, while the centres of all three fragments coincide. The distance between the planes of the porphyrin and the quinones is

3.42 Å. It has been shown for compounds (LXVI) and (LXVII) that the real conformation constitutes a superposition of both limiting steric structures.[76] From this, it follows that there is virtually no coordination between the donor and acceptor parts in the free bases (LXVI) and (LXVII).[77] In the absence of external ligands, the magnesium complexes (LXX) and (LXXI) have structures in which the carbonyl group of the quinone is coordinated to the central metal ion resulting in the formation of a pentacoordinate intramolecular complex.[76,77] When an external ligand (pyridine[63,76] or 3,5-lutidine[77]) is added, a hexacoordinate complex is formed. This has been confirmed by the bonding constants found. The coordination of the ligand from the sterically unhindered side of the porphyrin plane entails appreciable upfield shifts of the quinone ring proton signals [by 0.6 p.p.m. for compound (LXX) and by 0.3 p.p.m. for compound (LXXI)] and the signals of the protons of the ligand itself. In contrast to magnesium complexes, in the presence of a ligand the zinc complexes have a geometry very similar to that of the free bases (LXVI) and (LXVII), which is due to the pentacoordination limit for zinc itself and the probability of the intramolecular bonding diminishes appreciably.[77]

The determination of the mutual orientation of the fragments for linear P–Q compounds with a flexible bond involves considerable difficulties because of their conformational lability. The time-average conformations of the triads (LXXXVIa–f) and (LXXXVIIc) in solution have been determined[73] from ^{1}H NMR data by conformational analysis on a computer. It was established that in all cases the triads have a linear structure and the quinone rings are arranged at an angle of 90° relative to the covalent bond. The spatial organisations of each of these molecules differ from one another by the orientations of the quinone and carotenoid components relative to the porphyrin plane, which depends on the length of the polymethylene chain (n = 0–4, m = 0–1). For a series of other linear P–Q compounds, only tentative conclusions concerning the mutual disposition of the quinone and porphyrin fragments have been reached with the aid of ^{1}H NMR spectroscopy. Depending on the length of the linkage and its location in the porphyrin ring, there are two possible versions of the steric structure: (1) the molecule has a linear form in which the chromophores are remote from one another and (2) the molecule is characterised by a folded configuration in which the quinone component is located above the plane of the porphyrin ring. However, in the second case it is also impossible to determine the exact position of the acceptor above the plane of the donor. Thus, in the structures (Ia–c),[29] (IIa–c),[31], (XXXIII),[53] and (XCa,b),[74] the porphyrin ring current does not exert an appreciable influence on the chemical shifts of the protons in the quinone component. This finding suggests a linear conformation of the molecule. Upfield shifts of the signals due to the protons of the quinone ring and its closest substituents have been observed for compounds (V),[33] (VIa,b), (XCIa,b),[36] (VIIIa–e),[38] (X)–(XVb),[39,42] and (XXXIIIa)–(XXXa,b).[44,45] This indicates a folded structure of the P–Q molecule. For the more rigid structure (V), the shifts are 0.1 p.p.m. for H(1), 2.0 p.p.m. for H(2), and 3.0 p.p.m. for H(3). This suggests that the H(3) hydrogen is closest to the porphyrin and the H(1) hydrogen is most remote. In the models (VIIIa–e), the maximum shifts are shown by compound (VIIIb), in which there is no substituent in the 3-position in the naphthoquinone component. It has been demonstrated by three-dimensional modelling that the quinone in the structure (VIIIb) can readily rotate about the C–O bond and can assume a position in which the porphyrin and quinone planes are parallel. The π–π interaction between the molecular fragments is then a maximum. For the derivatives (VIIIc–d), the rotation is hindered and the orthogonal conformation, in which the influence of the porphyrin ring current on the quinone is weakened, is optimal.

In the zinc complexes (XIVa–c), the signals of the quinone protons are displaced more ($\Delta\delta$ = 0.42–0.89 p.p.m. depending on the bond length) than in the free bases (Xa–c) ($\Delta\delta$ = 0.24 to 0.34 p.p.m.). This may be associated with the additional coordination of the quinone to the metal ion. For the diquinone derivative (XVb), these values are smaller ($\Delta\delta$ = 0.17 p.p.m.) because of the influence of the second quinone, which apparently prevents the localisation of benzoquinone above the porphyrin ring. Several changes have been observed also for the zinc complexes (VIb) and (XCIb). The addition of pyridine to a solution of the triad (XCIb) induced the formation of a pentacoordinate complex with the external ligand and the simultaneous breakdown of the interaction between the zinc atom and the carbonyl group of the quinone. The signals of the protons of the quinone component then shifted to the level of the free base (XCIa). In the natural P–Q compounds (XXIIIa)–(XXVIa,b), $\Delta\delta$ = 0.23–0.47 p.p.m. for the naphthoquinone-containing compounds (XXIIIa) and (XXIVa,b). The shift of the singlet signals of the methyl protons of the quinone residues in compounds (XXIIIa)–(XXVIa,b) is 0.27–1.43 p.p.m. Thus the molecular conformation in the P–Q compounds with a flexible linkage can be estimated from the shift of the protons of the quinone residues and the nearest substituents.

As stated above, information about the mutual disposition of the fragments of the P–Q molecule is of great interest for the understanding of the mechanisms of charge separation in these systems.

The photochemical properties of the model systems can be considered also on the basis of the available data for their structural features.

VI. Photochemistry of porphyrin–quinone compounds

Among the questions arising in the study of the photochemistry of porphyrin–quinone compounds, the most important are the following: (1) what structural features of the bridging chain determine the efficiency of the electron transport; (2) how should the bridge be constructed so that the direct electron transfer from *P to Q is rapid and the reverse transfer is slow; (3) in what way does the efficiency of the charge separation depend on the oxidation-reduction properties of P and Q. The solution of these problems in the photochemistry of P–Q compounds is of interest as regards the answer to the main question—what features of the organisation of the photosynthetic apparatus in photosynthesising organisms ensure a high efficiency of charge separation.

Considerable advances have now been achieved in the elucidation of the photochemical properties of P–Q compounds. It is possible to distinguish three main aspects of the study of the photochemistry of structures differing in the characteristics of the intramolecular electron transport processes: (1) the photochemistry of P–Q compounds with a flexible linkage; (2) the photochemistry of P–Q molecules with a rigid bridge; (3) the photochemistry of triad systems containing a porphyrin bound covalently to a quinone and an electron donor. The photochemical studies on P–Q compounds have developed in this sequence from the moment of their initiation. The transition from systems with a flexible linkage to P–Q compounds with a rigid bridge made it possible to investigate in greater detail the dynamics of charge separation between the porphyrin and the quinone without the complicating influence of conformational

movements manifested in the study of systems with a flexible linkage. The covalently bound triads constituted the next step towards more adequate modelling of the reaction centres of photosynthesing organisms. In these systems, it is possible to achieve fairly long lifetimes of the light-separated charges. Following the logic of the development of the research into P–Q compounds, we shall consider initially photochemical processes in systems with a flexible linkage.

1. Porphyrin–quinone compounds with a flexible linkage

In the first studies on the synthesis of P–Q compounds, attempts were already made to investigate their photochemical properties. Thus an appreciable quenching of the fluorescence of the porphyrin fragment by the quinone in dioxan and petroleum ether was noted[28,29] for compounds (Ia–c). In petroleum ether, the quenching efficiency proved to be higher than in dioxan. No data concerning the mechanism of the quenching of the fluorescence were obtained in the above studies.

The hypothesis that the quenching of the fluorescence of the porphyrin by the quinone in the P–Q compounds is caused by intramolecular electron transfer was first put forward by Tabushi et al.[33] and Dalton and Milgrom.[56] Since low concentrations of P–Q compounds were used in these studies, it was concluded that an intramolecular mechanism of the quenching of the fluorescence of the porphyrin fragment operates. However, data permitting the exclusion of an alternative explanation of the quenching of the fluorescence, involving intramolecular energy transfer, were not obtained either.[33,56]

It has been observed[56] that the Soret band in the spectrum of compound (XXXVIII) is much broader than in that of the free porphyrin. According to the authors, this indicates the formation of an intramolecular charge-transfer state in the P–Q compound. The complete quenching of the fluorescence of the porphyrin fragment of the P–Q compound was noted (the fluorescence quantum yield was $\Phi < 10^{-3}$). The experimental results were explained by the high efficiency of the electron transfer from the singlet-excited prophyrin fragment to the quinone.

Subsequently the hypothesis that the quenching of the fluorescence of P–Q compounds is caused by electron transfer was used frequently to account for the non-exponential character of the decay of the fluorescence and the dependence of the fluorescence quenching efficiency on the length of the bridge connecting P and Q, the presence of the metal in the P–Q compound, and the nature of the solvent.[39,80,81]

In principle, four mechanisms of the quenching of the fluorescence of the donor D by the acceptor A are possible: (1) energy transfer from *D to A; (2) the mixing of the electronic states of D and A leading to an increase in the non-radiative transition of *D to the ground state; (3) the spin–orbital coupling of the $^1(\pi,\pi^*)$,$^3(\pi,\pi^*)$, and S_0 states of the donor by virtue of the addition of the acceptor; (4) electron transfer from *D to A.

We shall consider each of these quenching mechanisms for a covalently bound P–Q compound. The energy transfer from porphyrin in the S_1 state ($E_{S_1} \simeq 1.8$ eV) to the quinone is unlikely because the lowest excited state of the quinone is fairly high (2.6 eV for benzoquinone in solution[82]). This energy difference is also sufficient to rule out the hypothesis of the mixing of the electronic states of P and Q. The spin–orbital coupling of states also appears unlikely because the efficiency of the quenching of the fluorescence of porphyrins by quinones is determined mainly by their oxidation-reduction properties[83,84] and not by the capacity for spin–orbital coupling.[85] The hypothesis that the electron transfer from *P to Q responsible for the appreciable decrease in the efficiency of the luminescence of the porphyrin in P–Q compounds therefore appears reasonable. Measurements of the redox potentials of the P–Q compounds have shown that the singlet excitation energy of the porphyrin is indeed sufficient in many cases for the formation of the P^+–Q^- pair.[86]

The first study in which the formation of a radical-ion pair on irradiation of P–Q compound was demonstrated was that of Ho et al.[87] By a procedure similar to that used by Kong and Loach,[28,29] it was found that a much lower fluorescence intensity (~10%) is observed for compound (Ib) in methanol at room temperature than for a porphyrin without a quinone residue. At low temperatures, it is possible to detect the EPR signal of the photolysis products in vitreous methanol. Comparison of the EPR spectrum obtained with the individual EPR spectra of P^+ and Q^- enabled the authors[87] to interpret the light-induced EPR signal as a superposition of the EPR spectra of P^+ and Q^-. The efficiency of the formation of radical-ions for a P–Q compound was many times greater than the efficiency of the generation of P^+ and Q^- in a homogeneous solution of the porphyrin and the quinone at the same concentrations of the reactants, not bound to one another, as in the P–Q compound. The subsequent generation of the EPR signals on irradiation of compounds (Ia–c) and their zinc analogues has also been demonstrated in another study.[80]

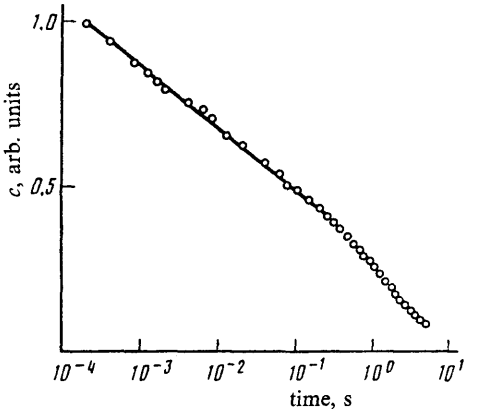


Figure 2. Kinetics of the destruction of the radical-ion pairs P^+–Q^- at T = 160 K in a 98 : 2 vitreous methanol–chloroform structure; c = concentration.[87]

At T = 160 K, the formation of the P^+–Q^- radical-ion pair is followed by the intramolecular recombination of charges, whose kinetics at low temperatures are described by a linear dependence of the number of P^+–Q^- pairs on the logarithm of the observation time (Fig. 2).[87] A similar relation had been observed earlier for the low-temperature recombination of charges in the reaction centres of the photosystems (I) of subchloroplasts.[88] On the grounds that the efficiency of the P^+–Q^- recombination depends strongly on temperature, the logarithmic character of the recombination of charges in compound (I) was explained[87] by the difference between

the activation energies for the recombination of different P^+-Q^- pairs. The difference may be caused by the presence of several conformations of the carbon chain linking the porphyrin and the quinone. However, it has been noted[88] that other causes of the logarithmic character of the kinetics of the recombination of charges in structures analogous to P–Q are also possible. These may be a difference between the distances over which an electron is transferred from Q^- to P^+ (if the electron transfer does not proceed via the bridge but directly from Q^- to P^+), a difference between the mutual orientations of P^+ and Q^-, or a difference between the values of some other parameter on which the efficiency of charge recombination depends exponentially.

At room temperature, the quantum yield in the separation of charges in compound (Ib) reaches 0.5%. The addition of tetrabutylammonium perchlorate lowers the rate of charge recombination in P^+-Q^-.[80] The observed[80] dependence of the fluorescence quenching efficiency on the solvent polarity (the increase in efficiency with increase in polarity) can be explained naturally within the framework of modern models of electron transfer in the condensed phase by the dependence of the charge separation energetics on the parameters of the medium.

Subsequently the light-induced charge separation in the model systems (IIIa–c) was observed by the EPR method. The high resistance of the diamide bridge to hydrolysis enabled the authors[89] to carry out optical, EPR, and luminescence studies on the separation of charges in P–Q compounds. It was observed that spin–exchange and dipole–dipole intramolecular interactions of the P^+ and Q^- radical-ions are manifested in the EPR spectra of vitreous P–Q solutions irradiated with light. The degree of the dipole–dipole interaction ($D \simeq 2.0\ mT$) made it possible to estimate the average distance between the unpaired electrons of P^+ and Q^-, amounting to 10–12 Å for compound (IIIa). Molecular models have shown that this distance corresponds to the conformation of the P–Q compound in which the quinone interacts with the nearest phenyl residue.

The quantum yield in the formation of the P^+Q^- radical-ion pair, measured by EPR, depends on temperature and increases markedly, to $\Phi \simeq 0.02$, when the temperature is reduced by ~20 K below the melting point of the solvent. On further reduction of temperature, Φ also falls. It has been suggested that charge separation quantum yield in P–Q compounds is determined by the microviscosity of the solvent. The increase in the temperature of the frozen matrix then increases the mobility of the P–Q fragments relative to one another promoting thereby the attainment of conformations favourable for electron transfer. In the temperature range near the melting point of the solvent, the recombination of charges becomes effective and, having reached a maximum, the charge separation quantum yield again diminishes.

The existence of different conformations of compounds (IIIa–c) has been established.[90] The most effective quenching of the fluorescence has been observed for the derivative (IIIb). These data agree with the results of EPR studies.[89]

The charge separation on pulsed irradiation of the derivative (IV) with light has been described.[32] The dependence of the efficiency of electron transfer from the porphyrin to the quinone on the refractive index n of the solvent was found: with increase in n, k_e increased from $1.4 \times 10^7\ s^{-1}$ for $n = 1.352$ (diethyl ether) to $7.7 \times 10^8\ s^{-1}$ for $n = 1.633$ (1-chloronaphthalene). The results of the above study show that for P–Q compounds the solvent can exert an appreciable influence on the process energetics even when the length of the bridge connecting P and Q is small.

The dependence of the rate of electron transfer from the electronically excited porphyrin fragment to Q and of the rate of the reverse process on the length of the bridge for the derivatives (Xa–c) has been described.[39,42,43] It was established that the reciprocal of the P–Q fluorescence decay time is $10^9\ s^{-1}$, $10^{10}\ s^{-1}$, and $10^{11}\ s^{-1}$ for $n = 6$, 4, and 2 respectively. A similar dependence has been observed also for the efficiency of the reverse electron transfer from Q^- to P^+. The pronounced dependence of the rates of the forward and reverse electron transfers on the length of the bridge connecting P and Q shows that the electron transfer takes place via the tunnel mechanism.[43]

The two-step electron transfer from the porphyrin to trichlorobenzoquinone in the molecule of compound (XV) [$P-(CH_2)_4-Q-(CH_2)_4-Q'$] has been investigated.[42,43] The charge separation takes place with participation of the intermediate state $P^+-(CH_2)_4-Q^--(CH_2)_4-Q'$:

$$P-(CH_2)_4-Q-(CH_2)_3-Q' \xrightarrow{h\nu} P^+-(CH_2)_4-Q^--(CH_2)_4-Q'$$
$$\searrow \qquad\qquad \swarrow$$
$$P^+-(CH_2)_4-Q-(CH_2)_4-(Q')^- .$$

The two-step electron transfer mechanism ensures rapid ($\tau < 10^{-11}$ s) charge separation. This time is much shorter than the time of the single-step charge separation in the molecule of compound (Xc) with a shorter bridge ($\tau > 5 \times 10^{-10}$ s). The greater length of the bridge in the molecule of compound (XV) ensures a comparatively long charge recombination lifetime $\tau = (3–4) \times 10^{-10}$ s. The present authors' data[42,43] confirm the results[91,107] showing that the multistep electron transfer along the redox potential gradient of the acceptor groups ensures a higher efficiency of charge separation than the single-step process.

2. Porphyrin–quinone compounds with a rigid bridge

The appreciable conformational mobility of the P–Q compounds with a flexible chain precludes the elucidation of the detailed mechanism of the intramolecular electron transfer. One of the ways of solving this problem has been the synthesis of "capped" P–Q structures.

Thus the parallel disposition of the fragments in compound (LXXXIV) ensured an appreciable (greater than 30%) P^+-Q^- quantum yield for its zinc complex.[92] For the metal-free derivative (LXXXIV), the intramolecular electron transfer was not observed. The appearance of additional luminescence quenching channel reduced the quantum yield and resulted in a two-component character of the P–Q fluorescence decay curve. The electron transfer rate constants, estimated from the biexponential curve, are $k_1 = 3 \times 10^8\ s^{-1}$ and $k_2 = 1.5 \times 10^3\ s^{-1}$. The electron transfer to the quinone is observed also with participation of the excited triplet state of the porphyrin fragment.

The diquinone compound (LXXX) has been investigated.[79] The small distance between the planes of the porphyrin and the quinone is apparently the cause of the almost complete absence of the luminescence of this derivative compared with its non-quinonoid analogue. A similar effect has been observed also for the monoquinone analogue of compound (LXXX).[69] The quenching of the fluorescence of compounds (LXXX) and (LXXXI) can be explained by electron transfer from the singlet-excited porphyrin fragment to the quinone.

Compounds with a linear structure and a rigid bridge [compounds (XLVI)–(LII) and (LXI)–(LXIII)] provide considerable possibilities for the elucidation of the factors determining the efficiency of the electron phototransfer in P–Q systems.[59,60,62,93] The absence from

the absorption spectra of any manifestations of the interaction of the porphyrin and quinone fragments, typical for systems with a flexible bridge, is characteristic of these compounds. A rigid structure prevents the interactions of the fragments in the ground state. Another characteristic feature of systems with a rigid bridge is the monoexponential character of the fluorescence decay curve, indicating the existence of only one P–Q conformation, in which an effective electron transfer takes place.

It has been observed for compounds (LXI)–(LXIII) that the fluoresence quantum yield of the porphyrin fragment of the P–Q compound is lower than for the individual porphyrin.[62] A correlation was then observed between the free energy of the electron transfer from the donor to the acceptor ($-\Delta G^0$) and the quenching efficiency (see Table 1). The free energy $-\Delta G^0$ was calculated from the formula

$$-\Delta G^0 = E(S_1) - E(P/P^+) + E(Q/Q^-),$$

where $E(S_1)$ is the excitation energy of the singlet state S_1 of the porphyrin fragment, $E(P/P^+)$ the oxidation potential of the porphyrin, and $E(Q/Q^-)$ the reduction potential of the quinone.

Table 1. The free energies $-\Delta G^0$ of the electron transfer from P to Q and the fluorescence quantum yields (Φ) for the P–Q compounds in CH_2Cl_2.[62]

Compound	Φ	$-\Delta G^0$, eV
Tetraphenylporphyrin (TPP)	0.14	—
(LXIIIa)	0.119	0.02
(LXIIa)	0.001	0.29
(LXIa)	<0.001	0.47
Zn complex of TPP	0.023	—
(LXIIIb)	0.002	0.43
(LXIIb)	<0.001	0.70
(LXIb)	<0.001	0.88

A similar correlation has been found for two other solvents: toluene and butyronitrile. The increase in $-\Delta G^0$ with decrease in the dielectric constant of the solvent led to an increase in the luminescence quenching efficiency. This character of the dependence of the luminescence quantum yield on the free energy change shows that the quenching of the luminescence is due to electron transfer from $^*P$ to Q.[91,94–97] This hypothesis is supported also by picosecond absorption spectroscopic data. Wasielewski and Niemczyk[62] were able to record the characteristic absorption bands of P^+ and Q^- in the absorption spectrum of a solution of the zinc complex (LXIIb) in toluene irradiated by a light pulse. The time of the intramolecular charge recombination $P^+-Q^- \rightarrow P-Q$ in this compound is 3.7×10^{-10} s.

The electron transfer rate constant for this process decreases with increase in $-\Delta G^0$.[93] This fact can also be explained within the framework of the modern theories of electron transfer. Indeed, the quantities $-\Delta G^0$ for charge recombination in compounds (LXI)–(LXIII) investigated by Wasielewski and Niemczyk[93] exceed 1 eV. The decrease in k_e with the increase in $-\Delta G^0$ is apparently caused by the fact that the quantity $-\Delta G^0$ exceeds the reorganisation energy (λ is a parameter determining, together with $-\Delta G^0$, the nuclear multiplier k_{nu} in the expression for the electron transfer rate constant):

$$k_{nu} = \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda RT}\right). \quad (1)$$

Eqn. (1) shows that the increase in $-\Delta G^0$ leads under these conditions to a decrease in the nuclear multiplier and hence in the electron transfer rate constant.

We may note that, in contrast to the "capped" P–Q compounds considered above, the effective electron transfer between the P and Q fragments observed by Wasielewski and Niemczyk[62] takes place over a considerable distance in the conformation hindering the overlap of the π orbitals of the reactants.

A dependence of the efficiency of the transfer from $^*P$ to Q on the dielectric constant and the refractive index of the solvent employed has been observed for the model systems (XLVI)–(LII).[59,60] The electron transfer rate constants reaches its maximum value for an intermediate and (and not the maximum) polarity of the solvent and varies from $k_e = 3.3 \times 10^7$ s^{-1} in propionitrile ($\varepsilon = 27.2$, $n = 1.3659$) to $k_e = 1.6 \times 10^6$ s^{-1} in 2-methyltetrahydrofuran (MTHF) ($\varepsilon = 7.6$, $n = 1.4060$) and falls almost to zero in dibutyl ether ($\varepsilon = 3.04$, $n = 1.3992$) and acetonitrile ($\varepsilon = 37.5$, $n = 1.3441$). Such variation is associated with the fact that the solvation energy of the P^+-Q^- state, which determines the energetics of the charge separation process, depends both on dielectric constants of the solvent and (to a greater extent) on its refractive index.[98] For solvents having similar structures, it is possible to obtain a quantitative correspondence between the quantities k_e, ε, and n.[60]

For the quantitative determination of the tunnelling parameters, the P–Q compounds (XLVIII) and (L) have been investigated.[99] The rate constant for electron transfer from $^*P$ to Q was estimated from the decrease in the luminescence decay time. Typical P–Q fluorescence decay curves are illustrated in Fig. 3. It is seen that the transition from the structure (LI) to compound (XLIX) results in a sharp decrease of the fluorescence decay time. The quantity k_e then increased from $k_e^2 \lesssim 10^7$ s^{-1} to $k_e^1 = 10^{10}$ s^{-1}. Using the maximum value of k_e for the derivative (LI), it is easy to obtain $a_e \leqslant 1.4$ Å and $\nu_e \geqslant 10^{19}$ s^{-1} from the exponential dependence of k_e on the distance R between the donor and acceptor: $k_e = \nu_e \exp(-2R/a_e)$.[97] If the minimum distance between P and Q is used instead of the intercentre distance, then ν_e may be estimated as $\nu_e \geqslant 10^{16}$ s^{-1}.

At $T = 77$ K, the kinetics of the quenching of the fluorescence of compound (XLIX) in vitreous MTHF are non-exponential. This effect is due to the existence in the frozen solution of several rotational conformations of the molecule. The monoexponential character of the decay curve at 298 K shows that at this temperature the rate of rotation exceeds k_e. The decay time of the principal component of the kinetic curve $\tau = 1.1 \times 10^{-10}$ s is almost identical with the value of τ at 298 K. Thus the rate of electron transfer from $^*P$ to Q in the structure (XLIX) is almost independent of temperature.

3. Model systems having a rigorous spatial orientation without a covalent bond between the porphyrin and the quinone

Together with the covalent bonding between the porphyrin and the quinone, a fixed distance between P and Q can be ensured, in principle, also in a number of other ways. Thus the synthesis of a porphyrin bound covalently to β-cyclodextrin (PC) has been described.[100] In a solution containing electron-accepting additives, cyclodextrin coordinates the acceptor molecules in its interior. On

irradiation with light at $\lambda > 550$ nm of a vitreous solution of PC containing added benzoquinone at 77 K, paramagnetic charge separation products are detected, their amount exceeding by a factor of 3–4 that in the control (P + Q solution). The efficiency of the charge separation depends on the oxidation-reduction potential of the electron acceptor. For an oxidation-reduction potential below –0.3 eV relative to the normal hydrogen electrode, a sharp decrease, greater than by an order of magnitude, in the intensity of the EPR signal of the charge separation products was observed when the oxidation-reduction potential changed from –0.3 to –0.6 eV. Such a decrease in the charge separation efficiency is caused, according to Gonzalez et al.,[100] by the rapid reverse charge recombination.

Yet another interesting example of a structure permitting the study of electron transfer between the porphyrin and the quinone, separated by a fixed distance, is provided by planar molecular assemblies obtained by the Langmuir–Blodget method. [101–103] The planar molecular assemblies constitute multilayer structures in which the acceptor layer is separated from the donor layer as a rule by a monolayer made up of saturated aliphatic acid molecules. The thickness of the monolayer and hence the distance between the donor and acceptor can be varied by increasing the number of CH_2 fragments in the acid molecule.

The electron phototransfer from chlorophyll to a quinone in a multilayer structure, where a layer of chloranil, bromanil, or *NN*-distearoyl-1,4-diaminoanthraquinone was deposited on a layer of chlorophyll *a* molecules, has been investigated.[104,105] The structural organisation was such that the phytol fragments of the chlorophyll molecules were turned towards the layer of quinone molecules. Thus the insulating layer consisted of the phytol fragments of the chlorophyll molecules. It was observed that irradiation of such a structure with light leads to electron transfer from chlorophyll to the quinone and the formation of the corresponding radical-ions. The charge separation took place via a two-quantum mechanism. The reason for the inefficiency of the one-quantum reaction channel is apparently the short lifetime of the excited state of chlorophyll *a* and the appreciable distance between the donor fragment of the chlorophyll molecule and the quinone. After the light had been switched off, charge recombination was observed. Its duration ($\tau_{1/2}$) amounted to 6×10^{-4} s and was almost independent of temperature in the range 100–300 K.

The introduction of ubiquinone, plastoquinone, or squalene (whose molecules have an unsaturated chain) into the system led to a tenfold increase in the charge separation efficiency for the given light intensity. The electron transfer became a one-quantum process and occurred with participation of the first excited triplet state of chlorophyll *a*. The observed effect was explained by a change in the form of the barrier to the tunnelling of the electron caused by the insertion of molecules or molecular fragments with a polyisoprene chain in the insulating layer. The use of molecules with a saturated chain in control experiments did not accelerate the electron phototransfer process. The results of the above studies[104,105] demonstrate the fruitfulness of the use of planar molecular assemblies for the investigation of the electron tunnelling mechanisms in porphyrin–quinone systems. However, the uncertainty in the interpretation of the results of experiments with molecular layers due to the non-rigid character of the linkage between the reacting species makes covalently bound P–Q compounds a preferable object for the modelling of photosynthesis and for the study of the mechanisms of electron phototransfer from the porphyrin to the quinone.

4. Covalently bound triads

As already mentioned above, the next step in the modelling of the charge separation process in photosynthesis involved the study of trifunctional molecules (D–P–Q) containing a porphyrin, a quinone, and a donor fragment.[72,73,75,106]

By analogy with photosynthesis, one might have expected that a fairly considerable increase in the lifetime of the separated charges compared with the bifunctional P–Q molecules would be achieved in the trifunctional compounds as a result of the two-step charge separation mechanism. Thus the excitation of the triads (LXXXVI)

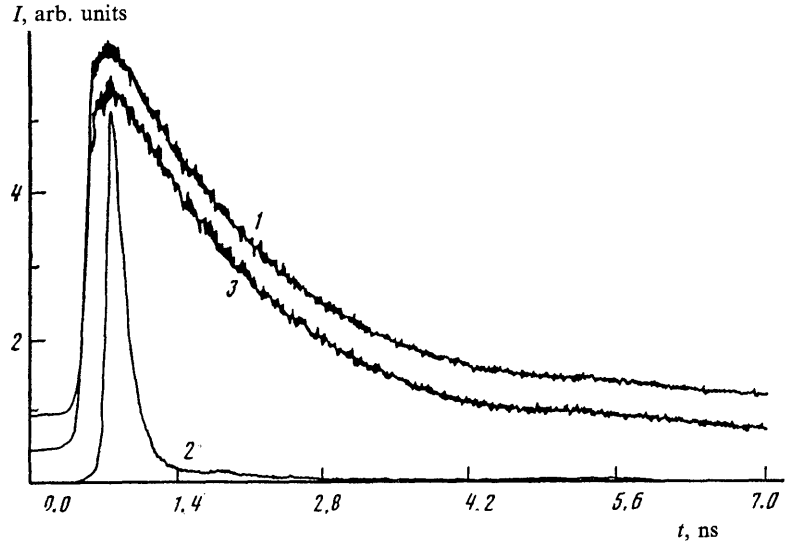


Figure 3. Kinetics of the decay of the fluorescence of compound (XLIX) (curve *1*), compound (LI) (curve *2*), and zinc 2,3,7,8,12,13,17,18-octamethyl-5-phenylporphyrinate (curve *3*); T = 298 K; I = intensity.[99]

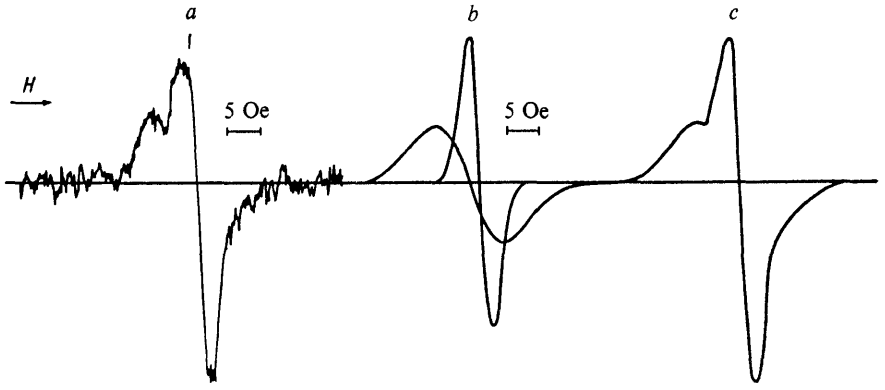
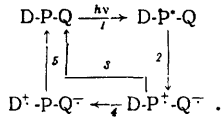


Figure 4. *a*, the EPR spectrum of a vitreous solution of compound (XXIIIa) (10^{-3} M) in triethylamine irradiated with the light from a DKSSh 1000 lamp (KS 10 filter); irradiation time 600 s; power of the light flux 2×10^{-3} W cm^{-2}; T = 77 K; the vertical line indicates the position of the EPR line of polycrystalline αα′-diphenyl-β-picrylhydrazyl;[108,109] *b*, EPR spectra of the radical-anion $P^{\cdot-}$ obtained by photoreduction in triethylamine and the radical-anion $Q^{\cdot-}$ obtained by reduction on a Na mirror; *c*, the calculated EPR spectrum representing a superposition of the EPR spectra of the radical-anions $P^{\cdot-}$–Q and $P–Q^{\cdot-}$; $P^{\cdot-}–Q : P–Q^{\cdot-} = 3:1$.

by a light pulse leads to the rapid (over a period less than 10^{-10} s) formation of $D^{+}–P–Q^{\cdot-}$:[72,73,106]



Charge separation is achieved via electron transfer from the excited singlet porphyrin to the quinone with formation of $D^{+}–P–Q^{\cdot-}$ [reaction (2)]. The formation of $D^{+}–P–Q^{\cdot-}$ [reaction (4)] competes with the charge recombination process [reaction (3)]. The quantum yield in the generation of $D^{+}–P–Q^{\cdot-}$ reaches 0.25. An amount of energy equal to 1 eV is then stored. The charge recombination time in $D^{+}–P–Q^{\cdot-}$ [reaction (5)] is several microseconds. This exceeds by a factor of 10^6 the charge recombination time for the analogue without a donor fragment.

As in the covalently bound triad considered above, the formation of $D^{+}–P–Q^{\cdot-}$ in compound (XCII) is achieved over a period $< 10^{-10}$ s.[75] However, the charge separation quantum yield and the energy stored were greater than $\Phi = 0.7$ and $\Delta G = 1.4$ eV. The charge recombination time [reaction (5)] was 2.45×10^{-6} s.

Thus the two-step mechanism of electron transfer from the donor to the acceptor ensures a rapid charge separation and makes it possible to attain high quantum yields and lifetimes of the separated charges. The results of studies described in the literature[72,73,75,106] constitute evidence in support of theoretical models of electron transport in photosynthesis,[91,107] according to which the stepwise character of the process actually ensures a high efficiency of the charge separation at the photosynthetic reaction centres.

VII. Modelling of the intermediate stage of the primary charge separation in photosynthesis with the aid of porphyrin–quinone compounds

A simple system for the modelling of the concluding stage of the primary charge separation has been proposed and investigated.[108,109] Electron phototransfer and dark transfer reactions in frozen vitreous matrices comprising solutions of covalently bound P–Q compounds (XXIII)–(XXVI) in an electron-donating solvent were investigated in the above studies. The solvent was triethylamine. The presence of the bridging heteroatom served as an additional lever for controlling the efficiency of the intramolecular electron transfer processes. It was observed that irradiation with light at 77 K of P–Q solutions in the region of the long-wavelength absorption bands of P leads to the formation of the radical-ions $P^{\cdot-}$ and $Q^{\cdot-}$, detected from their characteristic EPR spectra. Fig. 4 presents as an example the experimental EPR spectra of the light-irradiated solutions of compound (XXIIIa) (Fig. 4*a*), the EPR spectra of the individual radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ (Fig. 4*b*), and the EPR spectrum representing the superposition of the $P^{\cdot-}$ and $Q^{\cdot-}$ signals (Fig. 4*c*). The radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ were generated by irradiating the pigment in triethylamine with light at 77 K ($P^{\cdot-}$) or by reduction on a sodium mirror ($Q^{\cdot-}$). Fig. 4 shows that the calculated EPR spectrum describes satisfactorily the experimentally observed signal of the light-irradiated solution.

The analysis in the above studies of the possible mechanisms of the formation of the radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ showed that these species are formed in accordance with the following scheme:

$$P\text{-}Q \xrightleftharpoons[]{h\nu^1,\,(C_2H_5)_3N} (C_2H_5)_3N^{\cdot+} + P^{\cdot-}\text{-}Q \xrightarrow{h\nu^2,\,(P\text{-}Q)_y}$$
$$\rightarrow (C_2H_5)_3N^{\cdot+} + P\text{-}Q + (P^{\cdot-}\text{-}Q)_y \rightarrow (P\text{-}Q^{\cdot-})_y \ .$$

After the absorption of the first light quantum, the P–Q compound is reduced by the nearest solvent molecule $[(C_2H_5)_3N]$. The radical-anions $P^{\cdot-}$–Q formed are unstable and, together with charge recombination, there is a possibility of electron transfer from $P^{\cdot-}$ to Q. After the absorption of the second light quantum by the radical-anion $P^{\cdot-}$–Q, an electron is transferred to remote $(P–Q)_r$ species. The electron is then localised initially at the porphyrin fragment of the P–Q molecule. This is followed by the dark intramolecular electron transfer from the porphyrin fragment of the molecule to the quinone fragment. The kinetics of this process for compound (XXIIIa) are illustrated in Fig. 5. Evidently the intramolecular electron transfer $P^{\cdot-}–Q \rightarrow P–Q^{\cdot-}$ is described by a nearly linear relation between the concentration of the $P^{\cdot-}$–Q species and the logarithm of the observation time. This indicates a difference between the probabilities of the electron transfer from $P^{\cdot-}$ to Q for different P–Q molecules. The causes of this difference are so far obscure. They may involve, for example, different P–Q conformations in the frozen solution, which leads to a difference in the electron transfer distances and (or) different mutual orientations of the molecular fragments relative to one another.

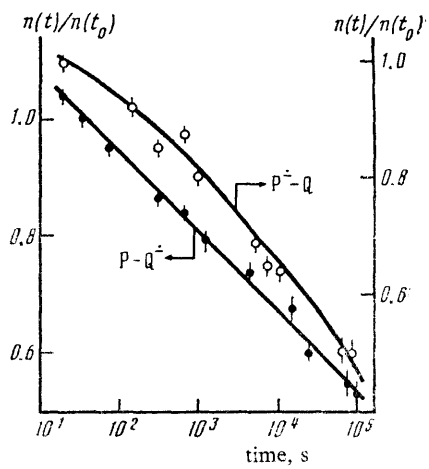


Figure 5. Kinetics of the dark destruction of $P^{\cdot-}$–Q and P–$Q^{\cdot-}$ in an irradiated vitreous solution of compound (XXIIIa) in triethylamine; the time is reckoned from the instant when irradiation ceases; T = 77 K;[108,109] $n(t)$ and $n(t_0)$ are the radical concentrations at times t and t_0.

The use of the quinone fragments of the P–Q molecules, differing in the electron-donating properties, and variation of the heteroatom in the bridge connecting P and Q make it possible to regulate the efficiency of the intramolecular electron transfer from $P^{\cdot-}$ to Q. It has been found that an increase in the oxidation-reduction potential of the quinone fragment of the P–Q molecule lowers the efficiency of the reduction of Q. This result can be explained if it is assumed that in the systems investigated the reorganisation energy is lower than the quantity $-\Delta G^0$ for the process[97] [see also Eqn. (1)].

The results of studies by Strekova and co-workers[108,109] demonstrate the possibility, in principle, of using solutions of P–Q compounds in electron-donating solvents for the modelling of one of the "elementary" stages of the charge separation process in photosynthesis—the stage involving electron transfer from phaeophytin to the primary acceptor. It is known that the electron transfer in photosynthesis from the electronically excited photosensitiser to the primary acceptor does not take place directly and occurs with participation of intermediate acceptors, one of which is phaeophytin.[110]

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We shall now formulate briefly the principal results of experimental studies on the intramolecular electron phototransfer in P–Q compounds, which are convenient models of the reaction centres in photosynthesis.

The possibility of the synthesis of such compounds with a fixed distance between the donor and acceptor and a definite mutual orientation makes it possible, as shown above, to investigate the influence of various factors on the efficiency of electron transport. As in photosynthesis, the transfer of an electron in the P–Q compounds takes place mainly with participation of excited singlet states of the pigments over distances reaching 15–20 Å. The electron transfer is manifested by the efficient quenching of the fluorescence of the porphyrin fragment and is recorded from the appearance of the characteristic EPR signals of the corresponding radical-ions and the appearance of new absorption bands in the optical spectra of the light-irradiated solutions. In conformity with the existing models of electron tunnelling, the probability of the process decreases exponentially with increase in chain length, depends on the mutual orientation of the porphyrin and the quinone, and is determined by the free energy of the reaction. The variation of the length and nature of the bridge and of the mutual orientation of the porphyrin and the quinone by specific synthesis makes it possible to control the electron transport process in the P–Q compounds. The ineffectiveness of the charge separation via the reaction channel involving the participation of the excited triplet state of the porphyrin is apparently caused by the lower energy of the triplet states compared with the singlet states. For $-\Delta G^0 < 1$–2 eV, this should entail, according to theoretical ideas about the mechanisms of electron transfer reactions, smaller rate constants for processes with participation of excited triplet states of the porphyrin. We may note in this connection studies[110–112] in which intramolecular electron transfer and the charge separation processes were investigated in covalently bound porphyrin–viologen and porphyrin–trinitroaryl compounds. According to preliminary data, the charge separation in these compounds takes place mainly with participation of the triplet states of porphyrins. Further investigation of the dependence of the electron transfer efficiency on the spin state of the pigment is of considerable interest for the theory of oxidation-reduction electron transfer reactions.

The solvent apparently plays an important role in the charge transfer in the P–Q compounds. The data obtained hitherto suggest that the medium influences only the process energetics. However, one must expect the involvement of the medium also in the dissipation of the energy of the resonance defect. This hypothesis is supported by the results of a study[113] of the influence of the isotope composition of the medium on the efficiency of the charge separation process in photosynthesis. The covalently bound P–Q compounds are convenient objects for the study of this interesting phenomenon, which is important for the theory of electron transfer and for the understanding of the mechanisms of charge separation in photosynthesis.

An appreciable increase in the lifetime of the separated charges is attained on passing from P–Q compounds to covalently bound triads. The stepwise character of the charge separation in these molecules ensures a high rate of charge separation and a low rate of their dark recombination.

Appreciable progress has now been achieved in the study of charge transfer processes in P–Q compounds. The results of these investigations promote a correct interpretation of data on the kinetics of electron transfer in photosynthesis. The synthesis and investigation of covalently bound triads with different donor fragments and bridging chains and other model structures containing P–Q fragments permit a deeper understanding of the mechanisms of electron transport in biological structures and will assist in progress towards the development of artificial molecular photocatalytic systems for the utilisation of solar energy.

References

1. U Govindjee (Editor) *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1987, Vol. 1, 728 pp
2. U Govindjee (Editor) *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1987, Vol. 2, 470 pp
3. R K Clayton *Photosynthesis: IUPAB Biophysics Series, Vol. 4, Physical Mechanisms and Chemical Patterns* (Translated into Russian from English), Izd. Mir, Moscow, 1984, 350 pp
4. D O Hall, K K Rao *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1983, 134 pp
5. V S Pshezhetskii, T S Lebedeva, A A Yaroslavov, et al. *Biofizika*, 1985, **30**
6. Y Nosaka, A Kuwabar, H Miyama *J. Phys. Chem.*, 1986, **90** 1465
7. K Mandal, M Z Hoffman *J. Phys. Chem.*, 1984, **88** 5632
8. T Sakata *J. Synth. Org. Chem. Jpn.*, 1981, **39** 909
9. D Dolphin, J Hiom, J B Paine *Heterocycles*, 1981, **16** 417
10. T Matsuo *J. Photochem.*, 1985, **25** 41
11. J H Fendler *J. Phys. Chem.*, 1985, **89** 2730
12. D Holten, M Gouterman, W W Parson, et al. *Photochem. Photobiol.*, 1976, **23**
13. D Huppert, P M Rentzepis, G Tollin *Biochim. Biophys. Acta*, 1976, **440** 356
14. A Harriman, G Porter, N Searle *J. Chem. Soc., Faraday Trans. 2*, 1979, **75** 1514
15. I N Ivanitskaya, I I Dilung *Biofizika*, 1974, **19** 647
16. D R Kemp, G Porter *Proc. R. Soc. London, A*, 1971, **326** 117
17. G Tollin, G Green *Biochim. Biophys. Acta*, 1962, **60** 524
18. G Tollin *J. Phys. Chem.*, 1976, **80** 2274
19. L V Natarajan, L R Humphreys, R Chang *Spectrosc. Lett.*, 1985, **18** 219
20. A Harriman, G Porter, A Wilowska *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**
21. N Mataga, A Karen, T Okada, et al. *Phys. Chem.*, 1984, **88** 4650
22. K Maruyama, H Furuta *Chem. Lett.*, 1986, 473
23. Y Degani, I Willner *J. Phys. Chem.*, 1985, **89** 5685
24. S M B Costa, M R Aires de Barros, J P Conde *J. Photochem.*, 1985, **28** 153
25. N B Joshi, J R Lopez, H T Tien, et al. *J. Photochem.*, 1982, **20** 139
26. I Tabushi, M Kinnaird, S-I Kugimiya *J. Photochem.*, 1985, **29** 217
27. M C Gonzalez, A C Weedon *Can. J. Chem.*, 1985, **63** 602
28. J L Y Kong, P A Loach *Frontiers of Biological Energetics: From Electrons to Tissues*, 1978, Vol. 1, p. 73
29. J L Y Kong, P A Loach *J. Heterocycl. Chem.*, 1980, **17** 737
30. J A Anton, J L Y Kong, P A Loach *J. Heterocycl. Chem.*, 1976, **13** 717
31. T-F Ho, A R McIntosh, A C Weedon *Can. J. Chem.*, 1984, **62** 967
32. J A Schmidt, A Siemiarczuk, A C Weedon, J R Bolton *J. Am. Chem. Soc.*, 1985, **107** 6112
33. I Tabushi, N Koga, M Yanagita *Tetrahedron Lett.*, 1979, **20** 257
34. J P Collman, R R Gagne, C A Reed, et al. *J. Am. Chem. Soc.*, 1975, **97** 7185
35. G M Sanders, M van Dijk, G P Koning, et al. *Recl. Trav. Chim. Pays-Bas*, 1985, **104** 243
36. G M Sanders, M van Dijk, A van Veldhuizen, H C van der Plas *J. Chem. Soc., Chem. Commun.*, 1986, 1311
37. K Maruyama, H Puruta, A Osuka *Chem. Lett.*, 1986, 475
38. A Osuka, S Morikawa, K Maruyama, et al. *J. Chem. Soc., Chem. Commun.*, 1987
39. S Nishitani, N Kurata, Y Sakata, et al. *Tetrahedron Lett.*, 1981, **22** 2099
40. D Arnold, A W Johnson, M Winter *J. Chem. Soc., Perkin Trans. 1*, 1977, 1643
41. D P Arnold, R Gaete-Holmes, A W Johnson, et al. *J. Chem. Soc., Perkin Trans.* 1, 1978, 1660
42. S Nishitani, N Kurata, Y Sakata, et al. *J. Am. Chem. Soc.*, 1983, **105** 7771
43. N Mataga, A Karen, T Okada, et al. *J. Phys. Chem.*, 1984, **88** 5138
44. R P Evstigneeva, V V Borovkov, E I Filippovich, S I Sviridov *Dokl. Akad. Nauk SSSR*, 1987, **293** 1130
45. V V Borovkov, E I Filippovich, R P Evstigneeva *Khim. Geterotsikl. Soedin.*, 1988(5), 608
46. C E D Chidsey, S G Boxer *Biophys. J.*, 1981, **33** 172a
47. J Deisenhofer, O Epp, K Miki, et al. *J. Mol. Biol.*, 1984, **180** 385
48. I Tabushi, N Koga, A Yazaki *Kukusokan Kagaku Toronkai Koen Yoshishu XII*, 1979, p. 246
49. M R Wasielewski, W A Svec, B T Cope *J. Am. Chem. Soc.*, 1978, **100** 1961
50. R R Bucks, S G Boxer *J. Am. Chem. Soc.*, 1982, **104** 340
51. C K Chang, I Abdalmuhdi *J. Org. Chem.*, 1983, **48** 5388
52. J A Cowan, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1985, 1214
53. Y Sakata, S Nishitani, N Nishimizu, et al. *Tetrahedron Lett.*, 1985, **26** 5207
54. J P Collman, A O Chong, G B Jameson, et al. *J. Amer. Chem. Soc.*, 1981, **103**
55. J E Guillet, Y Takahashi, A R McIntosh, J R Bolton *Macromolecules*, 1985, **18**
56. J Dalton, L R Milgrom *J. Chem. Soc., Chem. Commun.*, 1979, 609
57. A C Chan, J Dalton, L R Milgrom *J. Chem. Soc., Perkin Trans. 2*, 1982, 707
58. L R Milgrom *J. Chem. Soc., Perkin Trans. 1*, 1984, 1483
59. A D Joran, B A Leland, G G Geller, et al. *J. Am. Chem. Soc.*, 1984, **106** 6080
60. J R Bolton, T-F Ho, S Liauw, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 559

61. N Kobayashi, Y Nishiyama, T Ohya, M Sato *J. Chem. Soc., Chem. Commun.*, 1987, 390
62. M R Wasielewski, M P Niemczyk *J. Am. Chem. Soc.*, 1984, **106** 5043
63. K N Ganesh, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1980, 1129
64. K N Ganesh, J K M Sanders *J. Chem. Soc., Perkin Trans. 1*, 1982, 1611
65. H P Isenring, E Zass, K Smith, et al. *Helv. Chim. Acta*, 1975, **58** 2357
66. A Osuka, H Furuta, K Maruyama *Chem. Lett.*, 1986, 479
67. B Morgan, D Dolphin *Angew. Chem., Int. Ed. Engl.*, 1985, **24** 1003
68. J Weiser, H A Staab *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 623
69. J Weiser, H A Staab *Tetrahedron Lett.*, 1985, **49** 6059
70. J S Lindsey, D C Mauzerall *J. Am. Chem. Soc.*, 1982, **104** 4498
71. J Lindsey *J. Org. Chem.*, 1980, **45** 5215
72. T A Moore, D Gust, P Mathis, et al. *Nature*, 1984, **307** 630
73. D Gust, T A Moore, P A Liddell, et al. *J. Am. Chem. Soc.*, 1987, **109** 846
74. P A Liddell, D Barrett, L R Makings, et al. *J. Am. Chem. Soc.*, 1986, **108** 5350
75. M R Wasielewski, M P Niemczyk, W A Svec, E B Pewitt *J. Am. Chem. Soc.*, 1985, **107**
76. K N Ganesh, J K M Sanders, J C Waterton *J. Chem. Soc., Perkin Trans. 1*, 1982
77. P Leighton, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1985, 24
78. J E Baldwin, M J Crossley, J E Debernadis, et al. *Tetrahedron*, 1981, **37**
79. C Krieger, J Weiser, H A Staab *Tetrahedron Lett.*, 1985, **26** 6055
80. J L Y Kong, K G Spears, P A Loach *Photochem. Photobiol.*, 1982, **35** 545
81. M Migita, T Okada, N Mataga, et al. *Chem. Phys. Lett.*, 1981, **84** 263
82. G I Gleicher *The Chemistry of the Quinoid Compounds*, Wiley, New York, 1974, Part 1, p. 24
83. K P Quinlan *J. Phys. Chem.*, 1968, **72** 1797
84. P A Shakhverdov *Dokl. Akad. Nauk SSSR*, 1967, **174** 1141
85. M A Bergkamp, J Dalton, T L Netzel *J. Am. Chem. Soc.*, 1982, **104** 253
86. J H Wilford, M D Archer, J R Bolton, et al. *J. Phys. Chem.*, 1985, **89** 5395
87. T-F Ho, A R McIntosh, J R Bolton *Nature*, 1980, **286** 254
88. B Ke, S Demeter, K I Zamaraev, R F Khairutdinov *Biochim. Biophys. Acta*, 1979, **545** 264
89. A R McIntosh, A Siemiarczuk, J R Bolton, et al. *J. Am. Chem. Soc.*, 1983, **105**
90. A Siemiarczuk, A R McIntosh, T-F Ho, et al. *J. Am. Chem. Soc.*, 1983, **105** 7224
91. J Jortner *J. Am. Chem. Soc.*, 1980, **102** 6676
92. J S Lindsey, D C Mauzerall, H Linschitz *J. Am. Chem. Soc.*, 1983, **105** 6528
93. M R Wasielewski, M P Niemczyk, W A Svec, E B Pewitt *J. Am. Chem. Soc.*, 1985, **107**
94. J R Miller, J A Peeples, M J Schmitt, G L Closs *J. Am. Chem. Soc.*, 1982, **104** 6488
95. R A Marcus *J. Chem. Phys.*, 1956, **24** 966
96. B S Brunschwig, J Logan, M D Newton, N Sutin *J. Am. Chem. Soc.*, 1980, **102** 5798
97. K I Zamaraev, R F Khairutdinov, V P Zhdanov *Tunnelirovanie Elektrona v Khimii. Khimicheskie Reaktsii na Bol'shikh Rasstoyaniyakh* (Electron Tunnelling in Chemistry. Chemical Reactions over Long Distances), Izd. Nauka, Novosbirsk, 1985
98. N Mataga, M Ottolenghi *Molecular Associations* (Edited by R Foster), Acad. Press, London, 1979, p. 40
99. B A Leland, A D Joran, P M Felker, et al. *J. Phys. Chem.*, 1985, **89** 5571
100. M C Gonzalez, A R McIntosh, J R Bolton, A C Weedon *J. Chem. Soc., Chem. Commun.*, 1984, 1138
101. D Mobins *Ber. Bunsenges Phys. Chem.*, 1978, **82** 848
102. H Kuhn *Pure Appl. Chem.*, 1979, **51** 341
103. H Kuhn *Thin Solid Films*, 1983, **99** 1
104. A F Janzen, J R Bolton, M J Stillman *J. Am. Chem. Soc.*, 1979, **101** 6337
105. A F Janzen, J R Bolton *J. Am. Chem. Soc.*, 1979, **101** 6342
106. D Gust, T A Moore *J. Photochem.*, 1985, **29** 173
107. M A Vorotinzev, E M Itskovich *J. Theor. Biol.*, 1980, **86** 223
108. L N Strekova, et al. *Dokl. Akad. Nauk SSSR*, 1988, **298** 487
109. R F Khairutdinov, L N Strekova, V V Borovkov, et al. *Khim. Vys. Energ.*, 1988, **22** 520
110. A Harriman, G Porter, A Wilowska *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**
111. G Blondcel, et al. *Chem. Phys. Lett.*, 1985, **118** 77
112. H Nakamura, A Motonaga, T Ogata, et al. *Chem. Lett.*, 1986, 1615
113. L N Strekova, et al. *Biofizika*, 1988, **33** 495