CNDO/2 Calculations on Phlorin Trianion: a Model for a Bilatriene-type of Bile Pigment

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The ground-state energy levels and wavefunctions for phlorin trianion have been calculated using the CNDO/2 method. The calculations support the experimental observation that the phlorins are oxidised at lower potentials and reduced at higher potentials than the corresponding porphyrins. The frontier electron densities and superdelocalisabilities have been obtained from CNDO/2 wavefunctions and are compared with the corresponding PPP results as well as experimental data.

Phlorins are obtained by reversible hydrogenation of a methine bridge in a porphyrin ring system.[1,2] On the basis of kinetic and spectral evidence, phlorins (Figure) have been postulated as the first intermediates formed during photoreductions of porphyrins.[2-4] Pulse radiolytic studies of reduction of hematoporphyrin and its zinc complex by anion radicals had also revealed that the primary product is of the phlorin type.[5] Phlorins are highly reactive intermediates and can be stabilised by the presence of bulky groups.[6] The electronic spectra of phlorins and their metal complexes generally consist of two bands of nearly equal oscillator strengths occurring at ca. 440 and 880 nm. The visible absorption spectrum is nearly identical to that of ring-opened bilatriene (Figure). Hence phlorin serves as a model system for a bilatriene in a cis-cis configuration. Close and Close generated zinc tetraphenyl-phlorin anion which was rapidly converted into the corresponding chlorin.[7] Whitcock has converted chlorins into a phlorin by heating in tetrahydrofuran–potassium t-butoxide–t-butyl alcohol medium.[8] All the chemical data indicate that phlorin is highly reactive compared with a porphyrin. We have performed CNDO/2 calculations on phlorin trianion in order to understand its electronic structure by comparison with a porphyrin dianion.

PPP calculations do not distinguish between a phlorin and bilatriene. CNDO/2 calculations point to the participation of the CH_2 group in the π system. The phlorin trianion is chosen here because of its highly symmetric nature. It is easy to compare the behaviour of phlorin trianion and porphin dianion.

Methods

SCF calculations on phlorins in the PPP-π framework have already been reported.[9] The saturated methylene group was not included in the PPP calculations. In the present calculations, CNDO/2 formalism is used. The phlorin trianion has C_{2v} symmetry. Since crystal-structure data are not available for this system, the co-ordinates are taken to be the same as those for porphin dianion.[10] The saturated methylene group is taken to lie in the σ_v plane.

Results and Discussion

The energy levels obtained from CNDO/2 method for porphyrin dianion and phlorin trianion are presented in Table 1. The disruption of conjugation in the porphyrin macrocycle leads to the lifting of the near-degeneracy of the HOMO and the true degeneracy of the LUMO levels. In comparison with porphyrin dianion, the HOMO and LUMO of phlorin trianion are raised. Hence phlorin trianion is expected to have a lower oxidation potential and a higher reduction potential than the corresponding values of a porphyrin. This pattern of energy

Table 1. CNDO/2 molecular orbital energies of phlorin trianion and porphin dianion

Phlorin trianion		Porphin dianion	
Orbital no.	Energy (a.u.)	Orbital no.	Energy (a.u.)
63	0.6754	63 ⎫ e_g	0.5351
62	0.6697	62 ⎭	
61	0.6404	61	0.5284
60	0.4824	60	0.3809
59 (LUMO)	0.4412	59 ⎫ LUMO e_g	0.2876
58 (HOMO)	0.2082	58 ⎭	
57	0.1102	57 (HOMO 1)	0.0166
56	0.0519	56 (HOMO 2)	−0.0096

(a)

(b)

(c)

(d)

R^1 = vinyl or ethyl
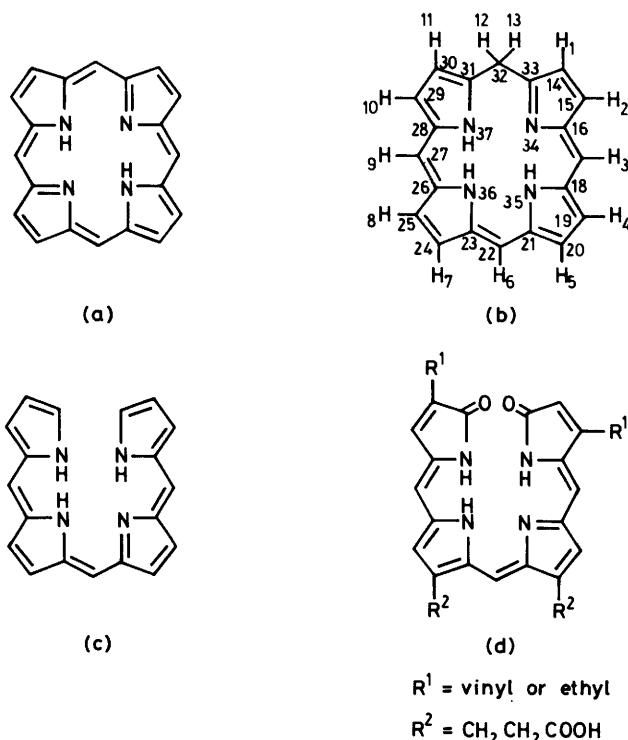
R^2 = $CH_2 CH_2 COOH$

Figure. (a) Free-based porphin; (b) free-base phlorin; (c) bilatriene with all-cis configuration; (d) R^1 = vinyl, biliverdin; R^1 = ethyl, meso-biliverdin

levels for phlorin trianion is different from that obtained from PPP calculations.

In the PPP calculations for phlorin, the nitrogen parameters are taken as the average of those for three pyrrole- and one

Table 2. Reactivity parameters for phlorin trianion

| | Electrophilic reactivity parameters | | | | Nucleophilic reactivity parameters | | | |
| | Frontier electron density | | Superdelocalisability | | Frontier electron density | | Superdelocalisability | |
Atomic centre	PPP	CNDO/2	PPP	CNDO/2	PPP	CNDO/2	PPP	CNDO/2
14	0.0094	0.0270	0.81	0.62	0.0051	0.0214	0.43	0.72
15	0.0490	0.0270	0.77	0.59	0.0575	0.0422	0.62	0.74
16	0.0330	0.0449	0.76	0.63	0.0024	0.0054	0.43	0.66
17	0.0883	0.0648	0.68	0.53	0.1777	0.1610	1.00	1.00
18	0.0500	0.0341	0.71	0.53	0.0035	0.0112	0.50	0.77
19	0.0074	0.0033	0.71	0.43	0.0733	0.0741	0.71	0.94
20	0.0518	0.0226	0.77	0.51	0.0086	0.0359	0.55	0.82
21	0.0019	0.0042	0.60	0.39	0.0854	0.0537	0.71	0.91
22	0.2056	0.1918	0.92	1.00	0.0000	0.0000	0.55	0.55
33	0.0610	0.0396	0.74	0.64	0.0494	0.0225	0.64	0.71
34	0.0039	0.0137	0.94	0.60	0.0142	0.0320	0.25	0.72
35	0.0405	0.1089	1.00	0.89	0.0226	0.0460	0.21	0.53

pyridine-type nitrogen atom. In a porphyrin the nitrogen parameters are the average of those for two pyrrole and two pyridine nitrogen atoms. Other parameters are identical for phlorin and porphyrin. Under this condition, if one compared the energy levels of porphyrin (D_{4h}) and phlorin (C_{2v}), the HOMO level for phlorin is higher and the LUMO level is lower than those of the corresponding values of porphyrin. Support for this pattern is indirect from the experimental data of biliverdins.[11] The oxidation and reduction potentials for metallobiliverdins are respectively lower than those of metalloporphyrins. But the biliverdins have terminal carbonyl groups and they do not truly represent a phlorin or a typical bilatriene. The arbitrariness in the choice of nitrogen parameters in PPP calculations should not be overlooked. The results of CNDO/2 calculations on phlorin trianion and porphin dianion are free from this factor. Regarding the oxidation potentials, both these methods predict that a phlorin system is more easily oxidised than porphyrin. This prediction is supported by experimental data. The first oxidation potential for ZnTPP (zinctetraphenyl-porphyrin) is 0.80 V versus saturated calomel electrode (s.c.e.) whereas the corresponding phlorin anion is oxidised to a porphyrin at a potential of -0.45 V versus s.c.e.[12] Regarding the case of reduction, the results of these calculations predict opposite trends. PPP calculations indicate that a phlorin has a lower reduction potential than that of a porphyrin, while according to the CNDO/2 results phlorin trianion should have a higher reduction potential than that of a porphyrin. There is experimental evidence in support of the results of CNDO/2 calculations. A detailed electrochemical and spectroscopic study by Lanese and Wilson has shown that ZnTPP is reversibly reduced to its monanion at -1.35 V versus s.c.e. while the corresponding phlorin anion, ZnTPPH$^-$, is reduced to its radical dianion, ZnTPPH^{2-}, at a potential of -1.85 V.[12] Additional support comes from photoreduction studies on metalloporphyrins. The photoreduction of porphyrins leading to phlorins and further hydrogenated products occurs only in acidic medium and not in alkaline medium. Further reduction of phlorin is very slow compared with the porphyrin→phlorin step.[13,14] These observations strongly support our calculations indicating that phlorins are more difficult to reduce than porphyrins. More experimental data on bilatrienes and stable phlorins are required to understand the relative reactivities of porphyrins and phlorins. Regarding the charge distributions there is very little difference between the results of PPP and CNDO/2 calculations. The saturated methylene group is at the nodal plane of the LUMO wavefunction. In the wavefunction corresponding to the HOMO level, the $2p\pi$-charge density of

the methylene carbon is very small. Thus the methylene group has very little interaction with the π-framework of the phlorin molecule and essentially disrupts the conjugation in the macrocyclic system.

We have complied the reactivity parameters for phlorin trianion. Table 2 lists the frontier orbital charge densities and superdelocalisabilities,[15] obtained from PPP and CNDO/2 wavefunctions. The superdelocalisabilities are normalised with respect to the centre having the highest reactivity value. There are only slight differences between the charge densities obtained by the PPP and CNDO/2 methods. Based on the charge densities in the HOMO level obtained by both the methods, the first three centres of high electrophilic reactivity in decreasing order, are 22 > 35 > 17 (PPP) and 22 > 17 > 33 (CNDO/2). Based on superdelocalisabilities, the order of electrophilic reactivities is: 35 > 22 > 14 (PPP) and 22 > 35 > 33 (CNDO/2). Summing up, the overall prediction of the order of electrophilic reactivity can be written as 22 > 17 > 33. Regarding the nucleophilic reactivities, there is a good agreement between the CNDO/2 and PPP charge densities for the LUMO level. The superdelocalisabilities also predict the same trends as the frontier electron densities. The predicted order of nucleophilic reactivity is 17 > 19 > 21. The limited experimental data on the reactivity of bile pigments[16–18] supports the above predictions.

In the porphin dianion, the charge density is uniformly distributed over all four methine bridge positions, while in phlorin trianion there is a larger concentration of charge at position 22 in the HOMO and at position 17 in the LUMO. Hence the electrophilic and nucleophilic reactivities are higher for phlorin than those observed for porphin.

In summary, we have observed that the PPP method predicts a phlorin to have lower oxidation and reduction potentials than those of a porphin while the CNDO/2 calculations indicate that a phlorin should have a lower oxidation potential and a higher reduction potential than the corresponding values of a porphin. The CNDO/2 results are supported by experimental data. Both the methods predict the same pattern of charge density distribution and reactivity parameters.

Acknowledgements

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