The Chlorophyll-a Radical-cation: Determination of Hyperfine Coupling Constants by Nuclear Magnetic Resonance Spectroscopy

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Summary By means of an n.m.r. line broadening method, all significant hyperfine coupling constants have been determined for the title compound in acetone solution; the rate of electron transfer at 300 K under these conditions is between 2×10^8 and 2×10^{10} l mol^{-1} s^{-1}.

THE fundamental step in photosynthesis is light-induced generation of chemical oxidising and reducing power, achieved[1] by a chlorophyll-mediated electron transfer (Scheme: D is an electron donor, A is an acceptor, and D^+ and A^- represent oxidising and reducing-power respectively). The first 'stable' product in this pathway is the radical cation of chlorophyll-a (**1**), and a knowledge of its electronic structure and electron transfer properties is central to the understanding of photosynthesis. In addition, this knowledge provides a good test of molecular orbital calculations.[2]

$$\text{D–chlorophyll–A} \xrightarrow[k\ ca.\ 10^{15}\ \mathrm{s}^{-1}]{h\nu} \text{D–chl}^{*}\text{–A} \xrightarrow[k\ ca.\ 10^{9}\ \mathrm{s}^{-1}]{}$$

$$\text{D–chl}^{+\cdot}\text{–A}^{-} \xrightarrow[k \leqslant 10^{3}\ \mathrm{s}^{-1}]{} \text{D}^{+}\text{–chl–A}^{-}$$

SCHEME

The e.s.r. spectrum of monomeric (**1**)$^{+\cdot}$ consists of a single broad resonance,[3] and ENDOR elucidates only a few large hyperfine couplings.[4] We report here detailed coupling information for (**1**)$^{+\cdot}$ determined by an n.m.r. line-broadening method.[5-7]

TABLE

Hyperfine coupling constants in (**1**)$^{+\cdot}$

Proton	Relative Broadening	Hyperfine coupling constant Relative	Absolute (MHz)[a]	Uncertainty (%)
α	0·09	0·30	2·2	10
β	0·01	0·10	0·75	15
δ	0·18	0·42	3·1	10
2a	0·018	0·13	0·99	15
2b′, 2b″	0·023	0·15	1·1	15
1a	0·64	0·79	5·9	10
3a	0·64	0·79	5·9	10
4a	(0·032)	(0·18)	(1·3)	(70)
5a	1·0	1·0	7·45	—
7	1·7	1·3	9·7	15
8	1·2	1·1	8·2	20
10	0·027	0·16	1·2	20
4b	0·005	0·07	0·53	25
7a, 7b	0·006	0·07	0·5	40
8a	0·0026	0·052	0·39	20
10b	<0·0006	<0·025	<0·2	—

[a] 2·8 MHz = 1 Gauss.

Radical-cations in fast electron exchange with their related neutral species cause line broadening (ΔT_2^{-1}) given[5] by equation (1), where [P] and [D] are the concentrations of the radical and neutral species, a_H is the relevant hyperfine coupling constant (in MHz), and k is the bimolecular rate contant for the electron transfer. Thus relative broadenings of different signals are equal to the squares of relative a_H's.

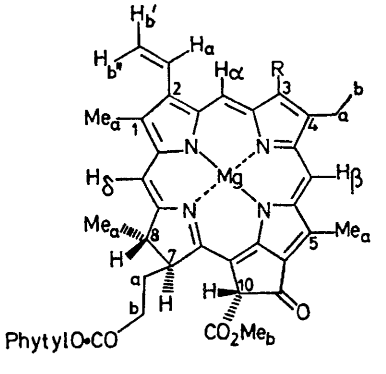
$$\Delta T_2^{-1} = \tfrac{1}{4}([P]/[D]^2)a_H^2k^{-1} \quad (1)$$

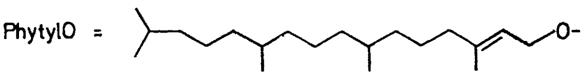
Dipolar broadening should be insignificant for disaggregated, monomeric (**1**).[6] We have assigned† all proton resonances of monomeric (**1**) *via* the nuclear Overhauser effect,[8] generated (**1**)$^{+\cdot}$ by electron transfer to added (**3**), and confirmed the fast exchange condition.[5] It is possible

$$(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+\cdot}\ \text{SbCl}_6^-$$

(**3**)

to broaden beyond detection the entire spectrum except for the phytyl and Me (10b) resonances, and the broadening can be abolished completely, restoring the diamagnetic spectrum, on prolonged exposure of the solution to air. The Table shows our measured values for relative hyperfine coupling constants and absolute values calculated assuming a_H (5a-H) = 7·45 MHz.[9] In general, uncertainties are *ca.* ± 15%, but for 4a-H, 7a-H, and 7b-H are particularly large owing to overlapping. No contact shifts have been observed, and therefore the signs of all hyperfine couplings are unknown.





(**1**) R = Me

(**2**) R = CHO

From the fast exchange condition[5] we calculate a minimum electron transfer rate of *ca.* 2 × 10^8 l mol^{-1} s^{-1}, and from the quantity of (**3**) added, and equation (1) we calculate a maximum rate of *ca.* 2 × 10^{10} l mol^{-1} s^{-1}. The electron transfer is very efficient, a finding which may have some functional significance.

Clearly, whilst ENDOR is invaluable in providing an absolute scale, n.m.r. spectroscopy can give much more detail and insight. We note also that although ENDOR and n.m.r. results are in good qualitative agreement with MO calculations of spin density (ρ),[2] quantitative agreement is poor unless Q in equation (2) is *ca.* eight times larger than expected. We find a similar effect for the radical-cation of bacteriopheophytin,[8] and these unexpected results are being pursued. In addition, our results[8] on chlorophyll-b$^{+\cdot}$

$$a_H = Q\,\rho \quad (2)$$

(**2**) indicate that it is considerably different in that the unpaired spin density is more evenly spread around the ring.

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† 100 MHz; (**1**) was 25mM in $(CD_3)_2CO$; 300 K.

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[7] A similar method is apparently being used to study the chlorophyll triplet state: S. G. Boxer and G. L. Closs, *J. Amer. Chem. Soc.*, 1975, **97**, 3268.

[8] J. K. M. Sanders and J. C. Waterton, unpublished observations.

[9] This is the only unambiguous single coupling constant determined by ENDOR.[4]