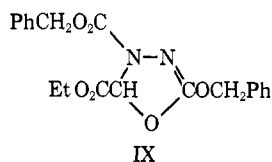
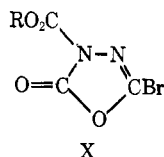


B and C, are observed. These continue to increase in area, but another signal, D, due to the CH₃ groups of (CH₃O₂C)₂NN=CCl₂, the final product, appears as the reaction progresses and grows at the expense of B and C. Clearly, an intermediate with nonequivalent OMe groups is formed initially and rearranges at room temperature to the final product. Similar information was obtained from the ¹³C nmr spectra of such reaction mixtures; the intermediate showed *two* different COMe and CH₃ carbon resonances (-25.8 and -23.1 ppm; +70.9 and +72.2 ppm, *vs.* C₆H₆). In an experiment where ir spectroscopy was applied, it was seen that the formation of the intermediate correlated with the growth of a band at 1640 cm⁻¹ (ν_{C=N}). This band disappeared with time with concomitant formation of a new band at 1580 cm⁻¹ (ν_{C=N} of (MeO₂C)₂NN=CCl₂). Although we have not yet been able to isolate these intermediates, the most likely structure which accounts for the data presented is III. The facile rearrangement of III to IV finds precedent in the thermal isomerization of IX to (PhCH₂O₂C)₂NN=CHCO₂Et.⁷



The reactive species which interacts with the azodicarboxylate ester could be either PhHgCCl₂Br or CCl₂ formed in its decomposition. That it is the latter is made likely by the observation that decarboxylation of CCl₃CO₂Na in the presence of EtO₂CN=NCO₂Et in refluxing 1,2-dimethoxyethane also gave IV (R = Et) in 69% yield. In terms of the final products obtained, there is a striking similarity between the reactions of azodicarboxylate esters with dihalocarbenes and diazoalkanes.^{7,11} However, we wish to emphasize that quite different reactions are involved. In the case of the latter reagents, direct attack of the diazoalkane as a carbon nucleophile at an azo ester nitrogen atom (rather than a carbene mechanism) was established.⁷ With the dihalocarbenes, we no doubt are dealing with an initial attack by these as electrophiles at nitrogen. It may well be that II is a transitory, nonobservable intermediate formed in the initial attack by CCl₂ at a nitrogen atom of the azodicarboxylate ester. None of our evidence speaks in favor of the formation of I as a stable intermediate, but it cannot be excluded as a transitory intermediate.

Similar reactions between azodicarboxylate esters and PhHgCClBr₂ and PhHgCBr₃ have been observed, but the (RO₂C)₂NN=CClBr and (RO₂C)₂NN=CBr₂ products formed are less stable thermally than (RO₂C)₂NN=CCl₂. Thermolysis of the dibromide gives X



in good yield, while thermal decomposition of the chlorobromo compounds results in a 10:1 mixture

(11) (a) H. Staudinger and A. Gaule, *Ber.*, **49**, 1961 (1916); (b) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 1979 (1966).

of VII and X. This new route to the difficult-to-prepare 2-halo-1,3,4-oxadiazolin-5-ones may well find useful application in synthetic chemistry.

Our studies of reactions of phenyl(trihalomethyl)-mercury compounds with azo compounds are continuing. In the case of azobenzene, a completely different reaction course is observed. Depending upon the reagent stoichiometry, the major product is either PhN=CCl₂ (azobenzene in excess) or 1-phenyl-2,2,3,3-tetrachloroaziridine (mercurial in excess). Such reactions with azoarenes, however, are not clean reactions, and the yields of these products under optimum conditions do not exceed 40–50%.

Acknowledgments. The authors are grateful to the U.S. Air Force Office of Scientific Research for generous support of this research (Grants AF-AFOSR-70-1971 and AF-AFOSR-72-2204) and to Dr. D. D. Trafficante for assistance in obtaining ¹³C nmr spectra.

Dietmar Seyferth,* Houg-min Shih

*Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*

Received December 29, 1971

Carbon-13 Fourier Transform Nuclear Magnetic Resonance Study of Some Porphyrins. Evidence for a Preferred Delocalization Pathway

Sir:

The application of Fourier transform techniques¹ for the observation of ¹³C in natural abundance has extended the range of accessible biological systems.^{2,3}

Porphyrins are a class of compounds which are extremely important, both from biological and theoretical standpoints, but whose natural abundance ¹³C spectra would be difficult to observe by continuous-wave methods. The understanding of porphyrin ring currents through proton magnetic resonance studies is frequently complicated somewhat by the dependence of proton chemical shifts on aggregation and solvation effects.⁴ This complication is not expected to arise with ¹³C nmr studies because ¹³C chemical shifts are largely determined by the paramagnetic screening term.⁵ Any through-space screening is likely to be of only minor importance, making ¹³C chemical shifts ideally suited for probing the electronic structure of the porphyrin ring. Here we report ¹³C chemical shift data which strongly support the concept that the main pathway of electron delocalization is the inner 16-membered ring of the porphyrin skeleton.^{4c,4d,6}

(1) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1965).

(2) A. Allerhand, D. W. Cochran, and D. Doddrell, *Proc. U. S. Nat. Acad. Sci.*, **67**, 1093 (1970).

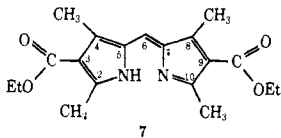
(3) A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, **93**, 544 (1971); A. Allerhand and D. Doddrell, unpublished results.

(4) (a) R. J. Abraham, P. A. Burbidge, A. H. Jackson, and G. W. Kenner, *Proc. Chem. Soc.*, 134 (1963); (b) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Amer. Chem. Soc.*, **85**, 3809 (1963); (c) W. S. Caughey, J. O. Alben, W. Y. Fujimoto, and J. L. York, *J. Org. Chem.*, **31**, 2631 (1966); (d) W. S. Caughey, J. L. York, and P. K. Iber in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Ed., Pergamon Press, New York, N. Y., 1967, p 25; (e) D. Doughty and C. W. Dwigins, Jr., *J. Phys. Chem.*, **73**, 423 (1969).

(5) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

(6) T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 2305 (1965); E. G. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

Table I. Chemical Shifts in Ppm from Neat Carbon Disulfide in the Proton-Decoupled Natural-Abundance Carbon-13 Spectra of the Porphyrin Derivatives Studied^a

Compound ^b	Resonances					
	1,3-CH ₃	C-2,4 ^c	5,8-CH ₃	6A,7A	6B,7B	Meso carbons
Deuteroporphyrin IX dimethyl ester (1) (0.23 M, 1650 scans) ^d	178.9	63.9	180.9	170.6	155.1	92.3, 93.1, 95.5, 96.5
Deuteroporphyrin IX diethyl ester (2) (0.31 M, 530 scans) ^d	178.9	63.7	181.0	170.6	155.5	92.5, 93.3, 95.6, 96.6
2,4-Diacetyldeuteroporphyrin IX dimethyl ester (3) (0.15 M, 2886 scans) ^{d,e}	178.9	-5.3	181.0	171.0	155.9	90.6, 92.8, 95.7, 97.2
2,4-Dipropionyldeuteroporphyrin IX dimethyl ester (4) (0.15 M, 2963 scans) ^{d,f}	178.6	-6.1	181.5			
Mesoporphyrin IX dimethyl ester (5) (0.12 M, 1568 scans) ^{d,h}	178.7	g	181.2	171.2	154.5 or 156.3	90.8, 92.7, 95.7, 97.4
Protoporphyrin IX diethyl ester (6) (0.22 M, 870 scans) ^{d,i}	174.7	172.6	180.9	170.4	155.0	96.2
	180.0	62.1	180.7	170.5	155.1	95.6 broad
	Resonances ^j					
	2,10-CH ₃	4,8-CH ₃	C-6	OCH ₂ CH ₃	OCH ₂ CH ₃	Carbonyl
	175.3	180.0	72.6	132.7	178.1	27.2

^a In chloroform at 15.08 MHz and 42°. ^b The estimated error in all chemical shifts is not more than ± 0.2 ppm. A recycle time of 5.43 sec was used in all cases. ^c In the C-2,4 protonated porphyrins 1 and 2 this listing refers to the chemical shifts of C-2 and C-4 while in the other porphyrins it refers to the chemical shift of the directly attached carbon of the side chain. ^d In the porphyrins 1-6 the carbonyl carbons of the ester side chains resonate between 19.0 and 19.3 ppm and the nonprotonated carbons of the pyrrole rings span the range 45.0-57.0 ppm. In the methyl esters the methyl resonance occurs between 140.7 and 140.9 ppm while in the ethyl esters the methylene occurs at 131.7 ppm and the methyl at 178.1 ppm. ^e The methyls of the acetyl groups occur at 159.4 and 159.7 ppm. ^f The methylenes and methyls of the propionyl groups showed broadened resonances at 154.5 or 156.3 and 183.4 ppm, respectively. ^g Unobserved. ^h The methyl groups of the ethyl side chains resonate at 180.9 ppm. ⁱ The methylene groups of the vinyl side chains resonate at 72.4 ppm. ^j In compound 7 there were additional resonances at 35.4, 47.9, and 59.6 ppm.

Carbon-13 nmr spectra were determined in natural abundance by the Fourier transform method as described previously.^{2,3} Spectral assignments were made by comparative methods and off-resonance single frequency decoupling experiments.⁷ The spectra of deuteroporphyrin IX diethyl ester (2) and 2,4-diacetyldeuteroporphyrin IX dimethyl ester (3) are shown in Figure 1. The carbon-13 chemical shifts of all the compounds studied are given in Table I. Except for unique differentiation between the four meso positions, the assignments for all the protonated carbons are straightforward. In general, the chemical shifts of the nonprotonated unsaturated carbons on the pyrrole ring span a very narrow range from about 45.0 to 57.0 ppm upfield from carbon disulfide with the outer carbons of the pyrrole ring probably falling in the upfield portion of this range. Evidence for this can be seen in the spectrum of 2 where there are three well-separated two-carbon resonances upfield at 52.3, 54.0, and 55.9 ppm. Individual assignment for this region of the spectra would be purely speculative at this time. However, this portion of the spectrum is potentially very informative as shown in Figure 1, where the expansion of this region for 3 shows 16 resolved resonance lines for the 16 nonprotonated carbons present. Unique assignment of the meso positions is also quite difficult. However, it should be noted that from a comparison of the spectra of 2 and 5 it appears that alkyl substitution at the adjacent pyrrole ring positions causes an upfield shift of about 3.0 ppm, and thus in the spectra of 1 and 2

the two upfield meso resonances can be allotted to the γ and δ positions, but not specifically.

Although there are a number of problems with the individual assignments, inspection of the gross chemical shifts shows that there is strong evidence for delocalization by the inner 16-membered ring. Consider C-2,4 and the meso positions of 1 and 2 which are all in β positions relative to the pyrrole nitrogens. C-2 and -4 resonate in the normal olefinic range⁸ at about 64 ppm upfield from carbon disulfide, while the meso carbons resonate at 90-98 ppm. The latter chemical shifts are comparable to those of unsubstituted C-3 of simple pyrrole derivatives.⁹ It is apparent that the meso positions are in a similar electronic environment to that of the β positions in simple pyrroles,¹⁰ while C-2 and C-4 behave like normal olefinic carbons. It is concluded that the meso positions experience strong resonance effects due to delocalization *via* the inner 16-membered ring with the β - β' carbon-carbon bonds left as nearly pure double bonds and little affected by the remainder of the structure. This is not a new proposal in porphyrin chemistry but has been put forward to explain the observed bond data for the porphyrin skeleton^{4a,4b,6} and has been substantiated by detailed theoretical calculations.¹¹ Further ¹³C chemical shift

(8) J. W. Emstley, J. Feeney, and L. H. Sutcliffe, "High-Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N.Y., 1966, p 988.

(9) T. F. Page, Jr., T. Alger, and D. M. Grant, *J. Amer. Chem. Soc.*, **87**, 5333 (1965).

(10) R. J. Pugmire and D. M. Grant, *ibid.*, **90**, 4232 (1968).

(11) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966); M. Gouterman and G. Wagmire, *J. Mol. Spectrosc.*, **11**, 108 (1963); H. Kobayshi, *J. Chem. Phys.*, **30**, 1362, 1373 (1959); C. Weiss, H. Kobayshi, and M. Gouterman, *J. Mol. Spectrosc.*, **16**, 415 (1965).

(7) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966); H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 7445 (1969).

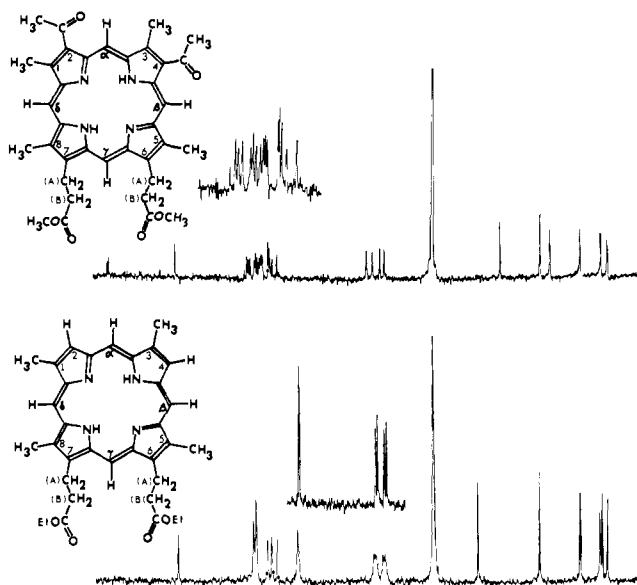


Figure 1. Proton-decoupled natural-abundance carbon-13 Fourier transform nmr spectra at 42° and 15.08 MHz of chloroform solutions of: top, 2,4-diacetyldeuteroporphyrim IX dimethyl ester (**3**) (0.15 *M* and 2886 scans) with the proton decoupling frequency set at about 4 ppm in the proton spectrum (insert, expansion of the region for the nonprotonated carbons of the pyrrole rings); bottom, deuteroporphyrim IX diethyl ester **2** (0.31 *M*, 530 scans) with the proton decoupling frequency set at about 4 ppm in the proton spectrum (insert, same as the bottom spectrum but with the proton decoupling frequency set at about 1 ppm in the proton spectrum). All spectra were recorded with a 90° pulse recycle time of 5.43 sec. The region shown is from -11.5 to 193.0 ppm from neat carbon disulfide. The intense resonance at 115.4 ppm is from the solvent.

information in support of this proposal is apparent from an inspection of the spectrum of the pyrromethene derivative **7**, where the bridging olefinic carbon resonates at 72.6 ppm. This carbon is in the same structural environment as the meso positions in the porphyrins, yet it resonates some 20 ppm downfield from them. This is consistent with a significantly reduced resonance interaction between the two pyrrole rings by the bridging carbon in **7** relative to that expected in a porphyrin.

Inspection of the spectra of **3** (Figure 1) and **4** reveals that the acetyl and propionyl groups, respectively, have removed the degeneracy¹² of the C-1,3 and C-5,8 methyl resonances encountered in the spectra of the other derivatives studied. In the case of **3**, separate resonances are observed for *all* methyl resonances, whereas in **4** some broadening of the methyl resonances was noted. A similar, but smaller, effect has been noted in studies of the pmr of these compounds^{4d} and it has been proposed¹³ that such side-chain groups exist in a preferred geometry with the methyl groups at C-1,3 trans to the carbonyl oxygen. Such a geometry would place the methyl groups in nonequivalent steric environments and could be responsible for the observed shift differences. However, a subtle electronic effect would be difficult to rule out.¹²

Although intermolecular ring current effects can be dismissed as being the cause of the pronounced upfield

(12) It should be noted that in all the porphyrin derivatives studied, the C-1,3 and C-5,8 methyls are structurally nonequivalent but appear to give rise to only two resonance lines, except in **3** and **4** where four separate resonances are encountered.

(13) W. S. Caughey, to be published.

shift of the meso positions, and it is apparent that the shift can be considered as a consequent of inner ring resonance, it is difficult to decide what the effect of the resultant large ring current has on the resonance position of these nuclei located directly on the periphery of this ring. At first glance one would guess that no conventional ring current effect would be observable because one is crossing from a shielding to a deshielding region. However, conventional ring current shift equations¹⁴ are based on the premise that one can factor the wave function of the group causing the shift from that being shifted.¹⁵ Clearly this is impossible for *any* position on the porphyrin ring and further theoretical work needs to be done in this area.¹⁶

The chemical shifts reported in this study will be useful in ¹³C investigations of diamagnetic heme proteins and other porphyrin derivatives. It is envisaged that the meso positions will be important in such studies because they fall in a region of the spectrum relatively free from overlap with other carbons.

Acknowledgment. We thank Professor Adam Allerhand for his help in this study. This research was supported by the National Science Foundation (Grant No. GP-17966, to Professor Allerhand), the donors of the Petroleum Research Fund of the American Chemical Society (Grant No. 4559-AC5 to A. A.), and the U.S. Public Health Service (Grant No. HE-13190 to W. S. C.).

(14) J. D. Memory, "Quantum Theory of Magnetic Resonance Parameters," McGraw-Hill, New York, N. Y., 1968, p 111.

(15) A similar approximation is used in the derivation of equations describing the screening from a group of atoms possessing anisotropy in their magnetic susceptibility: H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(16) Grant and coworkers have also briefly discussed this problem: A. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 2386 (1970).

(17) Contribution No. 2028.

* Address correspondence to this author at: Department of Organic Chemistry, University of New England, Armidale, N. S. W., 2351 Australia.

David Doddrell*

Department of Chemistry,¹⁷ Indiana University
Bloomington, Indiana 47401

Winslow S. Caughey

Department of Chemistry, Arizona State University
Tempe, Arizona 85281

Received February 24, 1971

Transition Metal Bicyclo[2.2.1]hept-1-yls

Sir:

Neutral compounds in which transition metals are attached only to saturated hydrocarbon ligands undergo thermal decomposition if processes such as α or β elimination of metal hydride, homolysis, or coupling of ligands at the transition metal atom occur.¹⁻⁴ Bridged or fused alicyclic ring systems of appropriate geometry are rather inert to β elimination, homolysis, or nucleophilic displacement of substituents bonded to bridgehead carbons.⁵⁻⁷ These characteristics enable

(1) R. P. A. Sneeden and H. Zeiss, *J. Organometal. Chem.*, **22**, 713 (1970).

(2) D. B. Denney and W. R. Davis, *ibid.*, **24**, 537 (1970).

(3) G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *J. Chem. Soc. D*, 1369 (1970).

(4) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968).

(5) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **92**, 948 (1970).