Restricted Internal Rotation in Cation Radicals Derived from Aminoethylenes. An Electron Spin Resonance Investigation[1]

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Abstract: Three closely related cation radicals have been studied by electron spin resonance spectroscopy. These radicals were obtained by one-electron oxidation of 1,2-bis(dimethylamino)ethylene, 1,2-bis(dimethylamino)ethylene-$[^2H_{12}]$, and 1,2-bis(diethylamino)ethylene, respectively. At 25° all 12 methyl protons in the 1,2-bis(dimethylamino)ethylene cation radical are magnetically equivalent, whereas at −70° and below two inequivalent groups of six protons each are observed. We interpret these observations in terms of restriction of rotation about the bonds between the ethylenic carbons and the amine nitrogens. The deuterated radical exhibits an interesting isotope effect: the deuterons exist in two magnetically inequivalent groups of six in the temperature range we were able to study, 35 to −30°. This result indicates that rotation about the carbon–nitrogen bonds is at least tenfold slower in the deuterated radical than in the protio radical. The inequivalence of two sets of methylene protons in the 1,2-bis(diethylamino)ethylene cation is maintained over the range of temperatures 60 to −70°. We have also examined the esr spectrum of the cation radical derived from perdeuteriotetrakis(dimethylamino)ethylene, a radical previously studied by Kuwata and Geske, and have resolved the two different deuterium coupling constants. The a_H/a_D ratios obtained from the tetrakis(dimethylamino)ethylene cations and the bis(dimethylamino)ethylene cations are compared and found to be similar.

Restricted rotation about carbon–nitrogen bonds has been observed by electron spin resonance (esr) spectroscopy in several classes of radicals including iminoxy radicals[3] and the anion radicals prepared from nitrosobenzene[4] and azobenzene.[5] In a related study, restricted rotation about nitrogen–nitrogen bonds was recently observed in the cation radical derived from tetramethyl-2-tetrazene.[6]

Kuwata and Geske[7] found two different methyl proton hyperfine coupling constants in the cation radical obtained by oxidation of tetrakis(dimethylamino)ethylene (TDE^+). Those workers found that the methyl protons exist in two magnetically inequivalent groups of 12 protons each over the range of temperature 0–120° and on that basis concluded that rotation about the carbon–nitrogen bonds between the amine groups and the central carbons is severely restricted. Since the TDE^+ radical is quite crowded, a desire to assess the relative importance of purely steric and electronic hindrance to rotation led naturally to the present investigation of the radical prepared by one-electron oxidation of 1,2-bis(dimethylamino)ethylene ($BDME^+$). We report here the results of esr investigations of three closely related species: $BDME^+$, the analogous radical deuterated at the methyl positions ($DBDME^+$), and the ethyl analog, the cation radical obtained by one-electron oxidation of 1,2-bis(diethylamino)ethylene ($BDEE^+$).

Kuwata and Geske[7] examined the spectrum of the perdeuteriotetrakis(dimethylamino)ethylene cation ($DTDE^+$), but were unable to resolve the different deuterium coupling constants. We have reexamined the spectrum of this radical under conditions of improved resolution and report experimental values of the two different deuterium hyperfine splittings. These values are of interest in comparing the a_H/a_D ratios for these radicals with the values obtained for the disubstituted radicals.

In addition, we have carried out a complete characterization of BDME and conclude that this molecule is the *trans* isomer. Electrochemical data for the oxidation of BDME and BDEE are also reported.

Experimental Section

Materials. Supporting electrolyte for electrochemistry and all solvents were commercially available and purified according to established literature methods. Chloroacetaldehyde, 30% in water, was obtained from K and K Laboratories, Inc. Dimethylamine and diethylamine were obtained from Distillation Products Industries and dimethylamine-$[^2H_6]$, 98.6% isotopic purity, was supplied by Merck Sharpe and Dohme of Canada, Ltd.

BDME. Synthesis of BDME was effected *via* a slight modification of the method described by Doss and Bost.[8] The product is acutely sensitive to atmospheric oxygen and required repeated purification prior to use. Several purification procedures were tried including preparative gas chromatography; however, the most satisfactory method proved to be trap-to-trap distillation in a vacuum train. Crude product was pumped from a trap held at 0° through a trap at Dry Ice temperature where purified material accumulated, while more volatile materials were collected in a final trap at liquid nitrogen temperature. Material purified by several repetitions of this procedure was a colorless liquid which could be stored satisfactorily *in vacuo* at Dry Ice temperature for several weeks.

The nmr spectrum of BDME in methylene chloride (at approximately 30°) consists of two singlets, δ 2.36 (12) and 5.15 (2). No significant difference was noted at −68° or when a neat sample was employed. Mass spectra were obtained at medium resolution on a CEC 21-103A spectrometer.[9] At 70 eV the base peak occurred at *m/e* 44 with the molecular ion peak (*m/e* 114) about 3% of the base peak. When the ionizing voltage was reduced to *ca.* 6 eV, the fragmentation pattern almost completely collapsed. Under these conditions, the molecular ion peak was the base peak and the $P + 1$ intensity was 8.1% (theoretical[10] $P + 1 = 7.47\%$). *Anal.*

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[6] W. M. Tolles, D. W. Moore, and W. E. Thun, *J. Amer. Chem. Soc.*, **88**, 3476 (1966).

[7] K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

[8] R. C. Doss and H. W. Bost, U. S. Patent 2,881,217 (1959).

[9] The complete 70-eV mass spectrum of BDME may be found in the Ph.D. thesis of R. H. S.

Calcd for $C_6H_{14}N_2$: C, 63.11; H, 12.36; N, 24.53. Found:[11] C, 60.10, 59.92; H, 12.47, 12.32; N, 24.51, 24.69.

DBDME. The deuterated material was synthesized and purified as described above, incorporating modifications suitable for small quantities of material: nmr (CH_2Cl_2) δ 5.20; high-resolution mass spectrum (AEI MS902) molecular ion (70 eV) *m/e* 126.1911, calcd for $C_6H_2N_2D_{12}$ 126.1909.

BDEE. The synthesis of this material was carried out in the same manner as those above. This material proved even more difficult to handle than BDME as it appears to be less stable and is less volatile. Purification using the three-trap vacuum technique described above gave a mixture of product and diethylamine in the Dry Ice trap. Removal of the diethylamine by bulb-to-bulb vacuum distillation left a colorless, viscous product which could not be further distilled without decomposition even at diffusion pump vacuum. (There was some indication that the presence of diethylamine helped to stabilize BDEE.) A medium-resolution mass spectrum (AEI MS902) showed the anticipated molecular ion, *m/e* 170; nmr (CH_2Cl_2) δ 5.15 (s, 2), 2.75 (q, 8, J = 6.5 Hz), 1.10 (t, 12, J = 6.5 Hz).

DTDE. A sample of DTDE as the dibromide salt originally synthesized by Professor K. Kuwata was available in these laboratories.

Radical Generation. Radicals were generated by oxidation of the parent amines with bromine. Substrate and solvent were degassed in high vacuum and then degassed bromine was condensed into the cooled sample vessel. The amount of bromine employed was varied to obtain good signal intensity and resolution in the esr spectra. It was also possible to generate these radicals by *in situ*[12] electrochemical oxidation; however, the line widths in the resulting esr spectra were broader than those obtained by bromine oxidation. The radical $DTDE^+$ was obtained by spontaneous reaction of the dibromide salt in absolute ethanol.[13,14]

Esr Spectra. The Varian V-4502-12 spectrometer system employed has been described previously[7] as has the method of magnetic field calibration.[15] The Varian V-4547 variable-temperature accessory was used to obtain spectra at temperatures other than 25°. A few of the spectra in this study were obtained on a Varian E-3 spectrometer in the Cornell University Department of Biochemistry. Simulations of esr spectra were computed using either a modification of the program devised by Stone and Maki[16] or the program written by Kaplan,[17] which permits use of nonuniform line widths. Both programs were executed on an IBM 360-65 computer.

Electrochemistry. Polarography was carried out using the three-electrode polarograph described previously.[7] Polarographic data were obtained in acetonitrile solution using 0.1 *M* tetraethylammonium perchlorate supporting electrolyte. Maximum, not average, currents are reported.

Configuration of BDME. In attempting to elucidate the configuration of BDME the spin-spin coupling of the vinylene protons was measured *via* the ^{13}C satellites using a Jeolco 100-MHz nmr spectrometer.[18] In addition, the infrared spectrum was measured with a Perkin-Elmer 521 spectrometer using a 1-m gas cell and a sample pressure of approximately 1 Torr. The Raman spectrum of the neat liquid was obtained with a Perkin-Elmer LR-1 laser Raman spectrometer in conjunction with a 25-μl. cell.[19]

Results and Discussion

Configuration of BDME. Spin-spin coupling constants obtained from the 100-MHz nmr spectrum of BDME are given in Table I. Included for comparison are the coupling constants for both the *cis* and *trans*

Table I. Nuclear Resonance Data

Compound	Spin-spin coupling, Hz J_{H-H}	$J_{C^{13}-H}$
BDME	12.3 ± 0.5	163
1,2-Diacetoxyethylene[a]		
cis	4 ± 0.5	195
trans	11 ± 0.5	192
1,2-Dichloroethylene[a]		
cis	5.2 ± 0.1	198
trans	11.1 ± 0.1	199

[a] R. A. Caldwell, personal communication.

Table II. Vibrational Spectra of BDME

Infrared spectrum		Raman spectrum		
Frequency, cm^{-1}	Intensity[a]	Frequency, $\Delta\nu$, cm^{-1}	Intensity[a]	Polarized
3070	W–M	480	W	
2978	S	587	W	
2949	S	805	W–M	No ρ_n = 0.848[b]
2864	W–M	910	W–M	Yes
2830	S	1078	W	
2780	S	1173	M	Yes
1660	W–M	1327	M	Yes
1475	S	1352	M	Yes
1459	W	1430	W	
1448	M–S	1455	W–M	No
1392	W	1495	W	
1215	S	1680	S	Yes ρ_n = 0.191[b]
1184	W–M	2793	W–M	Yes
1144	M	2848	W	Yes
1075	S	2965	W	Yes
1055	Sh	2993	W	
1048	Sh	3060	W	
1020	Sh			
900	M			
839	W			
777	W–M			
740	W–M			
724	W–M			

[a] W = weak, M = medium, S = strong, Sh = shoulder. [b] ρ_n is the degree of depolarization for unpolarized exciting radiation. For an unpolarized band ρ_n = 0.857.

Table III. Polarographic Data in Acetonitrile

Compound	$E_{1/2}$, V[a]	$E_{1/4} - E_{3/4}$, mV	I, μA $mg^{-2/3}$ $sec^{1/2}$ mM^{-1} [b]
BDME	−0.307 +0.354	58 21	−4.45 −2.55
BDEE	−0.420 +0.21	63 Ill-defined	*c*
TDE[d]	−0.75 −0.61		−3.6[e]
1,1-Bis(dimethylamino)ethylene	+0.44[f]		

[a] Potential *vs.* aqueous saturated calomel electrode. [b] Oxidative currents are by convention negative. [c] Difficulties of purification and transfer made the concentration, and therefore the diffusion current constant, uncertain. [d] Data from ref 7. [e] Diffusion current constant for the overall *two*-electron process. [f] Two-electron oxidation. Data from J. M. Fritsch and H. Weingarten, *J. Amer. Chem. Soc.*, **90**, 793 (1968), and Abstract No. 142, Electrochemical Society Meeting, New York, N. Y., May 1969.

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(10) J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960.

(11) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Samples were shipped packed in Dry Ice. Satisfactory nitrogen analyses were obtained only by the Dumas method.

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(14) (a) M.-K. Ahn and C. S. Johnson, Jr., *Proc. Colloq. AMPERE*, **14**, 253 (1966); (b) *J. Chem. Phys.*, **50**, 632 (1969).

(15) W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 4119 (1966).

(16) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

(17) M. Kaplan, Columbia University. A copy of this program was kindly made available to us by Professor J. H. Freed.

(18) The authors thank the Japan Electron Optics Laboratory Co., Ltd., Applications Laboratory, Medford, Mass., for their cooperation in allowing R. H. S. the use of their 100-MHz nmr spectrometer.

(19) The authors thank the Perkin-Elmer Corp., Norwalk, Conn., for their cooperation in allowing R. H. S. the use of their LR-1 Raman spectrometer.

Table IV. Electron Spin Resonance Data

Radical and conditions	Nucleus (no. equivalent)	Hyperfine coupling[a] constant, G	R[b]
BDME$^+$			
bromine oxidation, acetonitrile, 25°	N(2)	6.94 ± 0.018	
	H(12)	8.16 ± 0.024	1.18
	H(2)	4.35 ± 0.010	
	Line width	0.11	
BDME$^+$			
electrolytic, acetonitrile, 25°	N(2)	6.95 ± 0.06	
	H(12)	8.15 ± 0.10	1.17
	H(2)	4.35 ± 0.03	
	Line width	0.26	
BDME$^+$			
bromine oxidation, methylene chloride, 25°	N(2)	7.01 ± 0.024	
	H(12)	8.21 ± 0.025	1.17
	H(2)	4.23	
	Line width	0.26	
BDME$^+$			
bromine oxidation, methylene chloride, −70°	N(2)	8.07 ± 0.018	
	H(6)	8.39 ± 0.010	1.04
	H(6)	7.04 ± 0.010	0.87
	H(2)	4.36 ± 0.020	
	Line width	0.16	
BDME$^+$			
bromine oxidation, methylene chloride, −95°	N(2)	8.02	
	H(6)	8.43	1.05
	H(6)	7.02	0.87
	H(2)	4.40	
	Residual line width	~0.16	
BDME$^+$			
bromine oxidation, methylene chloride. −115°	N(2)	8.14	
	H(6)	8.58	1.05
	H(6)	7.09	0.87
	H(2)	4.50	
	Line width variable, see text		
DBDME$^+$			
bromine[c] oxidation, dimethylformamide–acetonitrile, 1:2 by volume, 25°	N(2)	6.98	
	D(6)	1.25	
	D(6)	1.07	
	H(2)	4.65	
	Line width	0.08	
DBDME$^+$			
bromine oxidation, dimethylformamide, 25°	N(2)	6.86	
	D(6)	1.24	
	D(6)	1.06	
	H(2)	4.58	
	Line width	0.10	
BDEE$^+$			
bromine oxidation, dimethylformamide, 60°	N(2)	8.12	
	H(4)	5.20	0.64
	H(4)	4.15	0.51
	H(2)	4.06	
	Line width	0.70	
BDEE$^+$			
bromine oxidation, dimethylformamide, 18°	N(2)	8.12	
	H(4)	5.12	0.63
	H(4)	4.06	0.50
	H(2)	4.06	
	Line width	0.70	
BDEE$^+$			
bromine oxidation, methylene chloride −10°	N(2)	8.12	
	H(4)	5.37	0.66
	H(4)	4.16	0.51
	H(2)	4.06	
	Line width	0.65	
BDEE$^+$			
bromine oxidation, methylene chloride, −70°	N(2)	8.12	
	H(4)	5.07	0.62
	H(4)	4.06	0.50
	H(2)	4.06	
	Line width	0.70	
TDE$^+$			
homogeneous reaction of TDE and TDE$^+$, dimethylformamide, 25°	N(2)	4.90[d]	
	H(12)	3.28	0.67
	H(12)	2.84	0.58
	Line width	0.06	

Table IV (*Continued*)

Radical and conditions	Nucleus (no. equivalent)	Hyperfine coupling[a] constant, G	R^b
$DTDE^+$			
spontaneous radical formation, ethanol, 25°	N(2)	4.87	
	D(12)	0.495	
	D(12)	0.427	
	Line width	0.03	

[a] Uncertainties given at the 95% confidence level. Where no uncertainty is given, the value was obtained from the best fit of a computer simulation of the spectrum and the accuracy believed to be 1% or better. [b] *R* is the ratio of the methyl (or methylene) proton hyperfine splitting to the nitrogen splitting. [c] E-3 spectrometer. [d] These values are only slightly different from those reported by Kuwata and Geske[7] and were obtained from reanalysis of the same spectra.

isomers of 1,2-diacetoxyethylene and 1,2-dichloroethylene. These data suggest that the sample of BDME is the *trans* isomer, although some ambiguity remains since some J_{H-H} values in the same range have been reported for *cis* compounds; however, these have usually been associated with hydrocarbons.[20] Infrared and Raman data are presented in Table II. No attempt will be made to give a complete assignment of either spectrum; rather, attention will be focused on the region of each spectrum associated with bands due to the ethylenic carbon–carbon stretching vibration, 1600–1700 cm^{-1}. Since absorptions due to totally symmetric vibrations are forbidden in the infrared, it is expected that this band will be weak or absent if the sample of BDME is *trans* and medium to strong if it is *cis*. We find a weak-medium absorption at 1660 cm^{-1}. *trans*-1,2-Dichloroethylene and *trans*-N,N-dimethyl-2-butene-1,4-diamine show absorptions of similar intensity in the region 1650–1680 cm^{-1};[21] however ,Moss[22] suggests that these are in fact combination bands. In the Raman spectrum the carbon–carbon stretching band for a *trans* symmetric olefin is expected to be intense and highly polarized,[23] while the *cis* isomer is expected to exhibit a band of comparable intensity but polarized to a lesser degree. The Raman spectrum of BDME contains an intense band at $\Delta\nu$ = 1680 cm^{-1} which is highly polarized. We conclude from these data that BDME is the *trans* isomer. It is possible that the sample contained a minor fraction of the *cis* compound, and other impurities are not excluded by these observations. In fact, esr evidence suggests that an impurity may be TDE (*vide infra*).

Electrochemistry. Polarographic data for BDME and BDEE are given in Table III. Both molecules are strong electron donors as indicated by the fact that they can be oxidized on a dropping mercury electrode at potentials negative with respect to the saturated calomel electrode. It is not surprising that these molecules are not so strong electron donors as TDE.

Assignments of Esr Spectra. Hyperfine coupling constants from analysis of the spectra obtained in this study are summarized in Table IV. Data in the Table show that the spectrum of $BDME^+$ is independent of solvent and methods of radical generation within the precision of the measurements. In Figure 1 a spectrum of $BDME^+$ obtained by bromine oxidation in acetonitrile at 25° is compared with a computer simulation. The assignment of this spectrum with a coupling constant of *ca.* 8 G for 12 equivalent methyl protons is unequivocal. The existence of some extraneous lines of low intensity (marked with small arrows in the figure) was considered carefully. These lines are too intense to be ^{13}C satellites from the spectrum of $BDME^+$; however, they appear in the correct positions to be assigned to TDE^+. These observations cannot distinguish whether TDE was present in the sample of BDME or formed as a product of the oxidation. The assignment given predicts 195 lines with a center-to-end intensity ratio of 5544:1; at high amplification we have observed 129 of the predicted lines.

In both acetonitrile and methylene chloride, oxidation of BDME produces highly colored solutions which show a reversible color change from yellow at 25° to purple at Dry Ice temperatures. Although $BDME^+$ was significantly more stable in acetonitrile than in methylene chloride, the greater liquid range of the latter solvent made it the more useful one in variable-temperature experiments. Esr spectra were obtained in this solvent at approximately 10° intervals over the range 5 to −115°.[24] The appearance of the spectra changed very significantly over this range as shown in Figure 2. These spectral changes were found to be reversible with temperature, thus assuring that they were due to changes in the sample temperature as opposed to some decomposition process. Parallel, but not identical, changes were found for $BDME^+$ in acetonitrile down to the freezing point of those solutions, *ca.* −45°. As illustrated in Figures 2e and 2f, in the temperature range −20 to −50°, a general broadening of the spectral lines took place. Sharper spectra were obtained at lower temperatures, with the sharpest lines found at about −70° (Figure 2c). At still lower temperatures, a selective line broadening process occurred which introduced a noticeable asymmetry into the spectra.

The spectra obtained at −70° and below clearly contain a larger number of hyperfine lines than the 25° spectrum. We attribute this phenomenon to restriction of rotation about the nitrogen–ethylenic carbon bonds and the consequent division of the methyl protons into two groups each containing six equivalent nuclei. Such an assignment predicts 735 lines (excluding accidental overlap) with a center-to-end intensity ratio of 2400:1. The spectrum at −70° contains approximately 230 identifiable lines. The overall

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(20) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(21) Sadtler Standard Spectra, midget ed, 1959.

(22) R. D. Moss and W. J. Potts, Jr., in "Applied Infrared Spectroscopy," D. W. Kendall, Ed., Reinhold Publishing Corp., New York, N. Y., 1966.

(23) J. H. Hibben, "The Raman Effect and Its Chemical Application," Reinhold Publishing Corp., New York, N. Y., 1939, pp 39, 66–76, 168–171.

(24) We estimate the uncertainty in the temperatures of these spectra as ±5°. The freezing point of methylene chloride is usually quoted as −97° (see, for example, Merck Index, 7th ed, p 676); we do not believe the temperature measurement was this much in error and suggest that the solvent supercooled.

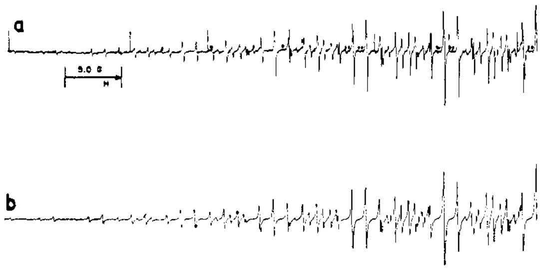

Figure 1. (a) Low-field half of the esr spectrum of BDME$^+$. Radicals were generated by bromine oxidation of BDME in acetonitrile and the spectrum was recorded at 25°. (b) Computed spectrum using the coupling constants and line width given in Table IV and Lorentzian line shape.

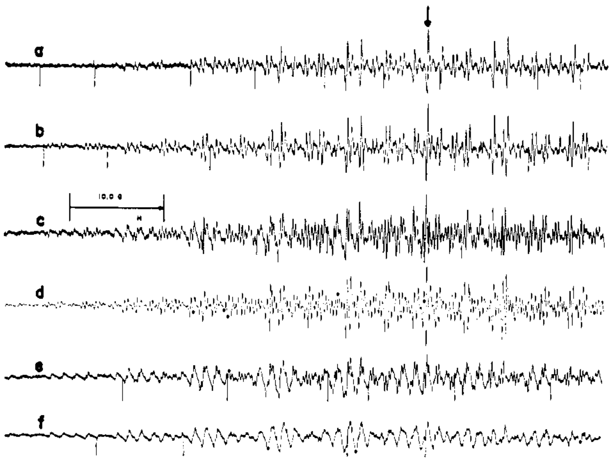

Figure 2. Spectra of BDME$^+$ produced by bromine oxidation of the parent amine in methylene chloride: (a) $-115°$; (b) $-95°$; (c) $-70°$; (d) computer simulation of the $-70°$ spectrum using $a_{H(6)} = 8.396$, $a_{H(6)} = 8.027$, $a_{N(2)} = 7.022$, and $a_{H(2)} = 4.391$ G and a Lorentzian line shape with 0.163-G width [interchange of the nitrogen splitting constant with the smaller methyl proton splitting constant yields a computation with the same line positions and only slightly different intensities; neither computation matches the experimental derivative amplitudes accurately (see text)]; (e) $-45°$; (f) $-25°$. Slightly more than half of each spectrum is shown and the center is indicated by the arrow.

broadening of spectra in the temperature range between 25 and $-70°$ is understandable in terms of an intramolecular exchange process which occurs at a rate close to the geometrically induced difference in hyperfine splittings in frequency units. At 25° we observe the exchange-averaged spectrum, whereas at $-70°$ we observe an approximation to the slow exchange limit. A spectrum computed using the parameters given in Table IV reproduced the line positions, but not the derivative amplitudes, of the $-70°$ spectrum. The differences between the observed and calculated amplitudes may be due to residual motional broadening of some of the lines, or to the onset of the asymmetric broadening process which is manifest at the lower temperatures. The uncertainty in line amplitudes and the fact that we could not achieve sufficient signal intensity to observe the end lines leave some ambiguity in the assignment. Thus, if the 7.04-G coupling is assigned to two equivalent nitrogen nuclei and the 8.07-G coupling is assigned to one set of six protons, the portion of the computed spectrum which can be compared with experiment is virtually unaltered (see Figure 2d). This ambiguity occurs because of the near identity of the intensity ratios of the lines for two equivalent spins of 1 (1:2:3:2:1) and those (excluding the outermost) for six equivalent spins of $^1/_2$ (1:6:15:20:15:6:1). In fact, the average value of 8.07 and 8.39 G is within experimental error of the 25° proton coupling constant as would be expected in the case of a motional process which causes rapid exchange of nonequivalent nuclei. Nonetheless, we prefer the assignment given in the table for reasons delineated below; a decrease in the average proton coupling constant of about 5% is not inconsistent with other data here (*vide infra*).

Inspection of the spectra obtained at $-70°$ and below reveals that they are closely similar except that with decreasing temperature certain lines decrease in derivative amplitude as a result of increasing width. All such lines belong to a single set which is characterized by a hyperfine splitting constant of *ca.* 8 G. The question is, from which group of nuclei does this splitting arise?

If this splitting were due to one set of methyl protons as inferred from the 25° average splitting, it would be necessary to invoke a second process which caused modulation of the isotropic hyperfine coupling constant. This process would have to affect one set of methyl groups strongly without appreciable effect on the second. It is possible to conceive of such a process;[25] however, all such processes cause line broadening which is symmetric about the center of the spectrum.[26] Out-of-phase correlated, in-phase correlated, and uncorrelated modulations give, respectively, line widths proportional to $(M_a - M_b)^2$, $(M_a + M_b)^2$, or the average of these, where M_a and M_b are the nuclear quantum numbers for the groups of nuclei with hyperfine splittings a and b which are undergoing exchange.

The low-temperature spectra of Figure 2 show that the lines selectively broadened have greater widths at high field than at low field. When the splitting in question is assigned to nitrogen, the origin of the asymmetric broadening can be understood in terms of the interplay of the hyperfine anisotropy and the g-tensor anisotropy which gives line widths proportional to M_N, while a contribution proportional to $M_N{}^2$ arises from anisotropic electron–nuclear dipolar interactions. Both of these effects are expected to become more pronounced as the temperature is lowered and rotational averaging of the anisotropies becomes less efficient. These effects are likely to be small for nuclei as far removed from a center of substantial π-electron spin density as the methyl protons since the anisotropic hyperfine interaction diminishes with r^3. Ahn and Johnson[14] have followed similar reasoning to suggest that at least part of the variation in nitrogen line widths observed for pyrazinium cation radicals at reduced temperatures results from anisotropic interactions.

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(25) One of the more plausible processes of this type involves a torsional motion of the amine groups about their equilibrium conformation. If the favorable resonance energy which tends to keep the radical planar is opposed by steric repulsions between the *endo* methyl groups and the vinylene protons, a potential minimum will exist when these methyl groups are slightly above or below the plane of the radical. The conformation which has both groups on the same side of the molecular plane will differ from that which has one on either side. The transition between these two conformations could modulate the methyl proton hyperfine splittings and would, presumably, affect the *endo* groups more than the *exo* groups. This process is considered further in the Ph.D. thesis of R. H. S.

(26) We include here all the motional processes which have been treated in the several publications of Freed and Fraenkel; these are summarized in ref 28.

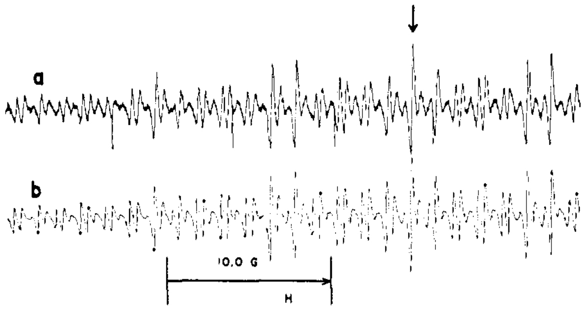

Figure 3. (a) A portion of the esr spectrum of BDME$^+$ at $-115°$. The center of the spectrum is indicated by the arrow. (b) Computed spectrum using the coupling constants given in Table IV and a Lorentzian line shape. The line width was varied as a function of the spectral index number for nitrogen (see text).

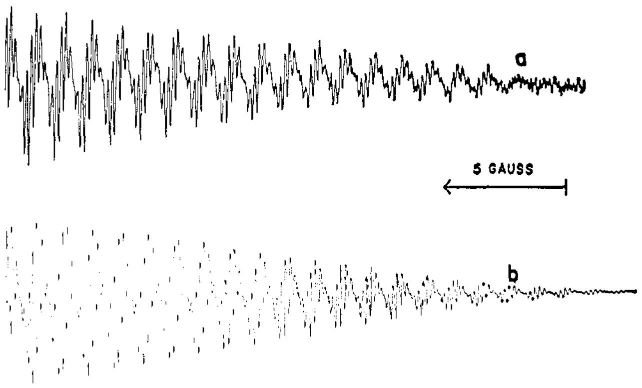

Figure 4. (a) Low-field half of the esr spectrum of deuterated BDME$^+$. Radicals were generated by bromine oxidation of DBDME in dimethylformamide and the spectrum was recorded at 25°. (b) Computed spectrum using the coupling constants and line width given in Table IV and Lorentzian line shape.

Such effects are well documented for other radicals in which substantial π-electron spin resides on nitrogen.[27]

We regard the asymmetry in the low-temperature spectra as compelling evidence to associate the coupling constant of *ca.* 8 G with the nitrogen nuclei. In Figure 3 a portion of the lowest temperature spectrum is compared with a computed spectrum which incorporates a selective line broadening and the coupling constants given in Table IV. The lines associated with the 8.14-G splitting were assigned widths according to the equation

$$\Delta H = A\tilde{M}_N{}^2 + B\tilde{M}_N + C \qquad (1)$$

where $A = 0.090$, $B = 0.030$, and $C = 0.160$ G, and $\tilde{M}_N$ is the spectral index number for nitrogen. As seen in the figure, good agreement between the computation and the experimental spectrum is achieved in this manner.

For this case of two equivalent nitrogen nuclei, eq 1 is an oversimplification and the line widths are correctly given by[28,29]

$$\Delta H = A'\langle J_N(J_N + 1) + {}^5/_3\tilde{M}_N{}^2\rangle + B\tilde{M}_N + C' \qquad (2)$$

where the quantum number J_N defines the nitrogen nuclear spin angular momentum and $\tilde{M}_N$ is again the nitrogen spectral index number, which may differ only in sign from the magnetic quantum number, M_N. Thus, the degenerate nitrogen lines are sums of components of different widths, depending on the value of J_N. If the width variations among the components are small, the observed line is of Lorentzian shape with a width given by eq 2 when the quantity in brackets is averaged over the possible values of J_N. The average width contributions of the first term of eq 2 to the lines with $\tilde{M}_N = \pm 2$, ± 1, and 0 are, respectively, ${}^{38}/_3A'$, ${}^{17}/_3A'$, and ${}^8/_3A'$. Using the widths of the principal nitrogen lines calculated *via* eq 1, we find $A' = 0.033$, $B = 0.030$, and $C' = 0.072$ G. Ahn and Johnson[14a] found $A' = 0.0144$ and $B = 0.0269$ G for the N,N′-dimethylpyrazinium cation radical. Since that radical has a nitrogen splitting of about 8 G and, therefore, approximately the same nitrogen spin density as BDME$^+$, the similarity of the anisotropic line-width parameters in the two cases supports our assignment of the low-temperature BDME$^+$ spectrum.

We had hoped to settle the question of the assignment of the nitrogen coupling constant unequivocally by examining the spectrum of DBDME$^+$. We found instead, however, an unexpected and most remarkable result: the deuterons exist in two magnetically inequivalent groups of six at 25°! The implication of this result, that the exchange of inequivalent groups of nuclei is substantially slower in the deuterated radical than in its protio counterpart, is considered further below.

In Figure 4 we compare a spectrum of DBDME$^+$ with a computed spectrum using the parameters given in Table IV. The smallest separation between adjacent lines represents the difference between the deuterium coupling constants. It proved impossible to obtain acceptable simulations of this spectrum using 12 equivalent deuterons. Attempts to study the nitrogen splitting as a function of temperature failed since cooling to about $-30°$ produced no changes except an increase in the line width, and below this temperature the continued increase in line width led to so great a loss of resolution that unambiguous assignment of the spectrum was no longer possible. Inequivalence of the two sets of deuterons persisted at 35°, the highest temperature we were able to attain.

Spectra of BDEE$^+$ are somewhat simpler to analyze. Under those conditions in which all four coupling constants are different, the spectra are predicted to have 475 lines with a center-to-end intensity ratio of 216:1, while in the cases in which the vinylene protons are accidentally equivalent to one set of methylene protons, the spectra should consist of 175 lines with a center-to-end intensity ratio of 360:1. It was, therefore, possible to observe the end lines of these spectra and, consequently, there are no ambiguities in the assignments given in Table IV. In Figure 5 the experimental spectrum of BDEE$^+$ obtained in dimethylformamide at 18° is compared with a spectrum computed using the parameters given in the table. Equally good fits were obtained for spectra recorded under the other experimental conditions listed. The large line width is due to unresolved splittings by the 12 methyl protons. In some experiments when particularly good resolution was achieved, further splittings of about 0.12 G, a value reasonable for protons γ to the π-electron center, were observed on each line. Simulations carried out using

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(27) See, for example, M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965). At low temperatures, the nitrogen lines of the spectrum of the azobenzene anion are so badly broadened that they are not detectable, ref 5.

(28) G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967).

(29) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

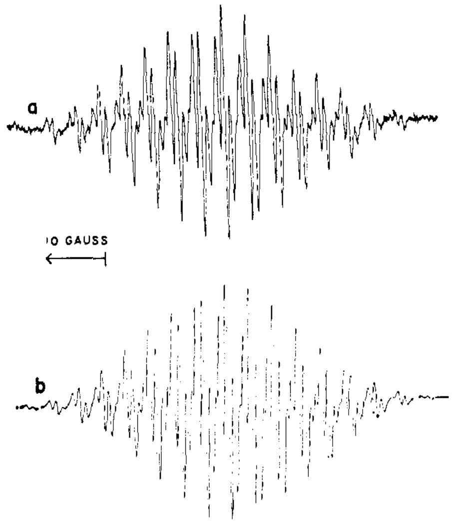
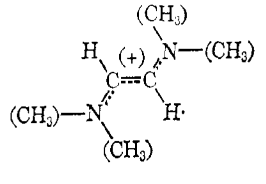


Figure 5. (a) Esr spectrum of BDEE$^+$ in dimethylformamide at 18°. Radicals were generated by bromine oxidation of the parent amine. (b) Computed spectrum using the parameters given in Table IV and a Lorentzian line shape.

this small splitting for 12 equivalent protons and a residual line width of 0.12 G gave a good approximation to the spectrum in the figure, albeit no better than that shown. For reasons still obscure, at temperatures below $-70°$ we were unable to secure sufficient intensity to obtain assignable spectra.

As a matter of secondary interest prompted by the results for DBDME$^+$, we reexamined the spectrum of DTDE$^+$ in an effort to resolve the two deuterium coupling constants experimentally. This attempt succeeded when the solvent employed was absolute ethanol. In Figure 6 we compare the spectrum of DTDE$^+$ with a spectrum computed using the parameters given in the table. Since we wished to make accurate comparison between the a_H/a_D ratio in the bis and tetrakis radicals, we reanalyzed the spectra of TDE$^+$ obtained by Kuwata and Geske.[7] The best fitting computation was achieved using the parameters in the table which differ only trivially from those reported previously.[7]

Kinetic Implications and Isotope Effect. The observation of two different coupling constants for the methyl protons of BDME$^+$ at low temperatures is clear evidence that there are two different stereochemical environments possible. For lack of a more precise description of these environments, we classify the methyl groups as *exo* and *endo* to the ethylenic double bond as idealized below.



The nature of the observed esr spectra of this radical depends upon the difference in hyperfine coupling for the two sites, $|a_{exo} - a_{endo}| = \delta a$, and the lifetime of the states, τ. From symmetry, the two states are equally probable, so the *exo-endo* interconversion can be described by a single rate constant, τ^{-1}. The observation of two discrete coupling constants requires the condition[28] that the exchange rate is small in comparison to the difference in hyperfine splittings in frequency units, *i.e.*

$$\tau > (|\gamma_e|\delta a)^{-1} \tag{3}$$

whereas at high temperatures when a single coupling constant is observed for 12 equivalent protons, the reverse of this inequality applies. Here γ_e is the magnetogyric ratio of the electron. Since data are available for both the high- and low-temperature (freely interconverting and "frozen") limits, in principle the kinetics of the interconversion can be elucidated *via* the line width effects observed in spectra obtained at intermediate temperatures.[29] This requires, however, sufficient resolution to permit distinguishing the contribution of isotropic modulation to the line widths from effects of overlap and other broadening processes. Inspection of spectra in Figure 2 shows that this condition is not fulfilled. Another limit may be placed on the interconversion rate. When two discrete methyl coupling constants are observed, the width of the hyperfine lines, ΔH, is related to the lifetime by[30]

$$\tau > (|\gamma_e|\Delta H)^{-1} \tag{4}$$

Equations 3 and 4 can be used to obtain crude estimates of the relevant kinetic parameters.

The data for BDME$^+$ in conjunction with eq 3 give $\tau_{25°} < 3.8 \times 10^{-8}$ sec for the high-temperature limiting spectrum. If we assume that the residual line width of the $-115°$ spectrum (C' in eq 2, 0.072 G) arises from this motional process, then $\tau_{-115°} > 7.9 \times 10^{-7}$ sec. Conversion to rate constants and absolute temperature gives $k_{298°} > 2.6 \times 10^7$ and $k_{158°} < 1.3 \times 10^6$ sec^{-1}. These values yield a *minimum* estimate of the activation energy for the first-order process of ~2 kcal mol^{-1}. The activation energy is undoubtedly larger than this value since it seems certain that factors other than motional broadening also contribute to C'; however, the available data do not permit estimation of an upper bound.

The most unusual aspect of the data reported here is the difference between BDME$^+$ and DBDME$^+$. Thus, for the deuterated radical we obtain $\tau_{25°} > 3 \times 10^{-7}$ from eq 3. Equation 4 and the line width 0.08 G yield $\tau_{25°} > 7 \times 10^{-7}$ sec. The interconversion rate is diminished by more than tenfold by deuteration, a decrease too large to be explained by the increase in the moment of inertia, I, for rotation about the ethylenic carbon–nitrogen bond. Assuming equal bond lengths for C–H and C–D, we calculate $I_D/I_H = 1.32$, a value larger than the most simplistic estimate, $^{18}/_{15}$, but not large enough

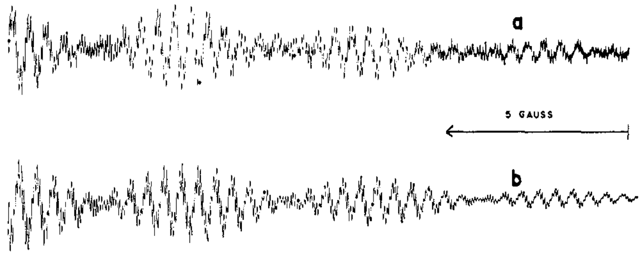


Figure 6. (a) Low-field half of the esr spectrum of deuterated TDE$^+$. Radicals were prepared by spontaneous reaction of the dibromide salt of DTDE^{2+} in ethanol and the spectrum was recorded at 25°. (b) Computed spectrum using the parameters given in Table IV and a Lorentzian line shape.

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(30) P. W. Anderson, *J. Phys. Soc. Jap.*, 9, 316 (1954).

to account for the difference in the rates of rotation. Thus, deuterium substitution apparently causes an increase in the ethylenic carbon–nitrogen bond order, an effect for which we find no precedent in the previous literature.

The ratio a_H/a_D is usually close to that predicted from the ratio of the magnetic moments, $\gamma_H/\gamma_D = 6.514$. Comparing TDE$^+$ and DTDE$^+$ we find ratios of 6.69 and 6.70 for the two kinds of methyl groups. For the BDME$^+$-DBDME$^+$ system we obtain 6.62 and 6.71 using the proton coupling constants from the $-115°$ spectrum and similar values from the other low-temperature spectra. Some uncertainty exists since the latter ratios must be computed from data obtained at two different temperatures. The alternative assignment of the low-temperature BDME$^+$ spectrum ($a_N \simeq 7$ G) results in a_H/a_D ratios of 6.7 and 7.5, values which seem less acceptable in view of the TDE$^+$ results.

Spin Densities and Molecular Orbital Calculations. In contrast to TDE$^+$, the disubstituted cations permit an immediate estimate of the spin density distribution *via* the vinylene proton coupling constant. Taking $Q_{CH}{}^H = -27$ G,[31] $\rho_C{}^\pi \simeq 0.16$ and conservation of spin density then requires $\rho_N{}^\pi \simeq 0.34$. We assume that the ethylenic carbons and amine nitrogens are approximately coplanar and form the basic π-electron system in these radicals. The origin of the alkyl proton couplings is assumed to be hyperconjugation.

Previous investigations[32,33] have indicated that the nitrogen coupling constant in this type of radical should be given by

$$a_N = Q_N{}^N\rho_N{}^\pi + Q_{CN}{}^N\rho_C{}^\pi \qquad (5)$$

The value of $Q_{CN}{}^N$ is small and of uncertain sign,[33] so the value of a_N depends primarily on the spin density on nitrogen. At the same time, for spin transmission to the alkyl protons *via* hyperconjugation, a relation of the form[34]

$$a_H = (B_0 + B\langle\cos^2\theta\rangle)\rho_N{}^\pi \qquad (6)$$

is expected, where θ is the projected angle between the p_z orbital on nitrogen and the psuedo-π orbital on the alkyl group and $B_0 \ll B$. Therefore, we expect an approximately constant ratio of the methyl proton to nitrogen coupling constant, R. For a number of radicals investigated previously, the value of R is close to unity.[35] Values of 0.96 and 1.07 were found for tetramethyl-2-tetrazine,[6] and more recently coupling constants have been reported[36] for two methylated 1,4-dihydro-*s*-tetrazine cations which give R values of 1.00 and 1.05. The value of R for BDME$^+$ at 25° is in accord with these results. The smaller value of R for BDEE$^+$ is anticipated since conformations which minimize nonbonded interactions of the methyl groups result in small values of $\langle\cos^2\theta\rangle$ for the methylene protons. This behavior is well known in nitroalkane anion radicals and has been reviewed recently by Geske.[37]

The spin density distributions in BDME$^+$ and BDEE$^+$ appear to be independent of temperature since little variation of the vinylene proton coupling constant is observed, and in BDEE$^+$ the nitrogen coupling constant is also temperature independent. The temperature variation of the methylene proton coupling constant in BDEE$^+$ is entirely consistent with this picture. At higher temperatures, larger torsional motions of the alkyl groups about their equilibrium conformation increase[34b] the value of $\langle\cos^2\theta\rangle$ in eq 6.

We suggest that the temperature dependence of the coupling constants in BDME$^+$ may also be explicable in terms of steric effects which alter the coefficients of *both* eq 5 and 6. If, at low temperature, the amine group is distorted slightly toward a pyramidal conformation, the s character of the orbital containing the unpaired spin on nitrogen will increase and enhance the value of a_N. At the same time, the decrease in π symmetry of this orbital will decrease its ability to participate in hyperconjugation and diminish the average methyl proton splitting. For steric reasons, this type of distortion might be expected to be more important in TDE$^+$ in accord with the anomalously small R values found for that radical.

We have carried out HMO calculations incorporating the approximate configuration interaction method suggested by McLachlan[38] and give the results which agree reasonably with the spin density estimates given above for BDME$^+$ in Table V. For comparison, results of calculations using the same parameters for TDE$^+$ are presented. Since we are fitting a single datum, it is not surprising that several combinations of parameters give essentially equivalent results. As suggested by the steric arguments of the preceding paragraph, the calculated nitrogen spin densities imply a larger value for $Q_N{}^N$ in TDE$^+$ than in BDME$^+$. The calculated π bond orders suggest the possibility of rotation about the ethylenic C–C bond; however, we found no experimental evidence that such a rotation occurs. Thus, while we believe that the molecular precursor of BDME$^+$ is *trans* and have presumed that the radicals studied here are also *trans*, we have no direct experimental substantiation of this presumption. Furthermore, there is no firm basis for assignment of the coupling constants to the *exo* or *endo* alkyl groups in BDME$^+$ and BDEE$^+$.

Table V. Molecular Orbital Calculations

	MO parameters[a]		Spin densities		π Bond order[b]	
Radical	δ_N	γ_{CN}	$\rho_C{}^\pi$	$\rho_N{}^\pi$	C–N	C–C
BDME^{+c}	0.60	1.00	0.159	0.341	0.636	0.611
TDE$^+$			0.240	0.130	0.423	0.531
BDME^{+d}	0.66	1.00	0.160	0.300	0.604	0.631
TDE$^+$			0.232	0.117	0.468	0.542
BDME^{+d}	0.80	0.80	0.161	0.299	0.550	0.687
TDE$^+$			0.240	0.115	0.437	0.601

[a] Usual definitions, $\alpha_X = \alpha_C + \delta_X\beta_{CC}$ and $\beta_{XY} = \gamma_{XY}\beta_{CC}$. [b] These are, respectively, the π bond orders of the ethylenic carbon–amine nitrogen bond and the bond connecting the ethylenic carbons. [c] Simplest case in which only the ethylenic carbons and amine nitrogens were included in the π system. [d] Methyl groups included in the calculations using the parameters suggested by Coulson and Crawford, *J. Chem. Soc.*, 2052 (1953).

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(32) M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961).

(33) P. T. Cottrell and P. H. Rieger, *Mol. Phys.*, **12**, 149 (1967), and references cited therein.

(34) (a) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960); (b) E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962); **38**, 1254 (1963).

(35) See Table I of ref 7 and data in ref 14.

(36) W. M. Tolles, W. R. McBride, and W. E. Thun, *J. Amer. Chem. Soc.*, **91**, 2443 (1969).

(37) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 179 (1967).

(38) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

We suggest, following previous workers,[7] that the groups with the smaller R values are likely to be those subjected to larger nonbonded interactions, and thus the smaller alkyl proton coupling constants should be associated with the *endo* groups.

The suggestion[39] that deuterium does not hyperconjugate so effectively as protium could account for the observation that in both BDME$^+$ and TDE$^+$ the a_H/a_D ratio is *greater* than 6.514. However, diminishing the value of the resonance integral between the methyl carbon and the H_3 pseudoatom in the HMO calculations predicts a small *decrease* in the ethylenic carbon–nitrogen bond order.

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Electrochemical and Electron Paramagnetic Resonance Studies of Metalloporphyrins and Their Electrochemical Oxidation Products

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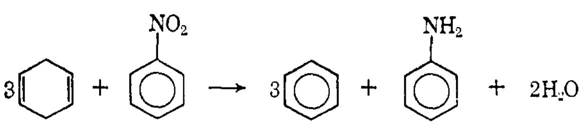
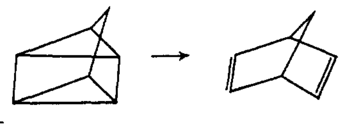
Abstract: The oxidation potentials of transition metal complexes of tetraphenylporphyrins (TPP) and phthalocyanine with bivalent Fe, Co, Ni, Cu, and Zn atoms were determined by cyclic voltammetry. The metallo TPP complexes and the products obtained by their controlled-potential electrochemical oxidation were studied by epr, magnetic susceptibility measurements, and optical spectroscopy. In the case of Fe, Co, and Ni, the first oxidation occurred at the central metal atom, whereas in the case of Cu and Zn, ligand oxidation was observed. Subsequent oxidations occurred at the ligand in all cases. The potentials of central metal oxidation showed a linear dependence on the third ionization potential of the ions. The ligand oxidation potentials were approximately independent of the metal ion for Fe, Co, and Ni, but dropped to a lower value for Cu and Zn, which was rationalized on theoretical grounds. A more or less stable Ni(III) square-planar complex was observed for the first time. ^{59}Co hf splitting of 5.7 G was observed in the epr spectrum of $[\mathrm{Co(III)TPP}]^{\cdot 2+}$ where the unpaired electron is of π-ligand character. The decrease in the ^{14}N hyperfine lines after the two-electron oxidation of [Cu(II)TPP] gave quantitative information about Cu–N overlap change with oxidation. Although Fe(III)TPP acetate has five unpaired spins, its oxidation product $[\mathrm{Fe(III)TPP}]^{\cdot 2+}$ has only two, one on the ligand and one on the central metal atom. For this kind of triplet species, which was also produced after the first oxidation of [Cu(II)TPP], no epr signal could be observed, but magnetic susceptibility measurements gave unequivocal evidence of their existence. The method of plotting oxidation potentials as a function of the third ionization potential of the metal ions appears to be of general importance and has been applied also to other complexes whose oxidation potentials had been reported in the literature.

Porphyrins and their metallo derivatives are significant in biological systems. Their properties and enzymatic activities have been studied extensively.[2] Recently Manassen and coworkers[3] demonstrated their catalytic activities in some pure chemical reactions, as oxidative dehydrogenation



(I)

and symmetry-forbidden rearrangements



(II)

Reaction I showed a decrease in conversion going from iron *via* cobalt to the nickel complex and then a slight increase going from nickel *via* copper to the zinc compound. In the rearrangement reaction, they found a high activity for the first three compounds and no reaction at all for the last two. In order to understand this behavior we have undertaken the current study of physical properties of some of the complexes by combining electrochemical with magnetic and optical spectroscopy measurements.

We have focused our attention on the complexes of tetraphenylporphyrins with first-row transition metal ions from iron to zinc, [M(II)TPP], and to a lesser degree to the corresponding phthalocyanine complexes, [M(II)Pc]. There are reports in the literature of electrochemical,[4] epr,[5,6] optical,[7-10] and combined electro-

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[1] On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, until Sept 1969.

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[6] P. T. Manoharan and M. T. Rogers in "Electron Spin Resonance