if the CH_3 and $Si(CH)_3$ substituents are deleted from the correlation: $\rho_1 = -9.147$; $\rho_R = -4.958$; $\lambda = 0.542$; $f = 0.101$. (b) Deletion of the CH_3 and $Si(CH_3)_3$ substituents from the 5α correlation leads to an improved correlation; $\rho_1 = -5.012$; $\rho_R = 0.021$; $\lambda = -0.004$; $f = 0.187$.
(58) Field effects from similar orientations in other model systems, 6-fluoro- and 7-fluoro-2-tetralone, have been shown to be the same (see ref 6c).
(59) G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **93**, 6984 (1971).
(60) Recent studies have clearly indicated the overwhelming importance of mesomeric phenomena as compared with field effects on carbon chemical shifts. See E. M. Schulman, K. A. Christensen, D. M. Grant, and C. Walling, *J. Org. Chem.*, **39**, 2686 (1974), and references therein.
(61) See footnote *g* to Table XII.
(62) S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc. B*, 1063 (1968).
(63) (a) P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **90**, 1767 (1968); (b) N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. V. Sinnott, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 2255 (1972).
(64) W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *Can. J. Chem.*, **51**, 1857 (1973).
(65) Electrophilic aromatic substitution studies have indicated that the dimethylsulfonium substituent is predominantly meta directing (90.4% meta). This observation is in line with a *net* electron-withdrawing mesomeric component (see H. M. Gislow and G. L. Walker, *J. Org. Chem.*, **32**, 2580 (1967)).
(66) (a) N. C. Cutress, T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 263 (1974), and references therein. (b) Recent studies suggest that this may be the result of polarization rather than p → d orbital conjugation: A. Streitwieser and S. P. Ewing, *J. Am. Chem. Soc.*, **97**, 190 (1975); A. Streitwieser and J. E. Williams, *ibid.*, **97**, 191 (1975).
(67) R. W. Taft, J. W. Rakshys, E. Price, G. Illuminati, A. Monaci, and S. Fatutta, *Gazz. Chim. Ital.*, **103**, 1019 (1973), and references therein.
(68) (a) C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Organomet. Chem.*, **55**, 97 (1973). The para (C_4) SCS for $Sn(CH_3)_3$ in $C_6H_5Sn(CH_3)_3$ is -0.1 ppm (*negative* sign implies upfield from internal benzene) and the shift separation of the meta and para carbons is zero. (b) D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching, and M. Bullpitt, *Aust. J. Chem.*, **27**, 417 (1974). Unfortunately, the ^{13}C chemical shifts for the metalloidal substituted benzenes in this study were not determined with respect to internal benzene as a standard. However, using the (C_4) SCS for $Sn(CH_3)_3$ determined by Schaeffer and Zuckerman and the ^{13}C chemical shift relative to TMS of C_4 in $C_6H_4Sn(CH_3)_3$, a chemical shift of 128.6 ppm (TMS) for benzene can be determined. This leads to the following (C_4) ^{13}C SCS (ppm): $Si(CH_3)_3$, 0.4; $Ge(CH_3)_3$, 0.1; $Sn(CH_3)_3$, -0.1; $Pb(CH_3)_3$, -0.9. It should also be noted that the shift separation of the meta and para carbons is only significant for $Si(CH_3)_3$ and $Pb(CH_3)_3$.
(69) ^{19}F SCS data taken from reference listed as footnote *g* to Table XII.
(70) C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Organomet. Chem.*, **78**, 373 (1974), and references therein.
(71) (a) C. Eaborn and K. C. Pande, *J. Chem. Soc.*, 1566, (1960), and references therein; (b) C. Eaborn, T. A. Emokpae, V. I. Sidorov, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1454 (1974).
(72) P. K. Bischof, M. J. S. Dewar, D. W. Goodman, and T. B. Jones, *J. Organomet. Chem.*, **82**, 89 (1974). An analysis of the photoelectron spectral data for compounds $(CH_3)_3MPh$ and $(CH_3)_3MCH_2Ph$ (M = C, Si, Ge, and Sn) suggests a constant inductive contribution by Si, Ge, and Sn. Further, that p_π–d_π conjugation is important for Si and Ge. However, the conclusions are not unequivocal because many of the spectra were poorly resolved and it is therefore difficult to estimate the various ionization energies accurately.
(73) (a) G. Fraenkel, *J. Chem. Phys.*, **39**, 1614 (1963); (b) G. Fraenkel and J. P. Kim, *J. Am. Chem. Soc.*, **88**, 4203 (1966).

ESR and X-Ray Study of the Structure of Diquat (6,7-Dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium) Cation Radical and Dication

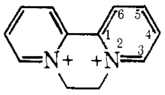
Paul D. Sullivan* and Michael L. Williams

Contribution from the Department of Chemistry, Ohio University, Athens, Ohio 45701.

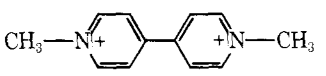
Received July 25, 1975

Abstract: The x-ray structure of diquat (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium dication) has been redetermined. The diheral angle between the rings is found to be ca. 20°. ESR studies on the diquat cation radical have been interpreted in terms of an intermediate rate of ring inversion. From the ESR spectra an upper limit can be estimated for the barrier to inversion. Molecular orbital calculations (HMO and INDO) are consistent with this interpretation and also provide some insight into the herbicidal action of diquat.

Diquat **1** (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium dication) and paraquat **2** (*N*,*N*′-dimethyl-4,4′-dipyridylium dication) are powerful herbicides.[1] Their herbicidal mode of action has been related to the relative ease with which these compounds may be photolytically and reversibly reduced to their cation radical.[2] The structure of the dications and cation radicals is also believed important to the herbicidal activity of these compounds.[3] The structure of the paraquat dication has been investigated by x-ray methods[4] and is found to be planar. The planar structure of the paraquat cation radical has been inferred from ESR studies.[5] The diquat molecule has been less thoroughly studied, a preliminary x-ray study of the dication has appeared[6] and an unresolved ESR spectrum of the cation radical has been reported.[7] It is the purpose of this paper to present an analysis of the ESR spectrum of the diquat cation radical and to rationalize this spectrum in terms of the probable structure of the cation radical. This is done by analogy to the structure of diquat dication which has been redetermined by x-ray methods. INDO calculations on the cation radical have also been used to aid in our analysis.



1



2

Experimental Section

Diquat dibromide was prepared by refluxing 2,2′-bipyridyl in excess 1,2-dibromoethane following previously described methods.[7] A deuterated derivative of diquat was prepared in a similar manner using 2,2′-bipyridyl and excess deuterated 1,2-dibromoethane-d_4 (99.9% from Stohler Chemical Co.). The cation radical of diquat was prepared by chemical reduction with zinc dust in ethanol, acetonitrile, or trifluoroacetic acid (TFA). The best resolved ESR spectra were obtained by zinc reduction in TFA of solutions approximately 2×10^{-4} M in diquat. The samples were submitted to several freeze–pump–thaw cycles before ESR observation. The ESR spectra were recorded on a Varian E-15 spectrometer in a dual cavity, the spectral analyses were carried out using the perylene radical anion as a secondary standard, and the splitting constants were obtained from a least-squares analysis.[8]

A purified crystal of diquat dibromide of approximate dimensions 0.4 × 0.15 × 0.1 mm was used for the x-ray analysis. Survey

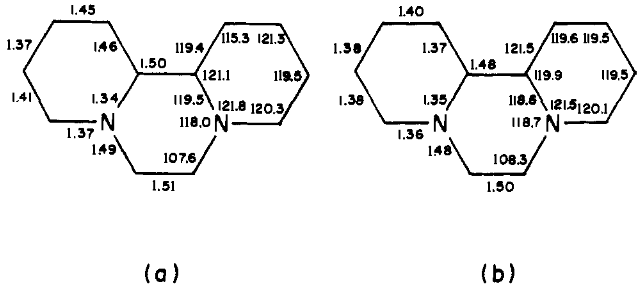


Figure 1. Mean values for the bond lengths and angles as determined by: (a) this work and (b) by Derry and Hamor.[6]

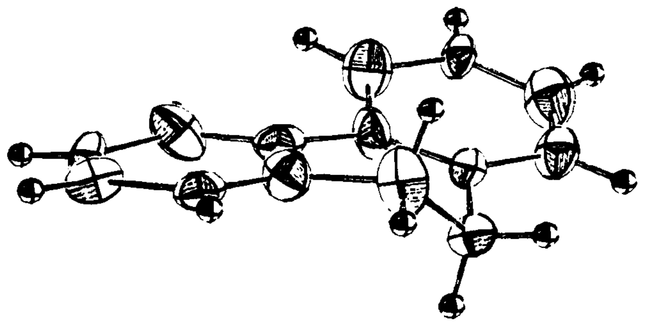


Figure 2. The molecular structure of the diquat dication as determined by x-ray methods. The view is looking down the x axis.

photographs taken with both Weissenberg and precession cameras indicated monoclinic symmetry with space group $P2_1/c$. The accurate unit cell dimensions obtained with a CAD-4 four-circle diffractometer from a least-squares refinement of the angular settings of 25 strong, independent reflections located using Mo Kα radiation are a = 8.402 (5) Å, b = 22.785 (8) Å, c = 7.0394 (5) Å, and β = 91.552 (3)°. An experimental density of 1.69 (1) g/cm^3 agrees with a calculated value of 1.695 g/cm^3 for four molecules per unit cell. Intensity data were collected by the θ–2θ scan method using a variable scan rate ranging from about 0.25 °/min for the weakest reflections to about 10 °/min for the strongest ones. During data collection two standard reflections were recorded every time a set of 24 reflections was collected and those were used to place all the reflections on a common scale. The change in the intensities of the standards was small and random, and the maximum fluctuation about the mean was ±4%. A total of 2986 reflections were scanned of which 555 had intensities with $I \geq 3\sigma(I)$ and have been included in the refinement. While the number is low the crystal chosen for the data collection diffracted most strongly of the single crystals obtained.

The data were corrected for Lorentz and polarization effects but not for absorption or extinction since the absorption coefficient along the cylindrical axis is small (μR = 0.15 cm^{-1}).

The position of the bromine atoms was determined from a three-dimensional Patterson map. Phases derived from the Br atoms were used to locate all other nonhydrogen atoms of the structure. After initial isotropic refinement the anisotropic thermal motion of all atoms was taken into account. At this point the position of the hydrogen atoms was added at idealized positions assuming a C–H bond length of 0.95 Å and the appropriate geometry. The final R factor was 0.067 where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and that of the weighted residual R_w was 0.094, where $R_w = (\Sigma w|F_o| - |F_c|^2/\Sigma wF_o^2)^{1/2}$. In all calculations the scattering factors were taken from the compilation of Hanson et al.[9] in the neutral atom form. A correction for anomalous dispersion (the real term only) was also included in the refinement. The hydrogen atom scattering factors were those given by Stewart et al.[10]

Results

Structure of Diquat Dibromide. The structure which we determined for diquat dibromide agrees closely with the previous study of Derry and Hamor.[6] Figure 1 shows the mean values for the bond lengths and angles as determined by ourselves and by Derry and Hamor. Figure 2 shows the structure of diquat as determined from the x-ray data. There are two important points to note from this structure. First the two aromatic rings are not coplanar; a mean-planes calculation gives the dihedral angle as 20.4° (compared with 19.7° obtained previously[6]). Second, the protons on the ethylene bridge can be seen to exist in pseudoaxial and pseudoequatorial positions.

ESR of Diquat Cation Radical. The ESR spectrum obtained from the diquat cation radical produced by zinc reduction in TFA at room temperature is shown in Figure 3a. A careful study of the wing lines and use of expanded scale recording led us to an initial analysis in terms of five pairs of protons with splittings of 0.36, 0.58, 2.54, 2.90, and 6.98 G and two equivalent nitrogens of 4.08 G. A simulation using these splitting constants was in fair agreement with the experimental spectrum (see Figure 3b) although some lines were not of the correct intensity. This together with the fact that only ten protons were accounted for by this analysis instead of the 12 present in the parent molecule prompted us to study the diquat analogue in which the bridging protons have been replaced by deuteriums. The spectrum obtained from this compound in TFA is shown in Figure 4a. This spectrum was carefully analyzed in terms of four pairs of protons of splitting 0.35, 0.55, 2.53, and 2.90 G plus two nitrogens of 4.07 G and two deuteriums of splitting 1.03 G. A simulation using these parameters (see Figure 4b) was again in fair agreement with the experimental spectrum. It thus appeared that the larger splitting in the diquat cation could be assigned to the methylene protons, their splitting being reduced by a factor of ca. 6.77 (cf. γ_H/γ_D = 6.51) in diquat-d_4. Two explanations for the apparent lack of splitting from two of the methylene protons are readily available. First, the molecule may be fixed in such a conformation that two of the β-methylene protons (presumably those in pseudoequatorial positions) have a dihedral angle relative to the spin in the nitrogen p_z orbital which results in a negligible splitting. The other two methylene protons being at such a dihedral angle as to give a large splitting. Second, one can consider the possibility of a ring inversion process which exchanges the pseudo-axial and equatorial protons. Such a process is known to occur in 9,10-dihydrophenanthrene[11-13] radical anion with an activation energy of approximately 6 kcal/mol. For such a process at intermediate rates of exchange line width alternation will occur leaving only three sharp lines of relative intensities 1:4:1.[14] A simulated spectrum using this intensity ratio for the largest (6.98 G) splitting is shown in Figure 3c. The agreement with the experimental spectrum is somewhat although not conclusively better than for a 1:2:1 ratio (compare Figures 3b and 3c). If the diquat-d_4 is also in the intermediate rate of exchange one predicts a 1:4:9:4:1 pattern of sharp lines as opposed to the normal 1:2:3:2:1 pattern for two equivalent deuterons.[14] The two simulations using these intensity ratios are shown in Figures 4b and 4c. In this case it is more obvious that the 1:4:9:4:1 ratio gives overall better agreement with the experimental spectra.[15]

Assuming an inversion process occurs, a change in temperature may change the rate of exchange sufficiently to affect the shape of the spectrum. In an effort to bring about such changes the spectrum of diquat cation radical in ethanol was studied at temperatures between −40 and +80 °C. At the lower temperatures little or no change in the spectrum was observed. At the higher temperatures small changes in the magnitudes of the splitting constants were observed but no effects which could be attributed to the onset of the rapid exchange limit were noted. Similarly the diquat-d_4 cation radical in ethanol was examined as a func-

Table I. Experimental Splitting Constants and Calculated Spin Densities and Splitting Constants for the Diquat Cation Radical

Position	1,1′	N,N′	3,3′	4,4′	5,5′	6,6′	CH_2 (or CD_2)
Diquat cation[a]		4.078 ± 0.002	0.577 ± 0.003	2.539 ± 0.006	2.898 ± 0.005	0.359 ± 0.004	6.982 ± 0.005
Diquat-d_4 cation[a]		4.068 ± 0.003	0.547 ± 0.013	2.534 ± 0.004	2.898 ± 0.006	0.349 ± 0.005	1.032 ± 0.003
HMO spin densities	0.1586	0.1470	0.0246	0.06598	0.1079	−0.0115	
Calcd splittings (HMO)		3.675[b]	0.66[c]	1.781[c]	2.913[c]	0.310[c]	3.97[d]
INDO calcd splittings		4.387	−2.463	0.451	−2.671	1.067	4.712[e] 0.844[f] 2.778[g]

[a] Experimental values obtained from a least-squares analysis of the data (all values in G). [b] $a_N{}^N = \rho_N Q_N$ where $Q_N = 25$ G. [c] $a_{CH}{}^H = \rho_C Q_{CH}{}^H$ where $|Q_{CH}{}^H| = 27$ G. [d] $a_{\beta-H}{}^H = \rho_N Q_{\beta-H}{}^H$ where $Q_{\beta-H}{}^H = 27$ G. [e] Pseudoaxial protons. [f] Pseudoequatorial protons. [g] Average of axial and equatorial protons.

tion of temperature; however, in this case line broadening at both low (less than −20 °C) and high temperatures (greater than +50 °C) prevented any firm conclusions from being drawn.

The experimental results are therefore consistent with an intermediate rate of inversion, although this cannot be conclusively proven from the experimental results alone. Further justification for this interpretation was therefore sought in molecular orbital calculations.

Molecular Orbital Calculations of Splitting Constants. The HMO approximation was first used for the diquat cation radical; the Coulomb and exchange integral parameters for the nitrogen atom and nitrogen-carbon bonds were those previously suggested for nitrogen-containing cation radicals[16] and the parameters for the methylene protons were those suggested by Iwaizumi.[13] The calculated spin densities were converted to splitting constants using appropriate Q values and the results are shown in Table I. On the basis of this calculation it appears that the two larger ring splittings are at the 4 and 5 positions on the ring and the smaller splittings are at the 3 and 6 positions. The averaged methylene proton splitting can be estimated from the spin density on the nitrogen as 3.97 G which is in good agreement with one-half of the largest experimentally observed splitting 6.98/2 = 3.99 G.

In order to provide more insight into the effects of molecular geometry on the calculated splitting constants a calculation was also performed using the INDO approximation.[17] The atomic coordinates were those generated from the x-ray structure of the diquat dication using symmetry averaged bond lengths and angles. It was felt that these coordinates would be the closest approximation to the actual structure of the cation radical without doing a prohibitively long geometry optimization. The splitting constants calculated in this way are also given in Table I. Unfortunately the HMO and INDO calculations do not agree with respect to the assignments of the ring proton constants. INDO suggests that the larger splittings should be assigned to the 3 and 5 positions as compared to the 4 and 5 positions for the HMO method. One might be able to resolve this difficulty with suitably substituted derivatives; however, the ESR spectrum of the 4,4′-dimethyldiquat cation radical is very complex and has not been analyzed in detail. The INDO method does, however, reproduce fairly well the magnitudes of the nitrogen and ring splittings; it also shows the pseudoaxial and pseudoequatorial splittings of the methylene protons, although their sum (5.56 G) is slightly less than the experimentally observed splitting of 6.98 G.

Barrier to Inversion in Diquat and Its Cation Radical. Assuming that an inversion process is occurring in the diquat cation radical one must be able to rationalize our failure to observe either the slow or rapid exchange limits in the temperature range −40 to +80 °C. In order to know by how much the exchange rate has to change before observable differences occur in the spectra it was necessary to compute spectra at various exchange rates by a density matrix method[18] using a two-jump model. As input for this program one needs the slow exchange splitting constants of the axial and equatorial protons. These are not available experimentally and had to be estimated by comparison with the crystal structure and with related compounds. Thus, the ratio of axial to equatorial splitting constants follows from the angular dependence of the β-proton splitting constants (most simply expressed as $a_\beta{}^H = B \cos^2 \theta$). Therefore, $a_\beta{}^a/a_\beta{}^e = \cos^2 \theta_a/\cos^2 \theta_e$, where $\theta_a = 0°$ and $\theta_e = 120°$, for the true axial and equatorial protons leading to a ratio of 4:1 (this ratio has been observed in several cases[14]). If, however, the β protons are not exactly axial or equatorial the ratio $a_\beta{}^a/a_\beta{}^e$ may change. This is the case for the 9,10-dihydrophenanthrene radical anion[11-13] in which $a_\beta{}^a/a_\beta{}^e$ is experimentally observed to be 9.25. This ratio is explained by a twisting of the two benzene rings by about 11° such that $\theta_a = 11°$, $\theta_e = 109°$. That such a twisting occurs for diquat is known from the crystal structure where the dihedral angle is found to be approximately 20°. Such an angle could lead to an axial-equatorial ratio as large as 29:1. However, the INDO calculation using a dihedral angle of 20° only predicts a ratio of 4.71/0.84 = 5.61. The above considerations lead us to believe that an axial-equatorial splitting constant ratio of 10:1 would not be unreasonable. Axial-equatorial splittings of 6.34 and 0.64 were therefore used as input parameters for the exchange simulation program. By calculating spectra at a series of exchange rates it was found that the rate must change by at least a factor of 100 before observable changes in the spectra would become apparent. That is, the intermediate type of spectrum exhibiting line width alternation would be predominant over an exchange rate range from 5×10^6 to 5×10^8 s^{-1}. Substituting these values into the Arrhenius equation together with the experimentally observed fact that no change in the spectrum is noted between −40 and +80° one calculates that the maximum possible inversion barrier is 7.25 kcal/mol. The actual barrier is undoubtedly less than this value.

Since INDO calculations are known to give reasonable estimates of rotational and inversion barriers[19-21] in both neutral compounds and radical ions, it was decided to estimate the barrier in diquat dication and cation radical. Using as input parameters the crystal structure of diquat dication the difference in total energy between the planar transition state and the nonplanar molecule was calculated to be 6.0 kcal/mol for diquat dication and 3.8 kcal/mol in diquat cation radical. This calculated barrier for the cation radical is in accord with the ESR results whereas the barrier calculated for the dication is perhaps somewhat surprisingly larger than that of the cation radical. No experimental evidence is available regarding the barrier in the dication save for the fact that the rate of exchange is fast on the NMR time scale.[22] Qualitatively the difference in inversion barriers can be understood in terms of the coefficients of the LUMO of the diquat dication and in the sum of the

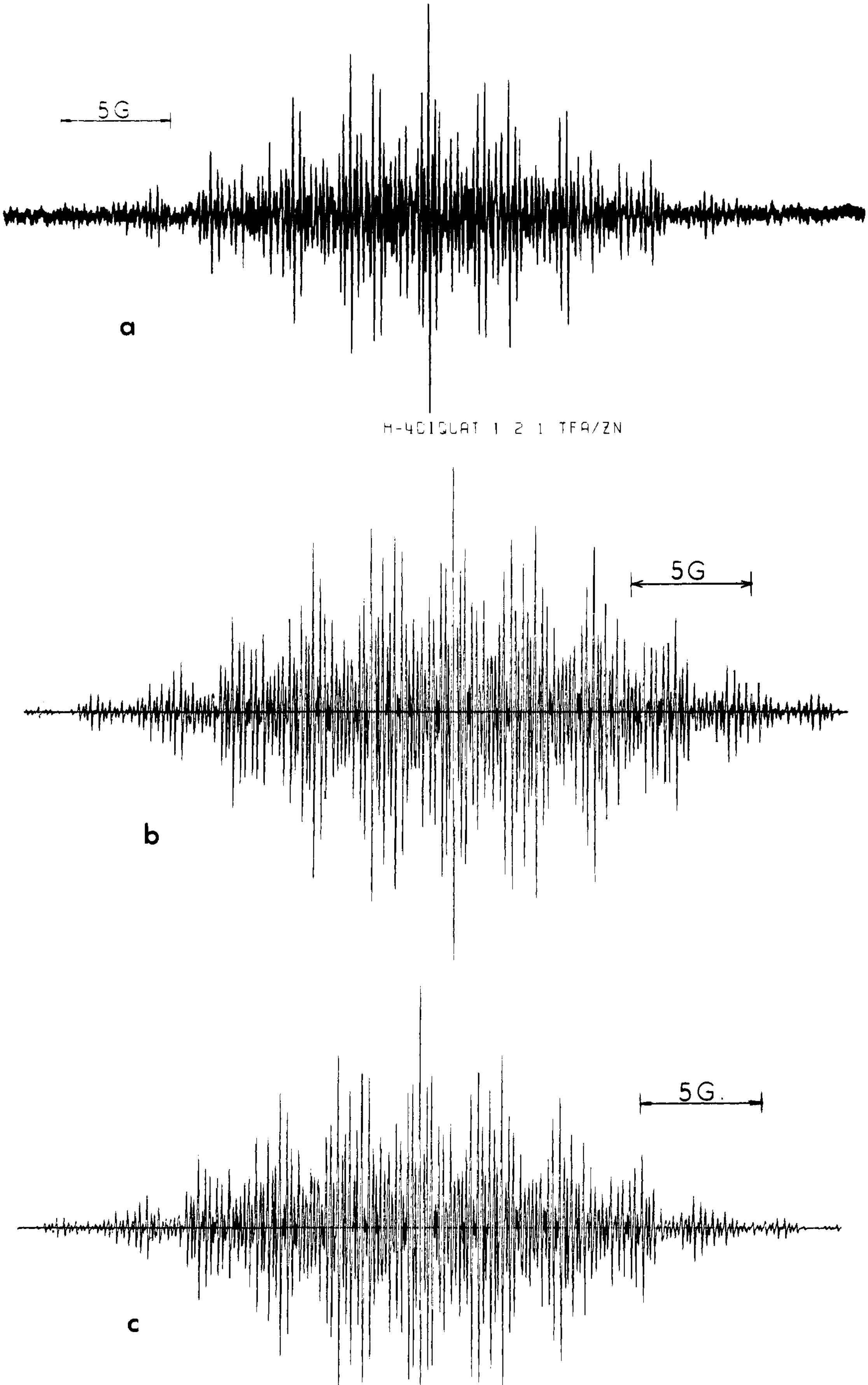


Figure 3. (a) The ESR spectrum of the diquat cation radical in TFA/Zn at room temperature. (b) A simulation of Figure 3a using the parameters in the text with a 1:2:1 intensity ratio for the largest splitting constant. (c) A simulation of Figure 3a using a 1:4:1 intensity ratio for the largest splitting constant.

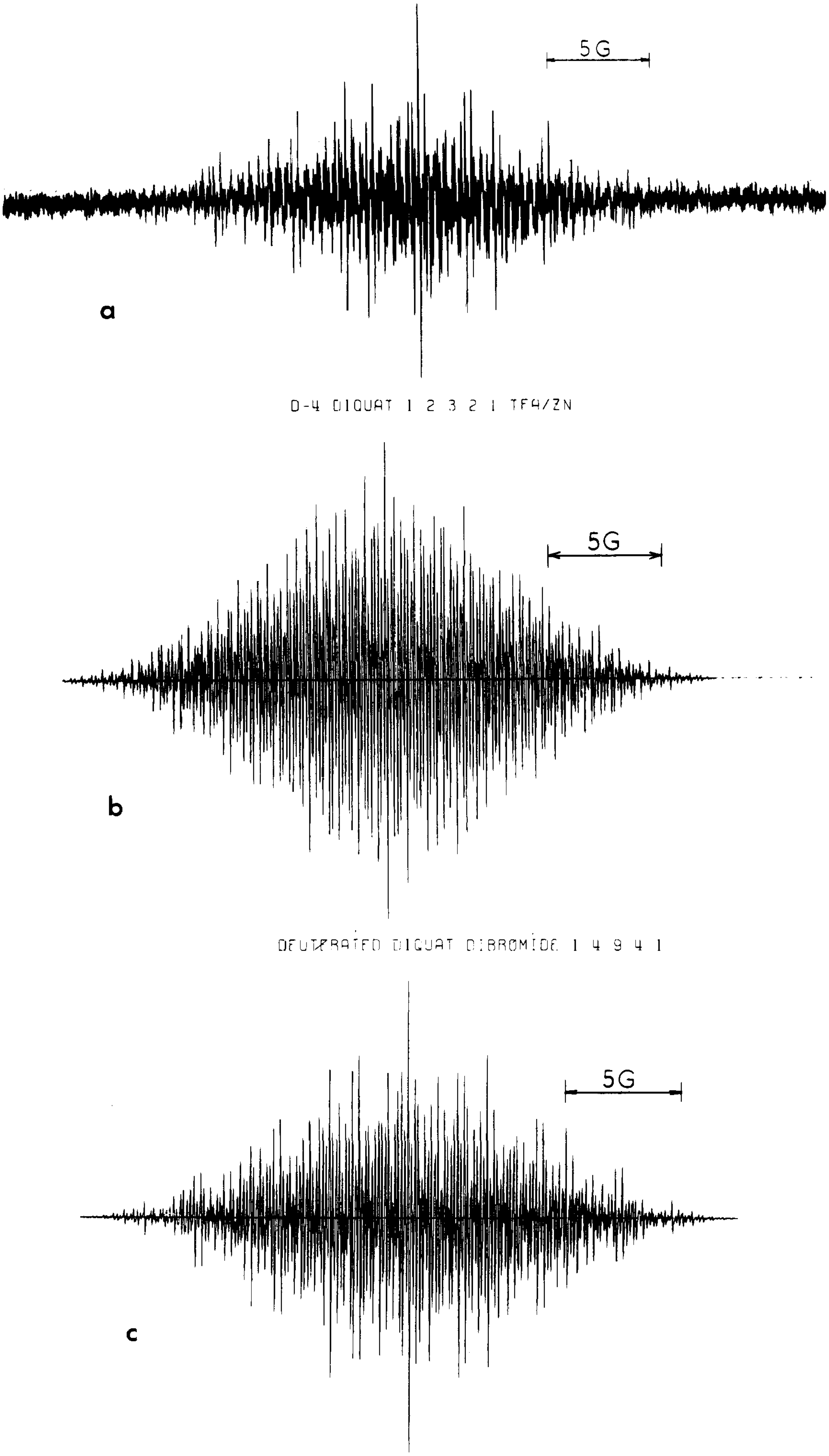


Figure 4. (a) The ESR spectrum of diquat-d_4 cation radical in TFA/Zn at room temperature. (b) A simulation of Figure 4a using the parameters in the text with a 1:2:3:2:1 intensity ratio for the two deuteriums. (c) A simulation of Figure 4b using a 1:4:9:4:1 intensity ratio for the two deuteriums.

bond orders of the C(1,1′)-N and C(1)-C(1′) bonds. The LUMO of the diquat dication is strongly bonding between C(1) and C(1′) and antibonding between C(1,1′)-N. This indicates that the 1,1′ bond in the cation radical may be shortened whereas the C(1,1′)-N bonds may be lengthened. The total bond orders of the N-C(1)-C(1′)-N fragment are, however, 1.490 in the dication and 1.392 in the cation radical which is consistent with a higher barrier in the dication. Interestingly this predicted lower barrier in the cation radical may be significant to the biological activity of diquat. It has been inferred from studies of many compounds that only those compounds which are reversibly reduced to a cation radical and which are essentially planar and of a certain size are good herbicides.[1-3,23] Therefore the observation that the diquat cation radical can more easily pass through the planar configuration than can the dication is probably important to the herbicidal action of diquat.

Conclusion

Molecular orbital calculations are consistent with the interpretation of the ESR spectra of the diquat cation radical in terms of an intermediate rate of ring inversion. Experimentally the barrier to inversion can be no more than 7.25 kcal/mol. The INDO calculated inversion barrier (using the atomic coordinates generated from the crystal structure of the dication) is 3.98 kcal/mol for the cation radical and 6.0 kcal/mol for the dication.

Acknowledgment. We would like to express our appreciation to Professor A. Clearfield and Dr. R. Gopal for their help in the crystal structure determination. Acknowledgment is also made to the Ohio University Research Institute for partial support of this research.

Supplementary Material Available: numbering scheme, atomic fractional coordinates, structure factors and bond lengths and angles for diquat dibromide (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. F. Homer, G. C. Mees, and T. E. Tomlinson, *J. Sci. Food. Agric.*, **11**, 309 (1960).
(2) F. M. Ashton and A. S. Crofts, "Mode of Action of Herbicides", Wiley, New York, N.Y., 1973.
(3) L. A. Summers and J. E. Dickeson, *J. Sci. Food Agric.*, **20**, 74 (1969).
(4) C. K. Prout and P. J. Murray-Rust., *J. Chem. Soc. A*, 1520 (1969).
(5) (a) C. S. Johnson and H. S. Gutowsky, *J. Chem. Phys.*, **39**, 58 (1963); (b) B. I. Shapiro, V. V. Minin, and Y. K. Syrdin., *Zh. Strukt. Khim.*, **14**, 642 (1973).
(6) J. E. Derry and T. A. Hamor, *Nature (London)*, **221**, 464 (1969).
(7) (a) J. E. Dickeson and L. A. Summers., *Experimentia*, **25**, 1247 (1969); (b) *J. Heterocycl. Chem.*, **7**, 719 (1970); (c) *ibid.*, **7**, 401 (1970).
(8) P. D. Sullivan, *J. Phys. Chem.*, **74**, 2563 (1970).
(9) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta. Crystallogr.*, **17**, 1040 (1964).
(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson., *J. Chem. Phys.*, **42**, 3175 (1965).
(11) F. C. Adam., *Can. J. Chem.*, **49**, 3524 (1971).
(12) J. Van Der Kooij, C. Cooijer, N. H. Velthorst, and C. Maclean., *Recl. Trav. Chim., Pays-Bas*, **90**, 732 (1971).
(13) M. Iwaizumi, T. Matsuzaki, and T. Isobe., *Bull. Chem. Soc. Jpn.*, **45**, 1030 (1972).
(14) P. D. Sullivan and J. R. Bolton, *Adv. Magn. Reson.*, **4**, 39 (1970).
(15) It should be emphasized that the compression of these spectra results in only the gross features being apparent. Close examination of expanded recordings of both the experimental and simulated spectra lead us to be fairly confident in the validity of our assignments.
(16) P. D. Sullivan and J. R. Bolton, *J. Magn. Reson.*, **1**, 356 (1969).
(17) J. A. Pople, D. L. Beveridge, and P. A. Dobosh., *J. Am. Chem. Soc.*, **90**, 4201 (1968).
(18) J. Heinzer, *Mol. Phys.*, **22**, 167 (1971).
(19) F. Bernardi, M. Guerra, and G. F. Pedulli, *J. Phys. Chem.*, **78**, 2144 (1974).
(20) L. L. Combs and M. Holloman, *J. Phys. Chem.*, **79**, 512 (1975).
(21) P. D. Sullivan, unpublished information.
(22) R. Haque, W. R. Coshow, and L. F. Johnson, *J. Am. Chem. Soc.*, **91**, 3822 (1969).
(23) W. R. Boon, *Chem Ind. (London)*, 782 (1965).

Molecular Structure of Ion Pairs from Electric Dipole Moments. IV. Ion-Pair Solvation in Acetic Acid[1,2]

Ernest Grunwald,* M. R. Crampton, A. Effio, and Ting-Po I

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received May 13, 1975*

Abstract. Electric dipole moments were measured in acetic acid for ion pairs of LiCl, KCl, KBr, LiTs (Ts = *p*-toluenesulfonate), KTs, CsTs, TlTs, *p*-toluidinium *p*-toluenesulfonate, and tetraisoamylammonium nitrate. Except for the latter, the dipole moments show considerable effects of solvation, deviating from intrinsic dipole moments measured in the gas phase or in inert solvents by amounts ranging from +4.8 D for KTs to −1.8 D for KCl. Measurements were made at 0.001–0.01 F concentrations. Corrections were made for solute-induced medium effects and for the effect of the free ions on the dielectric constant, the latter according to the theory of Onsager and Provencher which allows for dynamic equilibrium between free ions and ion pairs. Structure and dipole moment are considered for various models of solvated ion pairs. It is concluded, from the observed dipole moments and other properties, that the solvated ion pairs are best described as follows: LiCl·HAc, monodentate attachment of *cis*-HAc to cation; KCl·HAc and KBr·HAc, cyclic bidentate complex with *cis*-HAc; KTs·HAc, cyclic bidentate complex of *cis*-HAc with corner structure of KTs or monodentate attachment of *trans*-HAc to the axial structure of KTs. For (i-Am)$_4$NNO$_3$, the dipole moment indicates the absence of discrete solvation complexes with acetic acid.

The behavior of ion pairs in acetic acid is of special interest for practical as well as historical reasons. Considering the fairly low dielectric constant (ϵ_0 = 6.265 at 25 °C), acetic acid is a remarkably good solvent for electrolytes. It is perhaps for this reason that acetic acid has become a classic solvent for demonstrating the properties of ion pairs.[3-8] In particular, the isomerism between intimate and solvent-separated or "loose" ion pairs was first demonstrated by means of kinetic studies carried out in acetic acid.[6]

Our aim in this study is to examine ion-pair structure and solvation by measuring the electric dipole moment. In acetic acid, such measurements are extraordinarily difficult for