as 5.30 ppm) for the zwitterions. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

CH_2Cl_2 was purified by the procedure of Jones and Wood.[37] Freon 22, $CHClF_2$, and SO_2ClF were purified by double distillation on a vacuum line. The Al_2Cl_6 was sublimed *in vacuo*, mixed with aluminum powder, and resublimed.[38]

Preparation of 5-Acylpentamethylcyclopentadienes. To a solution of pentamethylcyclopentadiene (1.36 g) in anhydrous ether (100 ml) was added *n*-BuLi (3 ml of 22% in hexane). The reaction was stirred at room temperature for 30 min. The acid chloride (10 mmol) in anhydrous ether (25 ml) was added slowly, gentle refluxing being maintained. After 3 hr, water (300 ml) was added and the organic layer was separated, washed with aqueous $NaHCO_3$ (3 × 50 ml) and water (2 × 50 ml), and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on neutral alumina (activity 1), eluting with ether (5%) in pentane. The yields and properties of the 5-acylpentamethylcyclopentadienes are given in Table III. Samples for elemental analysis were prepared either by sublimation *in vacuo* (solids) or by vpc (liquids).

Preparation of Zwitterions (a). All manipulations were carried out in a drybox. Al_2Cl_6 (*ca.* 7.0 mg) was weighed out accurately into an nmr tube and dissolved in CH_2Cl_2 (1 ml) at room temperature. The solution was cooled to −78° and the acylpentamethylcyclopentadiene (0.9 of an equivalent amount of the Al_2Cl_6) dissolved in CH_2Cl_2 (0.2 ml) was added. The mixture was stirred to give a clear solution of the complex.

Table III. Properties and Analyses of 5-Acyl-1,2,3,4,5-pentamethylcyclopentadienes[a]

Compound	% yield	Mp, °C	$\nu_{C=O}$, cm^{-1}	Analysis Calcd C, %	Analysis Calcd H, %	Analysis Found C, %	Analysis Found H, %	m/e
3b	65	*b*	1691	81.18	10.50	81.35	10.63	192
3d	68	*b*	1668	84.94	8.40	84.72	8.31	240
3e	66	136	1655	79.95	8.22	80.07	8.20	270
3f	60	*b*	1662	84.97	8.73	84.71	8.53	254
3g	71	97	1660	85.07	9.54	85.41	9.48	296
3h	69	126	1666	74.28	6.98	74.08	6.94	274
3i	58	*b*	1677	70.10	6.22	70.28	5.99	308

[a] Nmr spectra are given in Table I. [b] Liquid.

(**b**) Higher concentrations of the zwitterions could be prepared by using a suspension of Al_2Cl_6 in CH_2Cl_2. The halide went into solution upon reaction with the ketone.

(**c**) Vacuum line procedure. Al_2Cl_6 (*ca.* 25 mg) was weighed out accurately into a 20-ml reaction vessel containing a stirrer bar and with an attached nmr tube. The vessel was attached to a vacuum line and the appropriate solvent, CH_2Cl_2 or $CHClF_2$ (5 ml), was distilled in. The mixture was stirred until solution of the Lewis acid occurred, when it was cooled in liquid N_2 and the ketone (0.9 of an equivalent) was distilled in. The reaction vessel was warmed to −78° and stirred for 10 min. Part of the solution was transferred into the nmr tube at −78° by tilting the vessel, and the tube was sealed under vacuum.

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[37] R. E. Jones and D. E. Wood, *J. Chem. Soc. A*, 1448 (1966).

[38] T. Birchall, McMaster University, personal communication, 1969.

Charge Delocalization in Saturated Systems. The Radical Cation of 1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}]dodecane

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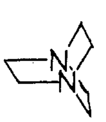
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 9, 1974*

Abstract: The photoelectron spectra of the title compound (**2**) and 1,4-diazabicyclo[2.2.2]octane (**1**) are compared, and the lone pair orbital ordering for **2** is assigned as B > E > A in energy (using S_4 molecular symmetry). The $A_1' > A_2''$ (assuming D_{3h} symmetry) ordering for **1** was previously established by Hoffmann, Heilbronner, and coworkers. The esr spectra of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ are discussed. From the observed nitrogen and hydrogen splitting constants, it is argued that the A_2'' orbital of $\mathbf{1}^{\cdot+}$ and the E orbital of $\mathbf{2}^{\cdot+}$ are singly occupied and thus highest in energy, requiring substantial shifts of relative orbital energies in going from neutral compound to the radical cation.

McKinney and Geske[1] first reported the remarkable stability of the radical cation of 1,4-diazabicyclo[2.2.2]octane (Dabco, **1**), and found that $\mathbf{1}^{\cdot+}$ was stable enough to show a re-reduction wave in a cyclic voltammetry (cv) experiment and also to give an esr spectrum at room temperature in a slow-flow system. That the stability of $\mathbf{1}^{\cdot+}$ is really quite unusual was shown in an electrochemical study[2] in which several analogs of **1** in which the two carbon bridges were replaced by one and three carbon bridges; most of these systems showed irreversible cv oxidation waves. One system which did show a re-reduction cv wave was 1,3,6,8-tetrazatricyclo[4.4.1.1^{3,8}]dodecane (**2**). Although $\mathbf{2}^{\cdot+}$ was somewhat less stable than $\mathbf{1}^{\cdot+}$ under similar conditions, an undeciphered, weak esr signal was detected upon electrolytic oxidation of **2**.[2] In this work, we compare the photoelectron spectra (pes) of **2** and **1** and the electron spin resonance (esr) spectra of their radical cations, and discuss the orbital ordering in these systems, as a means of understanding why the cations of **1** and **2** are so much stabler than those of other saturated amines.



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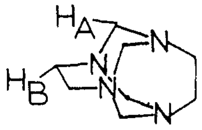

2

Results and Discussion

PES of 1 and 2. The through-bond lone pair–σ_{cc} interaction which raises the energy of the symmetric lone pair orbital of **2** (see A_1') above that of the antisymmetric (A_2'') orbital was predicted by Hoffmann

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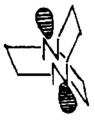
[1] T. M. McKinney and D. H. Geske, *J. Amer. Chem. Soc.*, **87**, 3013 (1965).

[2] S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **94**, 7114 (1972).

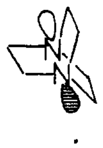
and coworkers,[3] and experimentally verified by Heilbronner and coworkers.[4] The balance of through-space and through-bond interactions in analogs of **1** with different-sized bridges was investigated using pes and extended Hückel calculations by Nelsen and Buschek.[5] The lone pair region of the pes of **2** is compared with that of **1** in Table I.

Table I. Photoelectron Spectra of **1** and **2**

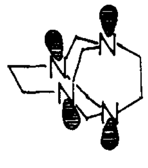
Compound	1^5	2
IP_1 (assignment)	7.60_9 (A_1')	7.389 (B_2)
IP_2 (assignment)	9.68_4 (A_2'')	8.659 (E)
IP_3 (assignment)		9.542 (A_1)



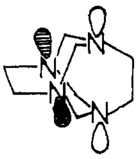
A_1'



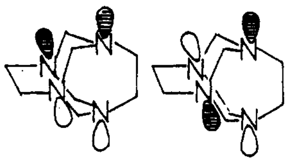
A_2''



A_1



B_2

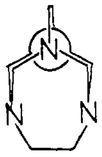


E

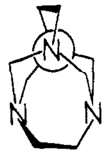
Although **1** is possibly torsionally twisted slightly out of the eclipsed conformation of maximum symmetry (**1**(D_{3h})) to give **1**(D_3),[5] previous workers[3,4] have used

1(D_{3h})

1(D_3)



2(D_{2d})



2(S_4)

calculations on **1**(D_{3h}) quite successfully in interpreting the orbital ordering and pes spectrum of **1**. Similarly, although **2** is quite probably torsionally twisted (see **2**(S_4)), we have used calculations on the eclipsed form, **2**(D_{2d}), and the appropriate labels in the assignments of Table I. An extended Hückel calculation, parameterized as in our previous work,[5] on **2**(D_{2d}) gave the principally lone pair (highest occupied) levels at -10.428_9 (B_2), -10.793_1 (E), and -11.134_7 (A_1) eV. We assign the first ionization observed (IP_1) to the B_2 level, IP_2 to E, and IP_3 to A_1, in agreement with this calculation. This assignment is also supported by the relative areas of the peaks (IP_1:IP_2:IP_3 areas are 1.09:1.72:1.00, consistent with IP_2 corresponding to the doubly degenerate E level), the observed weak vibrational structure in IP_1 and IP_3 (both showed progressions of about 730 cm^{-1}, consistent with B_2 and A_1 assignments), and our previous data showing that the calculations seriously underestimate the 1,3 nitrogen splitting,[5] so that the calculated A_1–B_2 gap should be considerably too small. The orbital labels would be B, E, and A in the S_4 symmetry of torsionally twisted **2**, but the qualitative arguments remain unchanged. The fact that the methylene singlets in the nmr spectrum of **2** remain unsplit, even at −90°, shows that the activation energy for interconversion of the mirror image S_4 forms must be quite low,[6] in spite of the fact that a model suggests otherwise. Force-field calculations on homoadamantane show that the barrier to torsional inversion of this analog of **2**, which contains one less carbon, is below 0.3 kcal/mol.[7]

Esr Spectra of $1\cdot^+$ and $2\cdot^+$. Because of the low stability of $2\cdot^+$, we were previously[2] unable to obtain a strong enough esr signal to attempt analysis. We finally discovered that chemical oxidation of **1** or **2** with tris(*p*-bromophenyl)aminium hexachloroantiminate (**3**)[8] in butyronitrile[9] gives excellent esr spectra of both radical cations. Although the $2\cdot^+$ esr signal fades slowly, even at −100°, we obtained our best spectra under these conditions. The line positions of the esr spectrum of $2\cdot^+$ (Figure 1) are well fit using three multiline splitting constants, in ratios 13:12:7. We assign these splittings as $a(8H_A)$:$a(4N)$:$a(8H_B)$, respectively, which gives the simulation shown in Figure 1 using ideal intensity ratios. At −100°, one would expect to see anisotropic line broadening[10a] because of the four interacting nitrogens, which will alter the observed apparent intensities from the ideal ratios. For the 52 lines on the high-field side of the center line, we obtained reasonable fit (the average deviation for estimated *vs.* observed peak heights, calculated as per cent of the center height, was 3.3%) using 1:0.95:0.75:0.5:0.25 for the peak height ratios as $|\bar{M}_n|$ varied from 0 to 4. These estimations are only approximate (we ignored the difference in peak heights expected for different signs of $\bar{M}_n$; since the spectrum is not exactly symmetrical on the left- and right-hand sides, this will introduce error), and there is far too much overlap for accurate determination of the anisotropic line-broadening parameters, but they show that the deviation of the observed intensities, calculated using ideal intensity ratios, is that expected for a fairly modest anisotropic line-width effect. There is no observable alternating line-width effect[10b] in the spectrum.

The splittings obtained are given in Table II. It may

Table II. Esr Splitting Constants (G) for $1\cdot^+$ and $2\cdot^+$ at −100° in Butyronitrile[a]

Nucleus	$1\cdot^+$	$2\cdot^+$
N	17.02 (2)	7.09 (4)
H	7.27 (12)	7.68 (8 H_A)
H		4.14 (8 H_B)

[a] The numbers in parentheses after the splitting constants give the number of equivalent nuclei.

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(3) (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); (b) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(4) (a) P. A. Bischoff, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969); (b) E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3878 (1970).

(5) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, submitted for publication.

(6) (a) G. Volpp, *Chem. Ber.*, **95**, 1493 (1962); (b) F. G. Riddell and P. Murray-Rust, *Chem. Commun.*, 1075 (1970).

(7) E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2525 (1972).

(8) F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. A*, 2719 (1969).

(9) R. P. Van Duyne and C. R. Reilley, *Anal. Chem.*, **44**, 142 (1972).

(10) (a) G. K. Fraenkel, *J. Phys. Chem.*, 71, 139 (1967); (b) P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970).

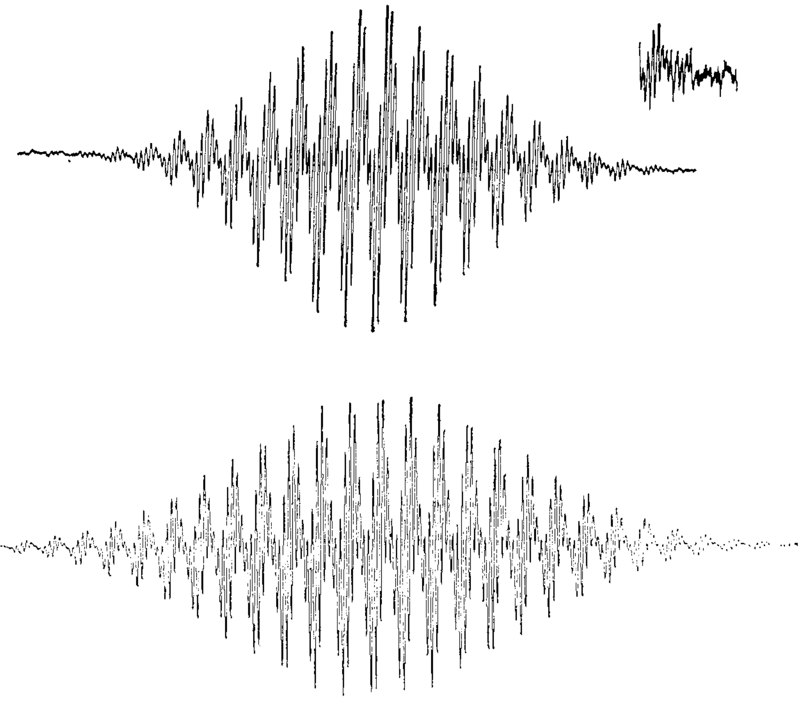

Figure 1. Experimental (above) and simulated esr spectra of $\mathbf{2}\cdot^+$ at −100° in butyronitrile. The simulation was carried out using the splittings of Table II and a 300-mG line width. See the text for discussion of the differences in intensity.

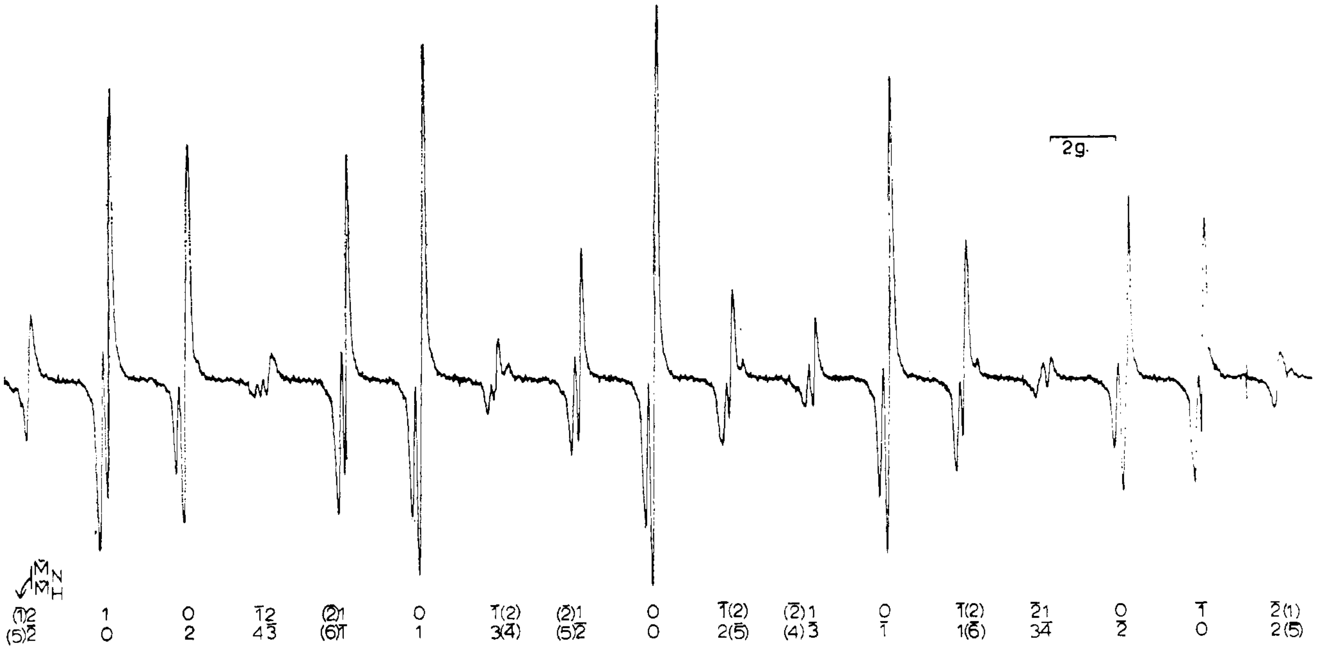

Figure 2. The central portion of the esr spectrum of $\mathbf{1}\cdot^+$ at −80° in butyronitrile. The $\tilde{M}_N$ and $\tilde{M}_H$ values of the lines are shown below (the lines in parentheses are very weak). Second-order splittings are partially resolved.

be seen that there is no splitting large enough to correspond to the nitrogen splitting if the positive charge were localized on two nitrogens (using $\mathbf{1}\cdot^+$ as a model), which is consistent with our assignment of a splitting for four equivalent nitrogens. We also determined the spectrum of $\mathbf{1}\cdot^+$ under conditions which allow direct comparison of the splittings.

Our splitting constants for $\mathbf{1}\cdot^+$ agree well with those of McKinney and Geske[1] in acetonitrile at room temperature (16.96 (2 N), 7.34 (12 H)). The line widths were substantially smaller, about 100 mG for the narrowest lines, allowing detection of second-order splittings[11] (see Figure 2). We believe that this is the first example of resolution of second-order splittings for nitrogen. Although there was a decrease in concentration during the 8-min scan shown in Figure 2, a fairly weak anisotropic broadening seems to be present, causing the Mn = −2 lines to be noticeably broader than the Mn = 2 lines. As McKinney and Geske pointed out, the symmetry observed in the esr spectrum (12 equivalent H, 2 equivalent N) only requires that electron transfer between the 2 nitrogens be relatively

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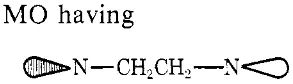
[11] R. W. Fessenden, *J. Chem. Phys.*, 37, 747 (1962).

rapid. In view of the current theoretical interpretation of n–σ_{cc} interaction,[3] it seems much more likely to us that both nitrogens of **1** are equivalent on an instantaneous basis, and that **1**$\cdot^+$ is either in a D_3 or a D_{3h} conformation. The observation of a splitting for 12 equivalent hydrogens requires that **1**$\cdot^+$ is either in the D_{3h} conformation or has a low activation energy for interconversion of D_3 conformations.

We suggest that all four nitrogens of **2**$\cdot^+$ are instantaneously equivalent because of 1,4 (principally through bond) and 1,3 (principally through space) lone pair interactions. The low IP_1 and electrolytic oxidation potential[2] for **2** would not be expected unless the charge were delocalized over all four nitrogens in the radical cation. We therefore propose that **2**$\cdot^+$ is an extensively delocalized cation which lacks the π bonds usually present in radical ions which are extensively delocalized (the delocalized polysilane anions of West and coworkers[12] represent an electronically very different case of delocalization in saturated systems).

The splitting constants of **2**$\cdot^+$ make an interesting comparison with those of **1**$\cdot^+$. The nitrogen splitting of **2**$\cdot^+$ is only 42% as large as that of **1**$\cdot^+$. We suggest that the reason for this ratio being lower than 0.5 is that **2**$\cdot^+$ is flatter at nitrogen than **1**$\cdot^+$ because of its seven-membered rings. An amine cation radical nitrogen splitting is predicted to increase several fold if the geometry at nitrogen is changed from planar to tetrahedral.[13] Taking into account the ρ_N differences, and comparing with the probably nearly planar trimethylamine cation radical (**4**$\cdot^+$), which has $a(N) = 18.0$ G[14] in a solid matrix, the ratio $2a(N, \mathbf{1}\cdot^+)/a(N, \mathbf{4}\cdot^+)$ is 1.89, compared to $4a(N, \mathbf{2}\cdot^+)/a(N, \mathbf{4}\cdot^+)$ of 1.58. This indicates greater flattening at the nitrogens of **2**$\cdot^+$ than of **1**$\cdot^+$. The observation of only two types of hydrogen splittings for **2**$\cdot^+$ requires that it is either in the eclipsed conformation (D_{2d}) or that the mirror image S_4 conformations are interconverting rapidly on the esr time scale at $-100°$.

The question of the symmetry of the MO containing the odd electron in the radical cations is a challenging one. Although the pes assignment is clear in both cases, making the highest occupied MO of **1** A_1', and that of **2** B_2, it is not necessarily true that these orbitals will be the ones containing the odd electron in the corresponding radical cations. Since removal of an electron from the highest occupied orbital of **1** is calculated[4b] not to cause appreciable flattening at nitrogen, one would expect a(N) for a **1**$\cdot^+$ cation which had a single occupied A_1' orbital to be that for a species having tetrahedral nitrogens, perhaps as high as 70 G.[13] The observed a(N) for **1**$\cdot^+$ is much more consistent with a single occupied A_2'' orbital, since this would lead to appreciable flattening at nitrogen.[4b] The flattening at the bridgehead nitrogens of **1**$\cdot^+$ deduced from the low value of a(N) observed is reminiscent of the calculated flattening at the carbons of 1,4-bicyclo[2.2.2]octyl dication.[15] We suggest the size of the methylene bridge hydrogen splitting for **2**$\cdot^+$, $a(H_A)$, is only consistent with the assignment of E symmetry to the singly occupied orbital in this molecule. Since the spin-bearing lone pair orbital bisects the HCH angles for both H_A and H_B of **2**$\cdot^+$, the angle dependent term in the hydrogen splitting formula must be about the same for both H_A and H_B. We shall use the observed value of $a(H_B)$ to predict $a(H_A)$ for the three possible symmetries of the lone pair MO. This ignores any contribution to $a(H_B)$ from spin at the nitrogen separated from it by a methylene group. Although this is not strictly valid, in the structurally related case of 1-bicyclo[2.2.2]octyl radical, the ratio of the adjacent to nonadjacent methylene splittings was 7.4,[16] so the error expected is not overwhelming. As Whiffen has pointed out,[17] for a methylene group simultaneously interacting with two spin-bearing orbitals (such as the H_A methylene), one must add the coefficients at the interacting centers before squaring them to give the proper spin density to use in a McConnell-type $a(H) = Q\rho$ relation. Therefore, if the a(H) splitting due to one adjacent nitrogen is A (A is about 4 G from the observed $a(H_B)$ splitting), and the odd electron is in the B_2 orbital, the coefficients would cancel, leading to a very small H_A splitting. If the odd electron MO had A_1 symmetry, the predicted $a(H_A)$ splitting would be 4A, or about 16 G. Neither is consistent with the observed H_A splitting. If the odd electron MO were of E symmetry, however, $a(H_A)$ would be about 2A, or 8 G, which is close to the observed value of 7.09 G. Thus, the esr splittings for both **1**$\cdot^+$ and **2**$\cdot^+$ are consistent with an inversion of highest and next highest occupied energy levels between neutral material and radical cation. In both **1**$\cdot^+$ and **2**$\cdot^+$, the cation prefers to have the odd electron in an MO having

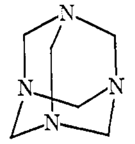


local symmetry, which leads to a flattening at nitrogen.

Rosenblatt and coworkers[18] established that **1**$\cdot^+$ is colored. Only a fairly faint brown color was observed when **1**$\cdot^+$ was formed at the approximately 5×10^{-3} *M* concentrations used in this work, but the tubes containing **2**$\cdot^+$ were intensely purple. Although we cannot prove conclusively that the color is associated with **2**$\cdot^+$, the fact that we saw esr signals when and only when the colors were present convinces us that both radicals are colored.

We are not aware of a good method for calculation of what would be expected for these systems, but as has been pointed out to us,[19] the $(A_1)^2(B_2)^2(E)^3 \rightarrow (A_1)^2(B_2)^1(E)^4$ electronic transition for **2**$\cdot^+$ (as well as the corresponding transition for **1**$\cdot^+$) is allowed, and a possible candidate.

We believe the difference in behavior observed upon oxidation of **2** and tetraazaadamantane (**5**) is quite



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[12] R. West and A. Indricksons, *J. Amer. Chem. Soc.*, **94**, 6110 (1972), and references therein.

[13] (a) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961); (b) J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

[14] A. D. Tench, *J. Chem. Phys.*, **38**, 593 (1963).

[15] G. A. Olah, G. Liang, P. v. R. Schleyer, E. M. Engler, M. J. S. Dewar, and R. C. Bingham, *J. Amer. Chem. Soc.*, **95**, 6829 (1973).

[16] P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 995 (1972).

[17] D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).

[18] (a) L. A. Hull, D. H. Rosenblatt, W. P. Giordano, G. T. Davis, C. K. Mann, and S. B. Milliken, *J. Phys. Chem.*, **73**, 2147 (1969); (b) G. T. Davis, M. M. Demek, and D. H. Rosenblatt, *J. Amer. Chem Soc.*, **94**, 3321 (1972).

[19] We thank Professor Hoffmann for this suggestion.

striking. Although both compounds have a set of four nitrogens held with their lone pairs directed outward, $5^{\cdot+}$ shows no more stability than an ordinary tertiary amine cation, having completely irreversible cv spectrum,[2] an unusually positive $E_{1/2}$ value,[2] and a first ionization potential,[5,20] which is higher than that of adamatane itself.[20] It is clear that the number of nitrogens over which the positive charge can be spread is not as important in observing the unique stability of $1^{\cdot+}$ and $2^{\cdot+}$ as is the necessity for conjugating these nitrogens with C–C single bonds in favorable geometry for $n-\sigma_{\mathrm{CC}}$ interaction. Apparently the C–N bonds of **5**, which are in the best possible geometry for $n-\sigma_{\mathrm{CN}}$ interaction, simply are too low lying to interact effectively with the nitrogen lone pair electrons.[2,5]

Experimental Section

The preparation and purification of the materials has already been described,[2] as have the pes[5] and esr[20] experimental and data handling techniques employed.

Esr Spectrum of $2^{\cdot+}$. A 5×10^{-3} M solution of **2** in butyronitrile was cooled in an ethanol slush (*ca.* $-100°$), with argon continuously bubbling through it. One equivalent of solid **3** was added, and the solution was agitated to hasten reaction. The solution rapidly developed a dark purple color. The mixture was transfered to a cooled 3-mm o.d. glass tube by forcing it through a steel capillary tube with pressure from the argon bubbler. After sealing, esr spectra were run at low temperature in the usual way. The purple color and the esr spectrum of $2^{\cdot+}$ fade very rapidly above $-80°$.

Acknowledgment. We thank the National Science Foundation for support of this work.

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[20] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

[20] S. F. Nelsen, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, *J. Amer. Chem. Soc.*, **96**, 2916 (1974).

Vinylic Cations from Solvolysis. XXII.[1] High Stereoselectivity in the Synthesis of and Ion Pair Return in the Solvolysis of (E)-α-Bromo-β-deuterio-p-methoxystyrene

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Abstract: Addition of HBr to α-anisyl-β-deuterioacetylene (**7-D**) in several solvents of low dielectric constants gives a mixture of (E)- and (Z)-α-bromo-β-deuterio-p-methoxystyrenes (**4-E** and **4-Z**) with little or no preference for the E isomer. More **4-E** is formed in chloroform in the presence of Et_4NBr, and the highest selectivity (80% **4-E**: 20% **4-Z**) is obtained in the presence of $HgBr_2$. The selectivity is ascribed to a syn addition of molecular or ion-paired HBr to **7-D**, while the nonselective addition takes place *via* the free vinyl cation **5-D**. Solvolysis of a mixture of **4-E** and **4-Z** in 50% EtOH gives mainly α-deuterio-p-methoxyacetophenone (**10-D**) and shows no **4-E** $\rightleftharpoons$ **4-Z** isomerization. In AcOH, p-methoxyacetophenone (**10-H**) is formed exclusively, Et_4NBr enhances the solvolysis rate, a **4-E** $\rightleftharpoons$ **4-Z** isomerization takes place during the solvolysis, the isotope effect k(**4-H**) k(60% **4-E** + 40% **4-Z**) is 1.21, and exchange of the vinylic deuterium with the solvent was not observed. It is suggested that the solvolysis proceeds *via* an ion pair which only gives products in 50% EtOH, while in AcOH 63% of the ion pairs give ion pair return to **4-E** and **4-Z** and 37% give **10-H**. The ion pair return in α-anisylvinyl bromides decreases on decreasing the bulk of the β substituents in aqueous EtOH, but the return in AcOH is insensitive to this factor. This is discussed in terms of capture and dissociation of the ion pairs.

The intermediacy of ion pairs in the SN1 solvolysis of vinylic substrates was suggested in several cases,[2,3] but quantitative information regarding the extent of ion pair return is scarce.[3] This is mainly due to the absence of an easy method for evaluating such return, which will be analogous to the loss of optical activity for evaluating ion pair return in the solvolysis of saturated substrates.[4] We recently suggested[1,5] that a cis–trans isomerization of the unreacted vinyl halide can serve as such a tool for detecting ion pair return in vinylic solvolysis, depending on three prerequisites. (a) It should be shown that the isomerization is not due to a non-SN1 reaction, such as electrophilic addition–elimination (Ad_E–E).[6] (b) For SN1 reactions account should be taken of possible isomerization *via* external ion return. (c) The vinyl cation should be as close to symmetrical as possible. Capture of the ion by nucleophiles occurs from its less hindered side,[7] and the ion pair return may be hidden, or the extent of cis–trans isomerization will be low, if the capture

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[1] Part XXI: Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, in press.

[2] (a) A. C. Day and M. C. Whiting, *J. Chem. Soc. B*, 991 (1967); (b) Z. Rappoport and Y. Apeloig, *Isr. J. Chem.*, **7**, 33p (1969); (c) R. C. Macomber, *J. Amer. Chem. Soc.*, **92**, 7101 (1970); (d) C. A. Grob and R. Nussbaumer, *Helv. Chim. Acta*, **54**, 2528 (1971); (e) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970); **93**, 1941 (1971); (f) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *ibid.*, **94**, 3626 (1972); (g) T. C. Clarke and R. G. Bergman, *ibid.*, **94**, 3627 (1972); (h) R. H. Summerville and P. v. R. Schleyer, *ibid.*, **94**, 3629 (1972); **96**, 1110 (1974); (i) R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *ibid.*, **96**, 1100 (1974).

[3] (a) G. Modena and U. Tonellato, *Chem. Commun.*, 1676 (1968); (b) *J. Chem. Soc. B*, 374 (1971).

[4] For an extensive review dealing with ion pairs in solvolysis reactions, see D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions," Vol. II, M. Szwarc, Ed., Wiley-Interscience, New York, N. Y., 1973.

[5] Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, in press.

[6] (a) P. E. Peterson and J. M. Indelicato, *J. Amer. Chem. Soc.*, **90**, 6515 (1968); (b) W. M. Schubert and G. W. Barfknecht, *ibid.*, **92**, 207 (1970); (c) Z. Rappoport, T. Bässler, and M. Hanack, *ibid.*, **92**, 4985 (1970).

[7] (a) Z. Rappoport and M. Atidia, *J. Chem. Soc., Perkin Trans. 2*, 2316 (1972); (b) A. Pross and Z. Rappoport, unpublished results.