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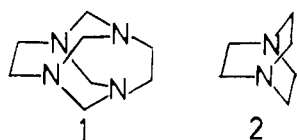
Three-Electron σ Bonding in the Radical Cation from 1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}]dodecane

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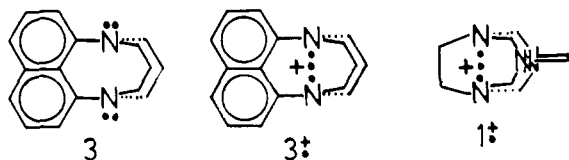
Abstract: Although the title tetraamine (**1**) is known to have four equivalent nitrogens, D_{2d} effective symmetry, and a highest occupied MO of b_2 symmetry, the ESR spectrum of the radical cation is incompatible with 2B_2 (D_{2d}) 1^+ , although it is consistent with a 2E (D_{2d}) species. It is argued that the cation observed in solution actually has C_{2v} symmetry with unequal NCH_2CH_2N distances, but the roles of the two sets of nitrogens are rapidly interchanging. MINDO/3 calculations are consistent with this explanation, and rationalize the low activation energy necessary for interchange.

The radical cation of the title tetraamine **1** is usually long lived in solution,¹ although not as long lived as that of Dabco (**2**),² with which it shares the structural feature of having



NCH_2CH_2N groups aligned for maximum lone pair, σ_{C-C} through-bond interaction.³ The photoelectron (PE) spectrum of **1** (which has D_{2d} effective molecular symmetry⁴) was assigned⁵ as having the b_2 MO (symmetric at each NCH_2CH_2N unit) 1.27 eV higher in energy than the e MO (antisymmetric at each NCH_2CH_2N unit), indicating that **1**, like **2**,³ has important through-bond interaction. 1^+ was argued to have its charge delocalized over all four nitrogens because of the low standard potential (E^0) for the **1**, 1^+ couple compared to model systems with NCH_2N structural units¹ and the longer wavelength absorption maximum for 1^+ than 2^+ . Although all four nitrogens of 1^+ were equivalent in its ESR spectrum, the NCH_2N proton splitting is far larger than would be observed for 1^+ with an odd electron in the b_2 MO,⁵ ruling out the species observed being 2B_2 (D_{2d}) 1^+ . This splitting was of the size expected for the 2E species, leading to the postulate that inversion of the highest occupied MOs had occurred between 1^+ (D_{2d}) produced in the gas phase and 1^+ (D_{2d}) produced in solution, and that by analogy such an inversion might also occur for 2^+ . We now present evidence that this postulation is incorrect, and that there is a fundamental difference between the bonding present in 1^+ as observed by PE spectroscopy and 1^+ as observed by ESR.

Alder and co-workers⁶ have recently shown that **3** has a low E^0 for oxidation and that 3^+ is both long lived and colored (λ_{max} 480 nm). 3^+ is best represented as having a through-space N,N interaction, a "three-electron σ bond" between the



nitrogens.⁶ Their data indicate that both the visible absorption of 1^+ and the low E^0 of **1** are entirely consistent with a through-space interaction between two of the nitrogens of 1^+ , which contains a bridgehead diazabicyclo[3.3.2]decyl system, rather closely analogous to the -[3.3.3]undecyl system of 3^+ . Such bonding would cause 1^+ to have C_{2v} symmetry, with unequal NCH_2CH_2N distances, in contrast to the D_{2d} symmetry of the neutral molecule. The ESR spectrum of 1^+ re-

quires that the roles of the two pairs of nitrogens would have to be interconverting rapidly.

To see if these structural hypotheses are reasonable, we have carried out MINDO/3 calculations. The PE spectrum of 1^5 (like that of 2^{3c}) shows vibrational splittings, requiring that great structural reorganization does not spontaneously take place when an electron is removed. Energy minimized MINDO/3 calculations bear this out. Such calculations on neutral **1** (D_{2d}) reproduce the experimental x-ray structure⁴ rather well (see Figure 1) as well as the orbital ordering assigned⁵ from PE data (see Table I). Similar calculations on 1^+ (D_{2d}) give only small changes in the energy minimized geometry, and the expected 2B_2 cation ground state (*no* orbital inversion). Subtraction of the calculated heats of formation gives an ionization potential in good agreement with the PE ionization potential. Although 1^+ is calculated to be stable in D_{2d} molecular symmetry, as shown by deforming the input coordinates toward a C_{2v} structure and letting the energy minimize back to the D_{2d} structure, it was found that *large* deviations of the input coordinates result in refinement to a second, stable, C_{2v} minimum energy structure (see Figure 1). Detailed calculations revealed the origin of this double minimum potential; see Figure 2. A b_2 distortion of the D_{2d} cation raises the 2B_2 curve, its symmetry species becoming 2A_1 in C_{2v} symmetry. However, this motion also splits the Jahn-Teller degeneracy of the excited 2E state of the original D_{2d} species, one component becoming strongly stabilized. Large enough distortion results in energy crossing of this component with the rising 2A_1 curve, and a new minimum for a truly isomeric C_{2v} cation evolves. Its ground-state symmetry is 2B_2 or 2B_1 depending on which pair of nitrogens becomes closer.

The vapor phase energies for minimum energy D_{2d} and C_{2v} 1^+ are calculated by MINDO/3 to be nearly the same; we are thus unable to predict the energetically favored molecular symmetry of isolated 1^+ . As the PE experiment starts out from neutral **1** of D_{2d} symmetry, the dominant Franck-Condon factors are those for transitions to ions of also D_{2d} symmetry. Analysis of the PE spectrum based on the vertical ionization energies thus provides the orbital structure of the D_{2d} ion. From the same calculations, however, we expect that in condensed phase the C_{2v} species is clearly favored owing to better solvation of its more localized charge. Gerson and co-workers⁷ have discussed several examples of charge localization in radical anion chemistry.

Rapid equilibration of the equal energy C_{2v} structures, which requires rapid electron transfer between the two sets of NCH_2CH_2N units, would lead for the temperature conditions used in ref 5, in view of the ESR time scale, to a time-averaged spin distribution corresponding to an average over the b_1 and b_2 orbitals: The intersection between the 2B_2 or 2B_1 curve with the 2A_1 curve lies rather low and avoided crossing will occur

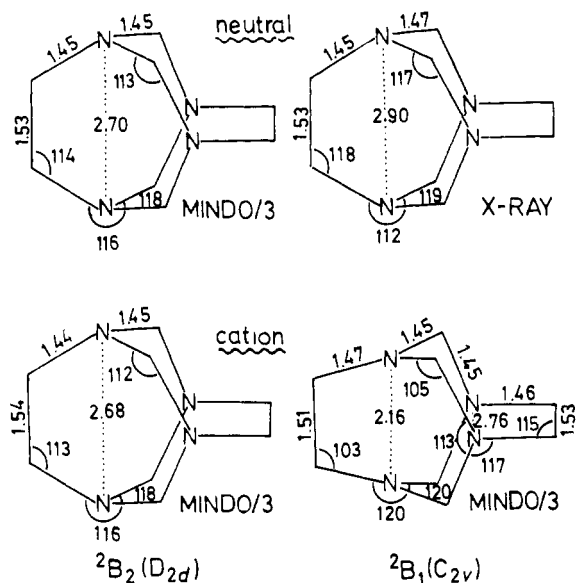


Figure 1. MINDO/3 energy minimized geometries for **1** and **1⁺**.

Table I. MINDO/3 Geometry-Optimized^a Energy Calculations for **1** and **1⁺**.

	1 (D_{2d})	1⁺ (D_{2d})	1⁺ (C_{2v})
State	1B_2	2B_2	2B_1 ^b
ΔH_f° , kcal/mol	89.2	255.3	256.0
Orbital energies, eV	-7.84 (b_2) ^c -8.40 (e) -9.25 (a_1)	[-7.76 (b_2)] ^d [-8.35 (e)] [-9.14 (a_1)]	[-7.49 (b_1)] ^d [-8.03 (a_1)] [-8.27 (b_2)] [-9.16 (a_1)]

^a See Figure 1 for the optimized geometrical parameters. ^b Interchanging the interatomic distances of the two sets of nitrogens changes the 2B_1 label to 2B_2 , and interchanges b_1 and b_2 . ^c Compare the PE results⁵ of 7.39 (b_2), 8.66 (e), 9.54 (a_1). ^d Orbital energies calculated for the neutral species using the optimized geometry of the cation.

under the influence of other asymmetric modes. The molecule thus oscillates from C_{2v} to C_{2v}' , not by climbing to the 2E (D_{2d}) state but by passing through the intermediate 2B_2 (D_{2d}) state, which leads to a much smaller barrier for the degenerate interconversion.

As the above mentioned b_1 and b_2 orbitals reflect the nodal characteristics of the degenerate components of the e orbital deduced from the PE spectrum for the D_{2d} ion, the ESR spectrum may operationally be interpreted as arising from a D_{2d} ion with 2E ground state as done in ref 5. The fundamental difference between the present and this earlier interpretation should, however, be clearly recognized. Earlier it was *in effect* assumed that the "unprecedented" crossing of states, as a result of solvation, occurred at the D_{2d} point itself. Hence, it was assumed that the different solvation of the 2B_2 ground state and the 2E excited state would lead to their interchange, being at most associated with nuclear displacements along the a_1 coordinate. This proposition is quite inconceivable in view of the 1.27-eV energy difference for isolated **1⁺**. The present version supports a less exotic mechanism: Solvation favors a ground state of a species which correlates with an excited state of a "valence isomeric" species. This latter shows up in the PE spectrum, the former in a rapid degenerate equilibration in the ESR spectrum.

The exceedingly rapid electron transfer between the two sets of two nitrogens of **1⁺** makes an interesting contrast with the very slow electron transfer between the two hydrazine units of tetraalkyl *sym*-hexahydrotetrazine radical cations (**4⁺**),⁸ despite the fact that **1** and **4** each possess two formally equiv-

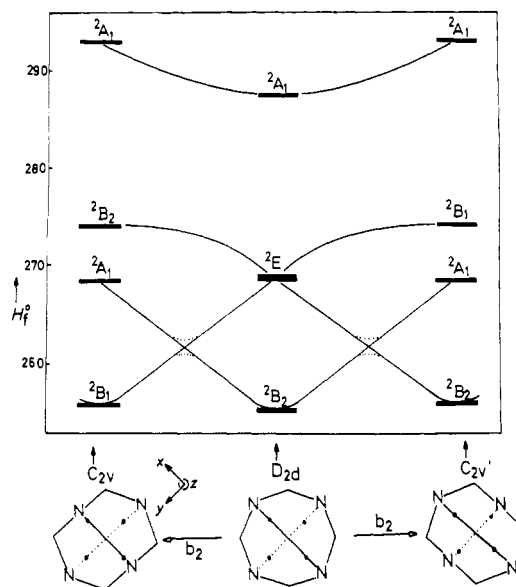
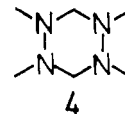


Figure 2. State correlation diagram for isolated **1⁺** (MINDO/3 calculations). The structures are viewed down the S_4 axis of the D_{2d} structure. Since calculations for the excited state of **1⁺** did not converge, the values given in Table I were used in conjunction with Koopman's theorem. In solution, the C_{2v} species might be stabilized with respect to the D_{2d} species.

alent nitrogen units, either of which can bear the charge, which are held in close proximity by linking methylene groups. Great structural reorganization is necessary to transfer an electron



in **4⁺**,⁸ while only fairly minor changes are necessary in **1⁺**.

The possibility of **2⁺** distorting to allow dominant through-space bonding does not appear feasible from MINDO/3 calculations which place such a species at considerably higher energy than that with through-bond interaction. Such a "three-electron σ bond" must introduce considerably more strain in the bridgehead diazabicyclo[2.2.2]-octyl system.

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