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Through-bond interaction in the radical cation of N,N-dimethylpiperazine. Resonance Raman spectroscopy and quantum chemical calculations

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Abstract

The radical cation of N,N-dimethylpiperazine is investigated by resonance Raman spectroscopy and ab initio calculations. The calculations strongly support the assignment of the vibrational spectrum to a chair conformation. It is shown that a dramatic geometry relaxation following ionization allows a much more efficient interaction between the nitrogen 'lone pairs' than in the neutral ground state.

1. Introduction

The interaction between the nitrogen lone pairs in 1,4-diazacyclohexane derivatives such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and piperazines has been the subject of numerous studies [1–15]. In this Letter we address the question of how this interaction affects the geometry of the radical cation of the semiflexible diamine N,N-dimethylpiperazine. We have used piperazines as double-electron-donor building blocks in multicomponent electron donor–acceptor systems [16]. The dipole moments of the charge-transfer states that we obtained suggested that in asymmetrically substituted piperazines a large extent of charge localization on one of the nitrogens occurs in the oxidized form. In general, if the interac-

tion between the donor groups is weak enough the radical cation character will be localized on one of the two sites, and two equivalent dissymmetric species will exist, as indicated schematically in Fig. 1. In the case of strong interaction, on the other hand, complete delocalization of charge and spin may occur and a single minimum will exist.

In this Letter we present evidence that the single-minimum situation prevails for dimethylpiperazine (DMP), and we establish the geometry of the radical

Fig. 1. Schematic potential energy curves for weakly coupled (double-minimum) and strongly coupled (single-minimum) double-donor radical cations.

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cation on the basis of resonance Raman spectroscopy and quantum chemical calculations.

Remarkably little is known about the DMP radical cation, in contrast with DABCO. The rigid cage structure of DABCO, with the nitrogen lone pairs aligned with the central C–C σ bonds, is favorable for through-bond interaction (TBI) [1]. This leads to a large splitting (2.1 eV) of the two lowest ionization potentials associated with the symmetric (n_+) and antisymmetric (n_-) combinations of the nitrogen lone pair orbitals [2–5]. In piperazine derivatives, on the other hand, the substituents at the nitrogens take up the equatorial positions, so that the lone pairs cannot be properly oriented. As a result, little or no interaction is found [4,6,7]. Oxidation of DABCO results in a stable radical cation, which has been studied by UV/VIS [8–10], ESR [3,9,11] and resonance Raman spectroscopy [12]. DMP, on the other hand, cannot be oxidized reversibly in conventional voltammetry experiments [13,14]. The radical cation apparently decomposes on the timescale of such measurements. It could be observed by optical absorption [15] and ESR spectroscopy [11] when generated by radiolysis in low-temperature matrices, but conclusive structural information could not be obtained from these experiments.

2. Experiments

The radical cation of DMP in CH_3CN (<0.005 M) was created as a transient species by means of a photoinduced electron transfer technique involving 1,4-dicyanonaphthalene (≈ 0.01 M) as the photoexcitable electron acceptor and biphenyl (≈ 0.25 M) as a cosensitizer. Electron-transfer quenching of the dicyanonaphthalene singlet by biphenyl and ion-pair separation lead to a high yield of biphenyl radical cation [17], which subsequently oxidizes the amine, present in a lower concentration. The optical absorption spectrum of the radical cation of DMP in CH_3CN ($\lambda_{\text{max}} \approx 600$ nm) is virtually identical with that in an alkane matrix [15]. In the time-resolved resonance Raman measurements the same cosensitization method could be used, but it proved advantageous to create the sensitizer radical cation by direct photoionization of biphenyl [18]. The transient pump-probe resonance Raman experiments were carried out

in the usual way using an excimer laser (Lambda Physik LPX220i) at 248 nm as pump source, an excimer-pumped dye laser (Lambda Physik EMG102E+FL3002) at 620 nm as the probe source and an intensified diode-array (Spectroscopy Instruments IRY-700) as detector. The resonance Raman spectrum ($250\text{--}1750\text{ cm}^{-1}$) of the DMP radical cation is shown in Fig. 2, together with the scaled UHF/6-31G* frequencies of the totally symmetric vibrations calculated for four different optimized molecular structures (see below). The experimental spectrum reveals eight totally symmetric fundamental modes ($451, 508, 761, 830, 995, 1155, 1263$ and 1443 cm^{-1}) and three combination bands at 1591 ($761+830$), 1660 (2×830) and 1710 cm^{-1} ($1263+451$). This interpretation is further supported by preliminary experiments on a deuterated isotopomer.

Fig. 2. Experimental resonance Raman spectrum (A) and computed Raman spectra ((B)–(E)) for different optimized geometries (for numbering see Fig. 3) of the radical cation of N,N-dimethylpiperazine.

3. Ab initio calculations

Several types of molecular structure were considered in the computational part [19] of this study. The optimized structures of DMP (1), its radical cation (2–5) and the excited state of the radical cation (6) are shown in Fig. 3. For the neutral ground state the chair conformation 1 (C_{2h}) with the methyl groups equatorial is definitely the most stable form. For the oxidized form results of UHF and UMP2 calculations are given in Table 1. Spin contamination of the UHF wavefunction was not a serious problem: in all cases the expectation value of S^2 was ≈ 0.78 , close to the theoretical doublet value of 0.75. The SCF cal-

Fig. 3. HF/6-31G* calculated molecular structures of N,N-dimethylpiperazine: neutral molecule (1), radical cation (2–5), 2B_u excited state of the radical cation (6).

culations predict that, in spite of the apparently equivalent nitrogens, a dissymmetric structure (2, C_s) is most stable, with one amino group planar (the typical structure of a radical cation), the other pyramidal (as in a neutral amine). The symmetric C_{2h} chair 3 is less stable at the SCF level. In structure 3 the methyl groups take up a pseudo-axial position, even though optimization was started from a pseudo-equatorial geometry. In addition to the chair forms we considered boat conformations (C_{2v}) of the radical cation. One of these (4) was set up to allow a direct through-space interaction to produce a three-electron bond. This type of bonding is known for certain diamines [20], and for the sulfur analogue 1,4-dithiane [21]. Another boat type geometry (5) is more favorable for TBI.

Vibrational analyses at the UHF/6-31G* level show that the C_{2h} and C_s chair forms are real minima. The boat forms 4 and 5 had one or two (low) imaginary frequencies, corresponding to transitions to nearby twisted-boats. These have slightly lower energies (0.2 kcal/mol), but their computed vibrational spectra are virtually identical with those of the corresponding C_{2v} form, except for the lowest frequency transitions. Optimal scaling factors used for the computed frequencies (Fig. 2) are 0.95 for the C_{2v} boat form 5, 0.91 for the other forms (2, 3 and 4). The scaling factors are close to the commonly used 0.9 for HF calculations [22].

Subsequent energy evaluations involving electron correlation (UMP2//6-31G*) yielded a dramatically different ordering of energies, and established that the C_{2h} symmetric conformation is *by far* the most stable. Finally, optimization of geometries at the MP2 level did not change the picture.

The computed normal modes reveal that most vibrations have contributions from various local coordinates. The normal modes corresponding to the most

Table 1

Computed energies (hartree) of the radical cation of N,N-dimethylpiperazine in various conformations optimized at the UHF/6-31G* and UMP2/6-31G* levels. Relative energies (in parentheses) in kcal/mol

Structure	UHF/6-31G*	UMP2/6-31G*//6-31G*	UMP2/6-31G*
chair (C_s) 2	–344.00167 (–11.7)	–345.06919 (+17.8)	–345.07185 (+17.7)
chair (C_{2h}) 3	–343.98296 (0)	–345.09751 (0)	–345.10009 (0)
boat (C_{2v}) 4	–343.96505 (+11.2)	–345.06541 (+20.1)	–345.06871 (+19.7)
boat (C_{2v}) 5	–343.96020 (+14.3)	–345.07377 (+14.9)	–345.07606 (+15.1)

Fig. 4. Computed normal modes and frequencies (scaled by 0.91) corresponding to the most intense bands in the resonance Raman spectrum of the radical cation of N,N-dimethylpiperazine.

prominent bands in the spectrum are depicted in Fig. 4.

The observed band at 830 cm^{-1} (computed 824 cm^{-1}) is due to a stretching mode of the central C–C bonds and the N-methyl bonds. Preliminary experiments indicate a lowering of the frequency upon deuteration of the methyl groups, in agreement with the nature of this vibration. The 995 cm^{-1} band (computed 999) can be attributed to methylene rocking, the 1263 cm^{-1} and (computed 1301) to wagging of the methylene groups. The latter is completely insensitive to isotope substitution in the methyl groups, whereas the former shifts to higher frequency upon methyl deuteration as it is decoupled from the methyl deformation.

The highest singly occupied MO is the symmetric n_+ orbitals. Thus, the ground state of the radical cation is 2A_g . Also shown in Fig. 3 is the UHF optimized geometry **6** of the lowest 2B_u excited state, corresponding to the promotion of one electron from n_- to n_+ . The vertical energy gap is $0.0823 E_h$ (MP2//6-31G*), corresponding to a transition wavelength of 554 nm.

4. Discussion

The observed vibrational frequencies are in good agreement with the calculated spectrum of the C_{2h} chair form **3**. The spectra calculated for the other geometries cannot account for some of the bands in the experimental spectrum, except perhaps for **4**. The computed energies at the MP2 level, however, favor structure **3** beyond reasonable doubt. The effect of electron correlation on the relative energies is un-

sually large. It favors, in particular, the through-bond coupled systems **3** and **5** relative to **2** and **4**.

There is a good correspondence between the calculated and observed Raman intensities. This is remarkable in view of the fact that calculated intensities pertain to normal Raman, while observed intensities are due to resonance Raman scattering. This suggests that a single low-lying electronic transition is responsible for the Raman activity [23]. For the C_{2h} structure **3** the resonant state is readily identified as the lowest excited 2B_u state. The computed vertical transition energy of 2.2 eV is in excellent agreement with the experimentally observed band at 600 nm (2.1 eV).

The large differences in geometry around the nitrogen atoms are striking. In the neutral molecule the interaction between the lone pair orbitals is small. The difference in energies of the two highest occupied MOs n_- and n_+ is only $\Delta\epsilon = 0.15\text{ eV}$. Because both MOs are doubly occupied, their splitting does not have an important energetic effect. Upon removal of an electron from the highest occupied ground state MO a considerable energy gain can be achieved by increasing the splitting of n_- and n_+ . Thus, a nuclear reorganization occurs in which the substituents move away from the equatorial orientation so that the n -orbitals are more favorably aligned with the central σ bonds. When the n_+/n_- splitting is evaluated (using the closed shell RHF orbital energies) at the relaxed geometry of the radical cation a value of $\Delta\epsilon = 2.82\text{ eV}$ is found, which is close to that computed for DABCO (3.1 eV) [5]. Interestingly, when an electron is promoted from n_- to n_+ to give the 2B_u excited state of the radical cation, the molecule responds by a nuclear reorganization that *reduces* the splitting again: at the optimized geometry of the 2B_u excited state the splitting is 0.32 eV.

5. Conclusion

We have presented evidence that N,N-dimethylpiperazine undergoes a dramatic geometry change following oxidation to the radical cation, while maintaining a symmetric chair-type conformation. The relaxed geometry is such that effective interaction between the nitrogen lone pair orbitals is possible, in contrast to the situation in the neutral molecule. An

interesting question is whether symmetry breaking and charge localization can occur in piperazine radical cations if the two nitrogen centers have clearly different oxidation potentials [16]. This is one of the issues we are currently addressing with the combined experimental and computational approach presented here.

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