

Localization Versus Delocalization in Diamine Radical Cations†

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Brouwer, A. M., Wiering, P. G., Zwier, J. M., Langkilde, F. W. and Willbrandt, R., 1997. Localization Versus Delocalization In Diamine Radical Cations. – Acta Chem. Scand. 51: 217–219. © Acta Chemica Scandinavica 1997.

The optical absorption spectrum of the radical cation of 1,4-diphenylpiperazine **2a** shows a strong transition in the near-IR, and only a weak band at 445 nm, in the region where aniline radical cations normally absorb strongly. This indicates that the charge and spin are delocalized over the two equivalent aniline moieties. Introduction of a 4-methoxy group on the aromatic ring allows increased stabilization of the radical ion character on one moiety, and charge delocalization across the piperazine ring is suppressed, as shown by optical absorption and resonance Raman spectroscopy. The possibility of coexistence of localized and delocalized radical cations of diphenylpiperazine and its derivatives cannot be ruled out at present. If that were the case, the effect of the methoxy substituents is to shift the equilibrium towards the localized species.

The interaction between the lone pair orbitals of diamines has been investigated in some depth in the early seventies^{1,2} in relation to Hoffmann's theory of through-bond interaction,^{3,4} which was so nicely exemplified by the 1,4-diazabicyclooctane system.⁵ In the case of *N,N*-dimethylpiperazine **1** only weak interaction has been observed in the photoelectron spectrum (PES),¹ but we recently demonstrated that in the radical cation of this molecule the interaction is in fact very large, and leads to a complete delocalization of the excess spin and charge.⁶ The large geometry change that occurs following ionization prevents the detection by PES of the interaction in the relaxed radical cation. In charge-transfer excited states in electron donor–donor–acceptor compounds in which piperazines are used as a double-donor building block, experimental evidence on the other hand indicates that the positive charge tends to be more or less localized on one of the two amino groups.^{7,8}

In this contribution we present some recent results on radical cations of *N*-phenylpiperazine derivatives **2** and **3** (Fig. 1), which were studied by optical absorption and resonance Raman spectroscopy.

Results

Radical cations were created as transient species in acetonitrile using pulsed laser induced electron transfer

† Contribution at the 14th International Conference on Radical Ions, Uppsala, Sweden, July 1–5, 1996.

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(cosensitization method)^{9,10} or direct photoionization, and were studied by means of nanosecond time-resolved spectroscopy. Some representative optical absorption spectra are shown in Fig. 2. A preliminary experiment on the symmetrical bis(4-methoxyphenyl)piperazine **2c** revealed an absorption band at 490 nm which is probably somewhat weaker than that of **2b**, **3** and **4**. In the resonance Raman spectra (Fig. 3) the probe laser (480 nm) was in resonance with the characteristic aniline radical cation absorption band.^{11,12}

Discussion

As we have recently shown, *N,N*-dimethylpiperazine upon one-electron oxidation forms a charge and spin *delocalized* radical cation in which a large structural reorganization occurs to facilitate the energetically favorable interactions of the three electrons that remain in the former lone pair MOs.⁶ The bonding situation is formally equivalent to that of dimer radical cations (Fig. 4).¹³

If there is a sufficiently large resonance interaction, there is a gain in electronic energy as a result of delocalization. On the other hand, additional nuclear reorganization energy is required to optimize the electronic interaction, which strongly depends on the orientation of the 'lone pair' orbitals. Apparently, in the case of **1** the energy gain is large enough for the geometry change to occur. This is in marked contrast with the recent report of Nelsen and Yunta¹⁴ that the symmetrical 1,4-bis(4-dimethylaminophenyl)piperazine **2d** forms a *localized* (symmetry-broken) radical cation, allowing this

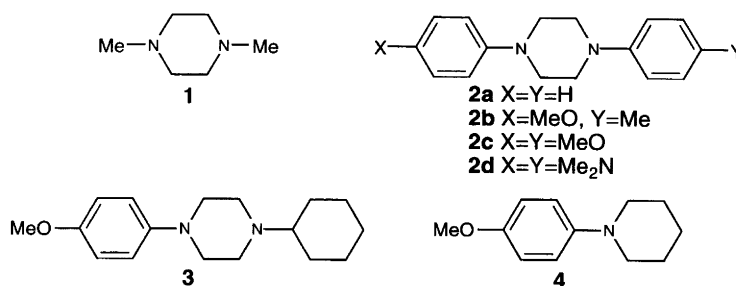
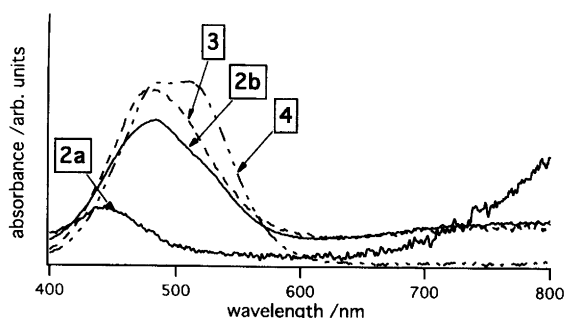
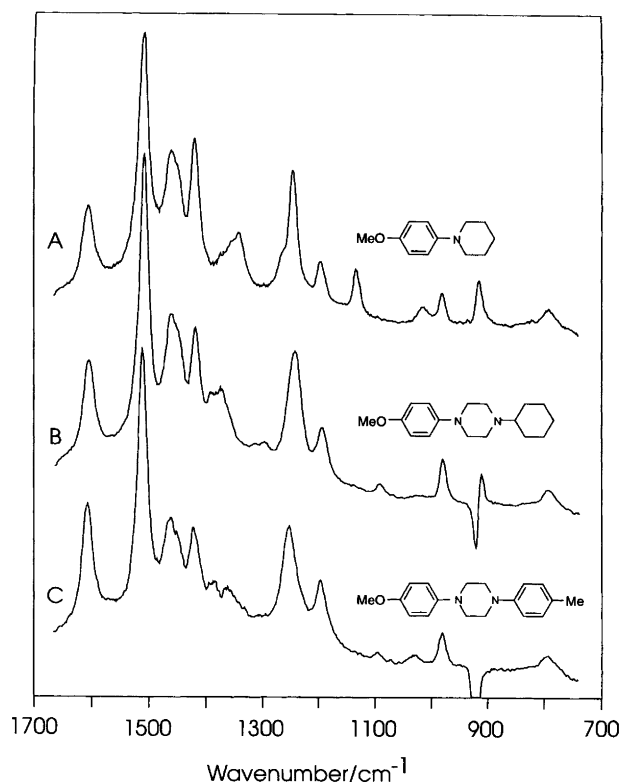
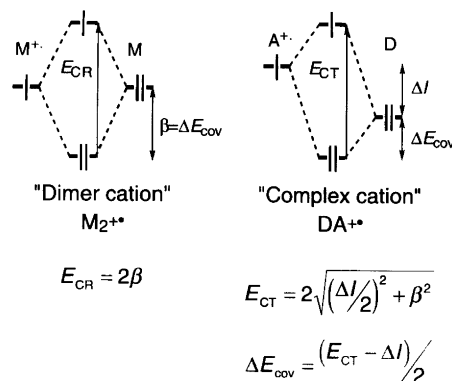


Fig. 1. Compounds discussed.

Fig. 2. Optical absorption spectra of radical cations of 1,4-diphenylpiperazine **2a**, 1-(4-methylphenyl)-4-(4-methoxyphenyl)piperazine **2b**, 1-(cyclohexyl)-4-(4-methoxyphenyl)piperazine **3** and 1-(4-methoxyphenyl)piperidine **4**.Fig. 3. Resonance Raman spectra of the radical cations of (A) 1-(4-methoxyphenyl)piperidine **4**; (B) 1-(cyclohexyl)-4-(4-methoxyphenyl)piperazine **3**; (C) 1-(4-methylphenyl)-4-(4-methoxyphenyl)piperazine **2b**.Fig. 4. Electronic interactions in (heterosymmetric) dimer radical cations.¹³ ΔE_{cov} is the 'covalent' stabilization energy, ΔI is the difference in ionization potential of the constituents in the heterosymmetric case. CR=charge resonance, CT=charge transfer.

molecule to be studied as a model for the electron self-exchange in *N,N,N',N'*-tetramethyl-*p*-phenylenediamine and its radical cation. The contrasting behavior of **1** and **2d** is likely to be due to the smaller resonance integral in the latter, which reduces the electronic energy gain of delocalization (see Fig. 4).

The optical absorption spectrum of the radical cation of diphenylpiperazine **2a** is indicative of a *delocalized* cation. The strong absorption characteristic of the aniline radical cation chromophore at 470 nm is virtually absent (although a weak and blue-shifted band remains), and an intense absorption at long wavelength is seen. The absorption maximum is outside the spectral range presently accessible to us, probably at ca. 1000 nm. The experiments did not allow a determination of the molar absorption coefficient, but based on comparison with other radical cations formed in the same way we estimate that it is at least of the order of $10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. This is much larger than the typical value for an 'intervalence' charge transfer band.¹⁴ The location of the absorption maximum corresponds approximately with the splitting energy 2β . For **2a**^{•+} the resonance integral is thus almost two times smaller than in **1**^{•+} ($\lambda_{max} = 600 \text{ nm}$).

In all methoxy-derivatives studied (**2b**, **2c**, **3** and **4**) the characteristic aniline radical cation band near 500 nm is present, and resonance Raman spectra show virtually identical vibrational frequencies for the aromatic ring vibrations in **2b**, **3** and **4**, which indicates that the radical

ion character is fully *localized* on the methoxyaniline moiety. Interestingly, the asymmetric derivatives show an additional broad long-wavelength absorption, which is most probably due to a charge-transfer transition. However, the hypothesis that the two bands in compounds **2a**, **2b** and **3** are due to two different (perhaps equilibrating) species cannot be rejected.

We tentatively conclude that the switch-over from delocalized to localized diphenylpiperazine radical cations can be achieved by introduction of a 4-methoxy group in the phenyl ring. This can be explained by the reduction of the spin density on the bridging nitrogen(s), which reduces the energy gain that can be achieved by delocalization. As a result the electronic energy gain cannot compensate for the energetic cost of the nuclear reorganization that is required for efficient delocalization.

When different substituents are present on the nitrogen atoms, creating a difference in ionization potentials ΔI , delocalization is also disfavored (see Fig. 4), but it seems that in the methoxy systems studied here the smaller electronic *N-N* interaction is the decisive factor. In the near future we will further explore the borderline region between localized and delocalized piperazine radical cations.

Acknowledgments. This work was supported by the Netherlands Organization for Scientific Research (NWO) which provided a travel grant to A.M.B. Grants from the Danish Natural Science Research Council and NATO (Grant No. 0137/88) are gratefully acknowledged. We

thank Dr. J. Fenger, Dr. K. B. Hansen, E. Engholm Larsen and H. J. van Ramesdonk for help with instrumentation.

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Received July 1, 1996.