

ELECTRONIC ABSORPTION SPECTRA OF ALIPHATIC DIAMINE RADICAL CATIONS. CONFORMATION-DEPENDENT CHARGE DELOCALIZATION

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Electronic absorption spectra of radical cations generated by steady-state and pulse radiolysis from a series of α,ω -diaminoalkanes ($R_2N(CH_2)_nNR_2$; $n = 1-6$, $R = CH_3$ or C_2H_5), 1,4-dimethylpiperazine and 1,4-diazabicyclo [2.2.2]octane (DABCO) were measured. In some cases spectral evidence was obtained for an interaction between the nitrogen atoms leading to charge delocalization in the radical cation. A delayed formation of radical cations was associated with a conformational change necessary for achieving the most stable structure having a favourable conformation for charge delocalization.

INTRODUCTION

Organic radical ions are important intermediates in a wide variety of electron-transfer reactions.^{1,2} They are produced in chemical reactions and also on electrolysis, photolysis and radiolysis. Direct exposure of low-temperature glassy solutions to ionizing radiation is a particularly useful method of radical ion generation for optical studies. Both steady-state and time-resolved detection are feasible. We have recently established that low-temperature pulse radiolysis can be successfully applied to studies of radical ion transformations with a very low activation barrier.^{3,4} This paper presents electronic absorption spectra of radical cations for several aliphatic diamines obtained in the steady-state and time-resolved modes. The problem of spectral evidence for the charge delocalization in diamine radical cations is considered in terms of the conformational requirements necessary to obtain the most stable structure characterized by the strongest interactions between the two nitrogen atoms of the diamine. In principle, two kinds of interactions, 'through-space' and 'through-bond,' can play a role.⁵ It has been suggested, and in some cases also documented,^{6,7} that both types of interactions are very dependent on the structure. Evidence is presented that charge delocalization in the diamine radical cations is a conformation-dependent process. This applies particularly to diamines that have great conformational freedom.

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EXPERIMENTAL



Materials. The structures and names of the α,ω -diaminoalkanes **1**, **2a**, **2b**, **3a**, **3b**, **4** and **6** and the cyclic diamines **2c** and **2d** used are given in Table 1.

The numbers of the compounds were chosen such that each is related to the number of methylene groups in the polymethylene chain separating two nitrogen atoms of the diamine. Hence there is no compound numbered **5** as we did not study 1,5-tetraalkyldiaminopentane derivatives. All the compounds were purchased from Aldrich, except **2b** and **3b**, which were synthesized according to the known procedure.⁸ They were purified by standard laboratory methods when necessary.

Methylcyclohexane (MCH) and 3-methylpentane (3MP) were used as solvents for the preparation of low-temperature glassy solutions. They were passed through a freshly activated silica gel column before use. Small amounts of 1-chlorobutane (1BuCl), acting as an electron scavenger, were added to the solution before sample preparation. The concentrations of the solute (0.02 M) and the electron scavenger (1 M) were kept constant during measurements.

Sample preparation and measurements. Since we have found that deoxygenation of the solution before sample preparation has almost no effect on the yield of radical cations, the samples were made from air-saturated solutions. The details of the sample preparation procedure and the description of the pulse

Table 1. Compounds studied

No.	Structure	Name
1	$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}-\text{CH}_2-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	<i>N,N,N',N'</i> -Tetramethyldiaminomethane
2a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}-(\text{CH}_2)_2-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1,2- <i>N,N,N',N'</i> -Tetramethyldiaminoethane
2b	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{N}-(\text{CH}_2)_2-\text{N} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	1,2- <i>N,N,N',N'</i> -Tetraethyldiaminoethane
2c		1,4-Dimethylpiperazine
2d		1,4-Diazabicyclo[2.2.2]octane (DABCO)
3a	$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}-(\text{CH}_2)_3-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1,3- <i>N,N,N',N'</i> -Tetramethyldiaminopropane
3b	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{N}-(\text{CH}_2)_3-\text{N} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	1,3- <i>N,N,N',N'</i> -Tetraethyldiaminopropane
4	$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}-(\text{CH}_2)_4-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1,4- <i>N,N,N',N'</i> -Tetramethyldiaminobutane
6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{N}-(\text{CH}_2)_6-\text{N} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	1,6- <i>N,N,N',N'</i> -Tetramethyldiaminohexane

radiolysis system and the steady-state radiolytic measurements are given elsewhere.^{3,4} For measurements at temperatures below 77 K a liquid helium-cooled cryostat (Oxford Instruments) was used.

RESULTS AND DISCUSSION

In aliphatic diamines, the nitrogen lone pairs can interact both directly through space and by mixing with other σ -bonds in the molecule (through-bond interactions). Photoelectron spectroscopy is particularly useful for probing such interactions. For example, for DABCO (**2d**), which has been thoroughly studied from that point of view, the photoelectron spectrum shows two bands ascribed to the ionization of electrons from the $a_1(n_+)$ and $a_2'(n_-)$ orbitals.⁹ Through analysis of the vibrational fine structure of the photoelectron spectrum, it was shown that the first ionization of DABCO corresponded to removal of an electron from the n_+ orbital.¹⁰ Since through-space interactions should lead to an orbital sequence $a_2'(n_-)$ above $a_1(n_+)$, this result suggests a dominant contribution of a through-bond interaction in DABCO.¹¹ The ESR spectrum of DABCO⁺ also indicated a delocalized structure.^{12,13} The picture for other diamines with more conformational flexibility is less clear. For example, for 1,4-dimethylpiperazine (**2c**), where both photoelectron and ESR spectra are known,^{6,13} there is spectral evidence for charge delocalization but there is no indication which interaction prevails.

Since both through-space and through-bond interac-

tions are dependent on geometry, one might expect that the electronic absorption spectra of radical cations obtained in the time-resolved mode would show features typical of such interactions. Absorption spectra themselves do not contain sufficient information for judging what type of interaction dominates. Without support from photoelectron spectroscopy it is even difficult to assign unambiguously the electronic transitions. Despite these drawbacks, we obtained evidence for a strong time dependence in the absorption spectra, suggesting conformational effects in the charge delocalization process. For all the diamines studied, except **2c** and **2d**,¹⁴⁻¹⁶ the absorption spectra of radical cations shown in Figures 1 and 2 are presented for the first time.

The spectra obtained for **1**, **2a-2d**, **3a** and **3b** show only the visible transition, in contrast to **4** and **6**, where only the UV transition is seen. In the case of **4** the spectrum shows a rising absorption in the UV region without a pronounced maximum. As the length of the polymethylene chain increases, the probability of achieving a favourable conformation for interactions decreases sharply.^{7,11} Also, viscosity effects introduced by the matrix can effectively quench the conformational mobility. Hence, radical cations generated from **4** and **6** may possess a charge localized on one nitrogen atom, similarly to the monoamine radical cations. For example, the radical cation of triethylamine generated in an argon matrix absorbs in the UV region ($\lambda_{\text{max}} = 324 \text{ nm}$).¹⁴

The visible absorption, being of the charge-resonance

type,^{7,17} indicates a structure with charge delocalization, already proved for **2c** and **2d**. The striking feature of the series **2a–2d** is that λ_{\max} is shifted to higher energy as the two nitrogen atoms are linked by additional ethylene bridges. Hence λ_{\max} observed at about 780 nm for **2a** and **2b** is shifted to 600 and 470 nm for **2c** and **2d**, respectively. This observation is fully compatible with a picture based on a dominant through-bond interaction in **2a–2d** in that an increasing number of ethylene bridges leads to a stronger interaction between the nitrogen lone pairs as manifested by a shift of the observed transition to higher energy.

The time-resolved observations of radical cations generated from a few diamines are summarized in Table 2. In all cases studied, with the exception of **2d**, the absorption increased with time after the electron pulse. This effect is particularly pronounced for **3a**. Transient absorption spectra for **3a** obtained at 90 K are pre-

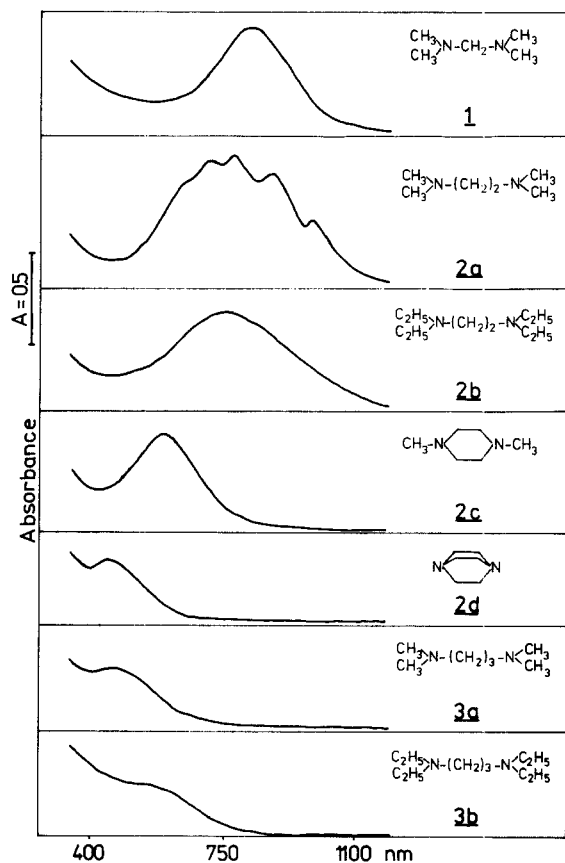


Figure 1. Absorption spectra of γ -irradiated (^{60}Co) **1**, **2a–2d**, **3a** and **3b** (0.02 M) in glassy matrices of MCH containing 1BuCl (1 M) at 77 K. The samples were 2 mm thick and received a radiation dose of 10^4 Gy

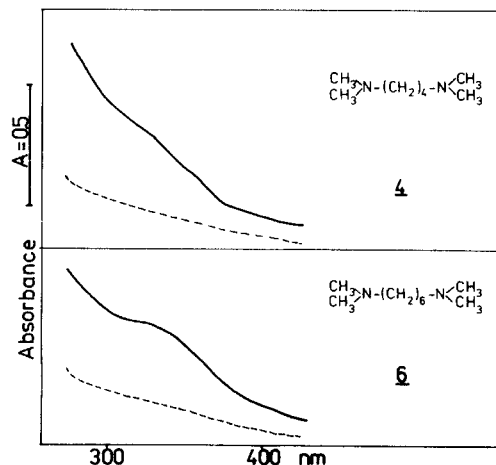


Figure 2. Absorption spectra of γ -irradiated (^{60}Co) **4** and **6** (0.02 M) in glassy matrices in MCH containing 1BuCl (1 M) at 77 K. The samples were 2 mm thick and received a radiation dose of 10^4 Gy. The dashed line shows the background before γ -irradiation

Table 2. Summary of pulse radiolytic observations^a

Diamine	λ_{\max} (nm)	$(A_{\infty} - A_{t=0})/A_{\infty}$ (%) ^b	t^c (s)	ϵ^d
2a	780	20	10^{-3}	1600
2b	780	30	10^{-3}	2700
2c	600	25	5×10^{-3}	1800
2d	470	—	—	650
3a	500	90	10^{-1}	1050

^a Measurements made in MCH matrices at 90 K.

^b Ratio of the increase in absorption ($A_{\infty} - A_{t=0}$) to the total absorption observed (A_{∞}).

^c Total rise time.

^d Molar absorptivity ($1\text{ mol}^{-1}\text{ cm}^{-1}$) of radical cation estimated from the total absorption formed after a $1\text{-}\mu\text{s}$ electron pulse (250 Gy) assuming a yield of scavengeable holes of $G = 3$.

sented in Figure 3. As can be seen, the initial absorption (curve a) is broad with a maximum at 510 nm. This absorption grows with time (see inset in Figure 3) and 2×10^{-3} s after the pulse a fairly strong absorption slightly shifted to a lower wavelength with a maximum at 500 nm is seen (curve b). This process can be rationalized in terms of conformational motion leading to an enhanced interaction between two nitrogen atoms of the diamine. Assuming dominant through-space interactions in this case, one would expect the formation of the three-electron σ -bond whose strength should depend strongly on the distance between the nitrogen atoms.⁷ As one would expect, the absorption maximum is shifted with time toward the ultraviolet region, indicating a stronger interaction. This intramolecular

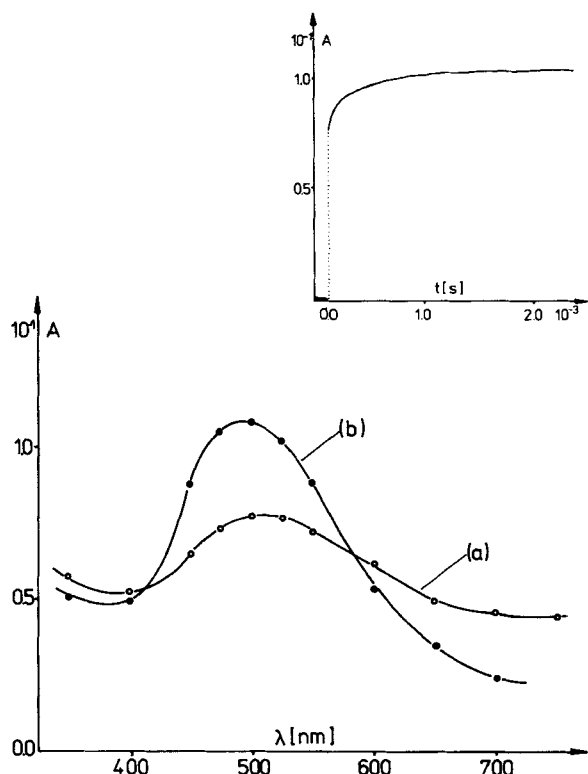


Figure 3. Transient absorption spectra of **3a** at 90 K obtained (a) 10^{-5} s and (b) 2×10^{-3} s after the $1\text{-}\mu\text{s}$ electron pulse delivering a dose of 250 Gy. The sample, 10 mm thick, contained **3a** (0.02 M) in MCH. Inset: absorption change calculated from the scope trace at 500 nm

rearrangement should follow first-order kinetics. This was not the case, as shown in Figure 4. The kinetics are more complex, suggesting a distribution of initial conformations leading to a distribution in the reaction rates.

Non-linearity, when the experimental data were treated by first-order kinetic equations, was also seen in the systems **2a–2c**. In our opinion, this problem deserves separate consideration, applying the kinetic model with a time-dependent rate constant.^{18,19} Interesting information comes from the effect of temperature on the transient absorption spectra of the radical cation generated from **3a**. As can be seen in Figure 5, the spectra of 30 K possess a maximum of 600 nm and hardly change with time if one corrects them for lowering of the background. Some motions can be quenched at very low temperature owing to intrinsic rotational barriers. Also at lower temperature the MCH matrix becomes more rigid, inhibiting conformational movement of the radical cation and a distinct change in the absorption is not seen with time evolution. The absorption maximum positioned at 600 nm

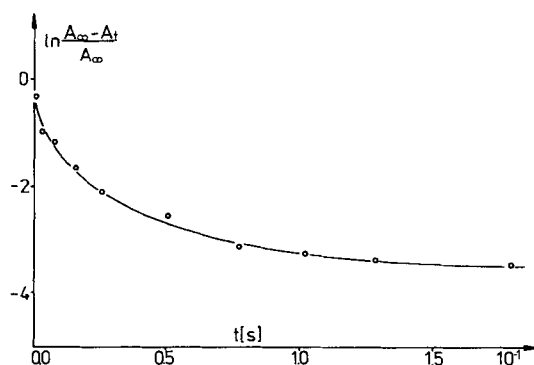


Figure 4. First-order kinetic plot of the absorption growth monitored at 500 nm as shown in Fig. 3

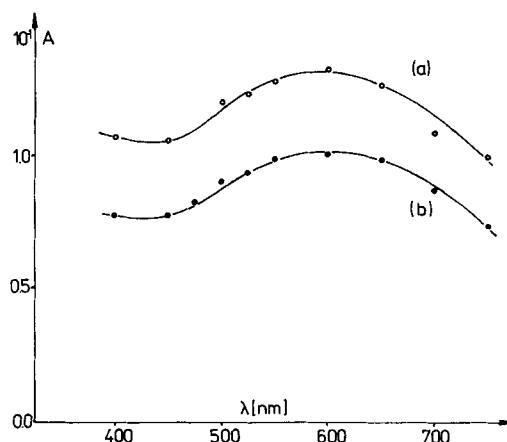


Figure 5. Transient absorption spectra of **3a** at 30 K obtained (a) 10^{-5} s and (b) 2×10^{-3} s after the $1\text{-}\mu\text{s}$ electron pulse delivering a dose of 250 Gy. The sample, 3 mm thick, contained **3a** (0.02 M) and 1BuCl (1 M) in MCH

as compared with 500 nm observed at 90 K points toward stronger effects on conformational mobility precluding the formation of a favourable structure for intramolecular interactions. This effect was also seen when we generated diamine radical cations in 3MP matrices. The ratios $(A_{\infty} - A_{t=0})/A_{\infty}$ obtained at 90 K were equal to 60, 25 and 100% for **2b**, **2c** and **3a**, respectively, and were higher than those obtained in MCH matrices (see Table 2). This indicates greater conformational freedom in 3MP, and is compatible with the known fact that 3MP is a much softer matrix than MCH, particularly in the region 80–100 K.^{20,21}

As one would expect, changes in the transient absorption spectra for **2a–2d** are much less pronounced (see Table 2) than for **3a**. For **2d**, where the bicyclic structure holds two nitrogen atoms in an almost fixed configuration, no change at all with time is seen in the absorption spectra.

All the above supports the view that conformational motion restricted by the rigid matrix environment leads to substantial changes in the time-resolved absorption spectra, which in turn reflects intramolecular interactions in diamine radical cations lowering their energy.

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