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The 1,2 migration of NH₃ in protonated β -aminoalkyl radicals

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Abstract

The enthalpy barriers for 1,2-migration of NH₃ in protonated β -aminoalkyl radicals, β -distonic isomers of primary amine radical cations, were determined with composite ab initio quantum chemical methods of the Gaussian and CBS families. The rearrangements are close to thermoneutral for small, protonated β -aminoalkyl radicals, and the barriers range from 60 to 100 kJ mol⁻¹, depending on the degree of substitution. The transition state resembles an NH₃ molecule symmetrically coordinated to an alkene radical cation. The heats of formation of the protonated C₂–C₄ β -aminoalkyl radicals are lower than those of the corresponding amine radical cations by 20–40 kJ mol⁻¹. The geometry and conformations of primary amine radical cations and their distonic isomers are briefly discussed. (Int J Mass Spectrom 199 (2000) 71–78) © 2000 Elsevier Science B.V.

Keywords: Transition states; NH₃ migration; Ab initio calculations; G3 method; Distonic ions

1. Introduction

The results of an early computational study by Golding and Radom [1] indicated that the enthalpy barrier toward the (at the time hypothetical) 1,2-migration of NH₃ in the protonated β -aminoethyl radical (Fig. 1) should be low enough to allow the reaction to take place under relatively mild conditions. Later, high-level ab initio calculations by Yates and Radom [2] provided a value for the barrier of 122 kJ mol⁻¹, substantially lower than that suggested by the results of less sophisticated calculations [1,3]. The results of experimental studies confirmed that the NH₃ migration is indeed a rapid reaction for $\cdot\text{CH}_2\text{CH}_2\text{NH}_3^+$ ions in the gas phase [4] and that 1,2 migration of NH₃

is a common reaction of protonated β -aminoalkyl radicals [5], also known as β -distonic isomers of amine radical cations [6].



Figure 1. 1,2-migration of NH₃ in the protonated β -aminoethyl radical *alias* the β -ammonioethyl radical *alias* the β -distonic isomer of the ethylamine radical cation.

1,2 migration of NH₃ in a β -distonic intermediate is a key step in the Audier mechanism for the skeletal isomerization of long-chain alkanamine radical cations (Fig. 2) [7]. The details of this transformation are examined in an accompanying article in this issue [8]; it has been suggested that the isomerization of secondary amine radical cations [9] proceeds analogously.

The present study was undertaken to determine the

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Dedicated to Henri Edouard Audier on the occasion of his 60th birthday.

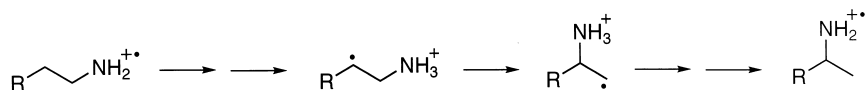


Figure 2. The key step in the Audier mechanism for the isomerization of metastable octanamine radical cations.

enthalpy barriers for NH_3 migration in a variety of β -distonic amine radical cations, to examine how the barrier height varies with substitution, and to resolve whether this step determines the enthalpy requirements of the isomerization of alkanamine radical cations by the Audier mechanism.

2. Methods

2.1. Computational thermochemistry

Heats of formation were obtained from the total energies calculated with the G3 method [10], slightly modified in that the geometry optimization was performed at the UMP2(full)/6-31+G(d,p) level. Additional results were obtained with other composite ab initio methods [11], G2(MP2) [12], G2(MP2,SVP) [13], and CBS-Q [14]. The calculations were performed with the Gaussian 94 suite of programs [15] and the total energies were converted to 298 K heats of formation as described by Nicolaidis et al. [16]; the required auxiliary thermochemical data were taken from the compilation by Wagman et al. [17].

The transition state region for NH_3 migration was located by stepwise variation of the NCC angle, and the subsequent optimization was performed in internal coordinates (z /G matrix). The transition states were characterized in each case by the calculated vibrational frequencies (one imaginary frequency) and by an intrinsic reaction coordinate calculation.

3. Results

The calculated heats of formation of the primary C_1 – C_4 amine radical cations are given in Table 1, together with the experimentally determined values [18]. The heats of formation of the corresponding

β -distonic isomers are in Table 2, and the results for the 1,2- NH_3 migration transition states are presented in Tables 3 and 4. Table 4 also includes results to indicate the thermochemical requirements of reactions that may compete with the NH_3 migration. The auxiliary thermochemical information in Table 5 was taken from the literature and supplemented with results obtained with the G3 method.

The UMP2(full)/6-31+G(d,p) geometries used in the energy calculations are in most cases not very different from those obtained with UMP2(full)/6-31G(d), except that the inclusion of polarization functions on hydrogen can change the predicted orientation of the C(1)–C(2) bond in alkanamine radical cations with respect to the $-\text{NH}_2$ plane.

The discussion in the present paper is based on heats of formation derived from G3 calculations. The G3 method is expected to provide quite accurate heats of formation for neutral molecules [10] as well as ions [19], even though the form of the empirical correction may introduce a small, systematic error [19]. The values determined with the G2(MP2) and CBS-Q methods are included in the tables for comparison. Thermochemical quantities derived from calculations with these composite ab initio methods have been shown to reproduce the values derived from experimental measurement quite well [19–24].

The G2(MP2,SVP) method is an economical alternative to G3 in terms of computer resources. The results in Tables 1–3 show that the G2(MP2,SVP) heats of formation of amine radical cations and distonic ions are close to those obtained with the G3 method, and G2(MP2,SVP) calculations should be useful for related species when the size of the system would make use of the G3 method too demanding.

The heats of formation obtained with the G2(MP2) method are slightly higher than those obtained with the other composite methods employed, particularly

Table 1
Total energies and heats of formation of C₁–C₄ primary amine radical cations^a

| | G3 | Exp ^b 298 | G2(MP2) | | G2 (MP2,SVP) | CBS-Q | G3 |
|--|------------|-------------------------|---------|-----|-----------------|-------|-----|
| | | | 0 | 298 | 298 | 298 | 298 |
| 1 CH ₃ NH ₂ ⁺ | -95.42761 | 842 ^c | 871 | 857 | 859 | 858 | 855 |
| 2 CH ₃ CH ₂ NH ₂ ^{+d} | -134.70672 | 807 | 835 | 815 | 815 | 815 | 812 |
| 3 CH ₃ CH ₂ CH ₂ NH ₂ ^{+e} | -173.98228 | 777 | 810 | 783 | 781 | 781 | 778 |
| 4 (CH ₃) ₂ CHNH ₂ ^{+f} | -173.98741 | 758 | 796 | 770 | 767 | 769 | 765 |
| 5 CH ₃ (CH ₂) ₃ NH ₂ ^{+f} | -213.25552 | 748 | 790 | 757 | 753 | 752 | 751 |
| 6 (CH ₃) ₂ CHCH ₂ NH ₂ ^{+g} | -213.25988 | 741 | 779 | 746 | 741 | 741 | 740 |
| 7 C ₂ H ₅ (CH ₃)CHNH ₂ ^{+h} | -213.26215 | 734 | 773 | 740 | 735 | 736 | 734 |
| 8 (CH ₃) ₃ CNH ₂ ⁺ⁱ | -213.26854 | 713 | 755 | 723 | 718 | 719 | 717 |

^a Total energies in Hartrees, heats of formation in kJ mol⁻¹, the same $\Delta H_{f,0} - \Delta H_{f,298}$ differences for all four methods. The geometry used in the G2(MP2), G2(MP2,SVP), and G3 calculations was determined at the UMP2(full)/6-31+G(d,p) level.

^b Experimental values taken from [18].

^c Experimental value may need revision [26].

^d The CC bond perpendicular to the -NH₂ plane. The G3 energy is 0.06 mH higher when the CC bond forms a 30° angle with the -NH₂ plane (calculated for QCISD/6-31G(d) geometries).

^e All-trans conformation, the α -CC bond perpendicular to -NH₂ plane, α -CC bond length 1.58 Å. The gauche conformation with the α -CC bond perpendicular to the -NH₂ plane: G3: -173.981 49, 780 kJ mol⁻¹, the α -CC bond length 1.58 Å. The results reported for this ion in [24] correspond to an incorrect geometry.

^f All-trans conformation, the α -CC bond perpendicular to the -NH₂ plane, the α -CC bond length 1.59 Å.

^g The α -CC bond perpendicular to the -NH₂ plane, the α -CC bond length 1.65 Å.

^h NCCC dihedral angle 180°, α -C₂H₅-CH bond perpendicular to the -NH₂ plane, α -C₂H₅-CH bond length 1.59 Å. The conformer with a CCCC dihedral angle of 180° and the α -C₂H₅-CH bond perpendicular to the -NH₂ plane: G3: -213.261 97 (734 kJ mol⁻¹). The conformer with a NCCC dihedral angle of 180° and the CH₃-CH bond perpendicular to the -NH₂ plane: G3: -213.260 74 (737 kJ mol⁻¹).

for the C₄ radical cations. A similar trend was apparent in a study of the heats of formation of imine and enamine radical cations [25]; preliminary results

for amine radical cations with up to three carbon atoms showed only small differences [24].

Spin contamination was not a problem in the

Table 2
Total energies and heats of formation of β -distonic isomers of C₁–C₄ primary amine radical cations^a

| | G3 | G2(MP2) | | G2 (MP2,SVP) | CBS-Q | G3 | Isom ^b |
|--|-------------|---------|-----|-----------------|-------|-----|-------------------|
| | | 0 | 298 | 298 | 298 | 298 | |
| 9 [•] CH ₂ CH ₂ NH ₃ ⁺ | -134.716 39 | 810 | 790 | 790 | 792 | 787 | -25 |
| 10 CH ₃ [•] CHCH ₂ NH ₃ ⁺ | -173.996 08 | 774 | 748 | 746 | 747 | 743 | -35 |
| 11 [•] CH ₂ CH(CH ₃)NH ₃ ⁺ | -173.996 55 | 772 | 746 | 744 | 747 | 741 | -24 |
| 12 CH ₃ CH ₂ [•] CHCH ₂ NH ₃ ^{+c} | -213.267 85 | 758 | 725 | 721 | 722 | 719 | -32 |
| 13 CH ₃ CH ₂ CH(CH ₂)NH ₃ ^{+d} | -213.269 66 | 753 | 720 | 716 | 718 | 714 | -20 |
| 14 CH ₃ [•] CHCH(CH ₃)NH ₃ ^{+e} | -213.276 11 | 736 | 704 | 699 | 701 | 698 | -36 |
| 15 (CH ₃) ₂ [•] CCH ₂ NH ₃ ⁺ | -213.275 50 | 738 | 706 | 702 | 704 | 700 | -40 |
| 16 (CH ₃) ₂ C(CH ₂)NH ₃ ⁺ | -213.277 43 | 732 | 699 | 695 | 698 | 694 | -23 |

^a Electronic energies in Hartrees, heats of formation in kJ mol⁻¹, the same $\Delta H_{f,0} - \Delta H_{f,298}$ differences for all four methods. The geometry used in the G2(MP2), G2(MP2,SVP), and G3 calculations was determined at the UMP2(full)/6-31+G(d,p) level.

^b ΔH_f (298 K) relative to the corresponding alkanamine radical cation.

^c All-trans (CCCC dihedral angle 150°); the gauche conformer (CCCC dihedral angle 90°) is slightly higher in energy, G3: -213.267 61 (720 kJ mol⁻¹).

^d CH₃/NH₃ gauche; the conformer with CH₃/CH₂ gauche interactions is slightly higher in energy, G3: -213.269 44 (715 kJ mol⁻¹).

^e All-trans; the conformer with CH₃/CH₃ gauche interactions is slightly higher in energy, G3: -213.275 13 (700 kJ mol⁻¹).

Table 3

Total energies and heats of formation of transition states for NH₃ migration in β -distonic isomers of C₁–C₄ primary amine radical cations^a

| Reactant | G3 | G2(MP2) | | G2 (MP2,SVP) | CBS-Q | G3 |
|---|-------------|---------|-----|-----------------|-------|-----|
| | | 0 | 298 | 298 | 298 | 298 |
| 9 $\cdot\text{CH}_2\text{CH}_2\text{NH}_3^+$ | –134.677 72 | 913 | 893 | 894 | 891 | 889 |
| 10 $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{NH}_3^+$ | –173.965 73 | 854 | 830 | 828 | 826 | 824 |
| 11 $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_3^+$ | –173.965 74 | 854 | 830 | 828 | 826 | 824 |
| 12 $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{NH}_3^+$ | –213.238 31 | 836 | 806 | 802 | 799 | 799 |
| 13 $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2)\text{NH}_3^+$ | –213.238 31 | 836 | 806 | 802 | 799 | 799 |
| 14 $\text{CH}_3\dot{\text{C}}\text{HCH}(\text{CH}_3)\text{NH}_3^{+\text{b}}$ | –213.253 00 | 799 | 770 | 765 | 761 | 762 |
| 15 $(\text{CH}_3)_2\dot{\text{C}}\text{HCH}_2\text{NH}_3^+$ | –213.253 54 | 796 | 768 | 763 | 764 | 760 |
| 16 $(\text{CH}_3)_2\text{C}(\text{CH}_2)\text{NH}_3^+$ | –213.253 54 | 796 | 768 | 763 | 764 | 760 |

^a Total energies in Hartree, heats of formation in kJ mol^{–1}, the same $\Delta H_{f,0} - \Delta H_{f,298}$ differences for all four methods. The geometry used in the G2(MP2), G2(MP2,SVP) and G3 calculations was determined at the UMP2(full)/6-31+G(d,p) level.

^b The transition state geometry corresponds to NH₃ migrating over *trans*-2-butene (see text). The transition state that corresponds to NH₃ over *cis*-2-butene: G3: –213.251 70 (765 kJ mol^{–1}).

present study. The calculated $\langle S^2 \rangle$ is between 0.76 and 0.78 for the alkanamine radical cations, their β -distonic isomers, and the transition states for isomerization.

4. Discussion

4.1. Amine radical cations

The calculated 298 K heats of formation of amine radical cations (Table 1) agree reasonably well with the experimentally determined values [18], with the

exception of the results for the methylamine radical cation. Gaud and Radom [26] suggested that the experimental value for this ion is too low and may need redetermination. The present results point to a similar conclusion; they show no serious discrepancies for the other small primary alkylamine radical cations, even though the G2(MP2) and CBS-Q values for the isopropylamine radical cation are outside the usual ± 10 kJ mol^{–1} target accuracy.

The conformational preferences of the small primary amine radical cations examined are for the most part unexceptional and can be illustrated by the

Table 4

NH₃ migration in protonated β -aminoalkyl radicals; heats of reaction, critical energies, and C–N bond lengths^a

| | $\Delta H_r(\text{isom})$ | E_0 | $r(\text{C–N})^b$ | | ΔH_r for alternative reactions | |
|--|---------------------------|-----------------|-------------------|------|--|--------------------------|
| | | | (1) | (2) | Dissociation ^c | Protonation ^d |
| 9 \rightleftharpoons 9 | 0 | 102 | 2.43 | 2.43 | 99 | — |
| 10 \rightleftharpoons 11 | 2 | 82 | 2.40 | 2.47 | 96 | –26 |
| 12 \rightleftharpoons 13 | 5 | 80 | 2.40 | 2.46 | 86 | –31 |
| 14 \rightleftharpoons 14 | 0 | 65 ^e | 2.48 | 2.48 | 69 | 6 |
| 15 \rightleftharpoons 16 | 6 | 60 | 2.44 | 2.51 | 73 | 9 |

^a G3 values in kJ mol^{–1} (298 K). Heats of reaction derived from the results in Tables 2, 3, and 5. Critical energies (E_0), $\Delta H_f(\text{TS}) - \Delta H_f(\text{reactant})$, derived from the results in Tables 2 and 3; energy differences given relative to lower-numbered reactant for nondegenerate isomerization reactions. The G2(MP2), G2(MP2,SVP) and G3 methods yield critical energies that agree to within ± 2 kJ mol^{–1} for ΔH_r and E_0 ; the CBS-Q results are within a few kJ of the G3 results.

^b C–N bond lengths in the transition state; geometries determined at the UMP2(full)/6-31+G(d,p) level.

^c $\Delta H_f(\text{alkene}^+) + \Delta H_f(\text{NH}_3) - \Delta H_f(\text{TS})$.

^d $\Delta H_f(\text{alkenyl}^+) + \Delta H_f(\text{NH}_4^+) - \Delta H_f(\text{TS})$.

^e Same barrier for the isomerization of the *trans* and *gauche* conformers.

Table 5
Auxiliary heats of formation^a

| | Exp ^b | G3 ^c |
|--|------------------|-----------------|
| C ₂ H ₄ | 52 | 52 |
| C ₃ H ₆ ⁺ | 959 | 966 |
| 1-C ₄ H ₈ ⁺ | 924 | 931 |
| <i>trans</i> -2-C ₄ H ₈ ⁺ | 866 | 877 |
| <i>cis</i> -2-C ₄ H ₈ ⁺ | 871 | 881 |
| <i>iso</i> -C ₄ H ₈ ⁺ | 874 | 879 |
| NH ₃ | -46 | -43 |
| NH ₃ ⁺ | 934 | 936 |
| NH ₄ ⁺ | 630 | 634 |
| CH ₂ =CHCH ₂ | 161 | 164 |
| CH ₃ CH=CHCH ₂ | 133 | 134 |
| CH ₂ =C(CH ₃)CH ₂ | 121 | 135 |

^a 298 K heats of formation in kJ mol⁻¹.

^b Taken from [18] unless otherwise noted.

^c Calculated with the G3 method; geometry optimization for the alkenyl radicals at the UMP2(full)/6-31+G(d,p) level.

properties of the propylamine and *sec*-butylamine radical cations. The nitrogen atom and its ligands lie almost in the same plane. The preferred orientation of the α -CC bond is to form an angle of approximately 90° with the -NH₂ plane (MP2 calculations without polarization functions on hydrogen atoms indicate that the α -CC bond in the *gauche* conformers will form a 30° angle with the -NH₂; this is not reproduced at higher levels). The *sec*-butyl amine radical cation possesses two α -CC bonds; in the lower-energy conformer the ethyl group is perpendicular to the -NH₂ plane. The propylamine radical cation in the *gauche* conformation is slightly higher in energy than the all-*trans* conformer (by 3 kJ mol⁻¹); in the *sec*-butyl system, the energy difference between the conformers with CH₃/CH₃ *gauche* interactions and CH₃/NH₂⁺ *gauche* interactions is quite small, less than 1 kJ mol⁻¹.

The α -CC bond is slightly elongated when perpendicular to the -NH₂ plane, e.g. the two α -CC bonds in the isopropylamine radical cation are 1.52 and 1.56 Å long, in the lower-energy conformer of the *sec*-butylamine radical cation the bond lengths are 1.59 Å (CH-C₂H₅) and 1.52 Å (CH-CH₃), respectively; the difference does not appear to be particularly dependent on the basis set employed. In isobutylamine, the α -CC bond length is found to be close to 1.65 Å.

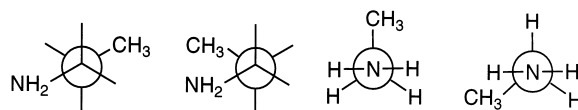


Figure 3. The principal conformations of the ethylamine and propylamine radical cations. (a) and (b) propylamine *trans* and *gauche*; (c) and (d) ethylamine with the methyl group at 90° and 30° with respect to the -NH₂ plane.

Elongated C-C bonds in simple aliphatic radical cations have been reported previously; in a careful *ab initio* study of the ethanol radical cation [27] it was concluded that the unusual C-C bond length is not a computational artefact.

The C-C bond in the ethylamine radical cation can form an angle of 30° or 90° with the -NH₂ plane. The G3 energies of the two conformers are less than 1 mH different when the geometry is optimized at the UMP2(full)/6-31+G(d,p) level; very similar results are obtained with geometries determined at the QCISD/6-31G(d) level. The C-C bond length differs between the two conformations: 1.57 Å (90°) and 1.53 Å (30°).

The calculated C-N bonds in amine radical cations are significantly shorter than in the corresponding neutral amines, e.g. 1.41 vs 1.47 Å for the propylamine radical cation and its neutral counterpart.

4.2. β -distonic ions

The heats of formation of the β -distonic ions examined are lower than those of the corresponding amine radical cations by between 20 and 40 kJ mol⁻¹ (Table 2). The enthalpy difference is to a good approximation equal to the difference between the hydrogen atom affinity [28] of the -NH₂⁺ and the appropriate CH bond dissociation energy. We find that $\Delta H_f(\text{amine } M^+) - \Delta H_f(\text{distonic ion})$ is ~ 23 kJ mol⁻¹ for β -distonic amine radical cations with the unpaired electron at a primary site; the average difference is 34 kJ mol⁻¹ when the β -distonic ion has the unpaired electron at a secondary site (Table 2). These differences correspond well with the enthalpy difference between primary and secondary alkyl radicals [29], which is in good agreement with the

conclusions of Gauld et al. [30], that the heats of formation of distonic ions with charge and radical in non-neighboring positions can be estimated by simple additivity.

Yates and Radom [31] have shown that there is a substantial enthalpy barrier toward the isomerization of amine radical cations to their β -distonic isomers by a 1,3-hydrogen atom shift, and direct spontaneous interconversion is not to be expected under ordinary conditions. The relay mechanism proposed by Audier et al. [7] accounts for the observed relatively facile isomerization of long-chain amine radical cations to the corresponding β -distonic isomers.

We find only slight differences between the heats of formation of the pairs of β -distonic ions that can interconvert by 1,2-NH₃ migration, **10** and **11**, **12** and **13**, and **15** and **16** (Table 4), possibly a slight preference for the isomer with the NH₃⁺ bonded to the more substituted carbon atom and the unpaired electron at a primary site. This illustrates that stabilization of the positive charge by charge-induced dipole interactions between the -NH₃⁺ and the neighboring groups is not much more important than stabilization of the radical site.

The preferred geometry of the β -distonic ions examined is such that the tricoordinate carbon atom is almost planar, and the neighboring C–N bond is nearly perpendicular to this plane. The C–N bonds in the distonic ions are significantly longer than the C–N bonds in the corresponding amine radical cations, e.g. 1.54 Å in **10** and 1.41 Å in **3**. The bond angles around the nitrogen-bearing carbon atom are unexceptional, e.g. the NCC angle in **10** is 110.3°.

4.3. 1,2 migration of NH₃

Experimental studies of the reactions of distonic ions [5] show that the NH₃ group in β -distonic isomers of aliphatic amine radical cations readily migrates to the neighboring radical site. The present results confirm that the enthalpy barriers involved (Table 4) are sufficiently low as to allow facile isomerization in this manner, and they show that the barriers vary with the degree of substitution in the carbon skeleton, from some 100 kJ mol⁻¹ for the

unsubstituted case, **9** \rightleftharpoons **9**, to some 60 kJ mol⁻¹ for **15** \rightleftharpoons **16**.

The energy required for 1,2 migration of the NH₃ is of the same order of magnitude as the heat of reaction for dissociation to give NH₄⁺ and an alkenyl radical (the predominant reaction of small β -distonic amine ions [5]) or the energy required for intramolecular 1,4-hydrogen atom abstraction (the energy-limiting step of the predominant reaction of β -distonic amine ions with long alkyl groups [5,7,8]). The energy required for 1,4-H-atom transfer in alkyl radicals is reported to be between 80 and 100 kJ mol⁻¹ [32].

The isomerization of the β -distonic ions by 1,2 migration of NH₃ involves a three-membered cyclic transition state whose geometry can be described as that of an NH₃ molecule almost symmetrically coordinated to the double bond of an alkene radical cation. The transition state forms an isosceles triangle in the degenerate isomerization reactions, **9** \rightleftharpoons **9** and **14** \rightleftharpoons **14**, and the transition states for the other transformations examined are not very different in this respect. The transition state C–N bond lengths vary from 2.44 Å for **9** \rightleftharpoons **9** to 2.51 Å for **15** \rightleftharpoons **16** (Table 4); in the slightly unsymmetrical transition states, the NH₃ group is closer to the more substituted carbon atom. The carbon skeleton is almost planar (ignoring the terminal CH₃ group in **12** \rightleftharpoons **13**) and the C–C bond is slightly shorter than in the corresponding alkene radical cation, e.g. the C(1)–C(2) distance in **10** is 1.48 Å in the **10** \rightleftharpoons **11** transition state 1.38 Å and in the propene radical cation 1.42 Å. When the gauche conformer of **14** undergoes NH₃ migration, the transition state resembles NH₃ coordinated to ionized *cis*-2-butene, whereas the transition state for isomerization of the *trans* conformer resembles NH₃ coordinated to the *trans*-2-butene radical cation. The energy of the reactant as well as the transition state is slightly lower in the latter case, so that the barrier toward rearrangement is almost the same for the two conformers.

The geometry of the transition state could indicate that the isomerization bears some resemblance to a dissociation–recombination reaction; this would be in line with the observation [33–35] that the bimolecular

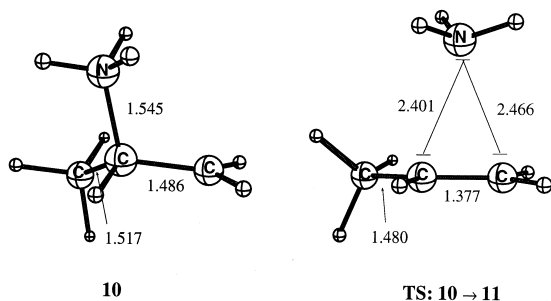


Figure 4. (a) The β -distonic isomer of the propylamine radical cation **10**. (b) The transition state for the interconversion of **10** and **11** by NH_3 migration

reactions of gas-phase alkene radical cations with NH_3 can result in addition, albeit in low yield, with formation of a β -distonic ion. However, the resemblance does not extend to other properties of these systems. The transition state energy is in all cases well below that of the corresponding separated alkene⁺ + NH_3 pair (see Table 4), indicating that considerable covalent bonding is preserved during the isomerization. Furthermore, the reactions of metastable alkan-1-amine radical cations [7,8] illustrate that the NH_3 is tightly bonded during the isomerization. The major reaction of these ions proceeds via 1,2 migration of NH_3 in a β -distonic intermediate; NH_4^+ is formed only as a minor product, even though the energy of the transition state for NH_3 migration is some 30 kJ mol⁻¹ higher than the energy of the products of proton transfer from the alkene radical cation to NH_3 , an alkenyl radical and NH_4^+ (Table 4).

5. Conclusions

The energy barriers for 1,2 migration of NH_3 in protonated β -aminoalkyl radicals are relatively low and the heats of formation of isomers capable of interconversion are not very different, which suggests that protonated β -aminoalkyl radicals should often behave like an equilibrium mixture of the two interconverting species. This is in line with experimental observations regarding these ions in the gas phase, and they could well exhibit similar properties in the condensed phase, inasmuch as the energy of solvation

of the interconverting ions should not be very different. The energy barrier toward migration of NH_3 to a neighboring radical site is sufficiently low as to make it likely that the skeletal rearrangement of straight-chain gaseous alkanamine radical cations, in which the nitrogen moves between neighboring carbon atoms, proceeds by the mechanism suggested by Audier et al. [7].

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