Figure 4. van't Hoff plot. $K = N_G/N_A$.

has been removed from S_G°. The van't Hoff plot shown in Figure 4 yields the results $\Delta E^\circ = 2.2$ ($2\sigma = 1.1$) kcal mol^{-1} and $\Delta S^\circ + R \ln 2 = +0.35$ ($2\sigma = 2.2$) cal mol^{-1} K^{-1}.

To the extent that torsion around the conjugated single bond is a good representation of one of the normal coordinates in DCB, our parameter σ_A provides a crude estimate of the wavenumber for the torsional mode.[11] The result, calculated from the formula $\omega = (2\pi c)^{-1}(k/\mu_1)^{1/2}$ with $k = 0.24$ ($2\sigma = 0.06$) aJ rad^{-2} ($k = V^*/2 = RT/\sigma_A^2$; the value is a weighted average), is 87 ($2\sigma = 11$) cm^{-1}, in excellent agreement with the observed 80 cm^{-1}.

Hydrazinium Radical Cation (NH3NH3+·) and Dication (NH3NH3 2+): Prototypes for the Ionized Forms of Medium-Ring Bicyclic Compounds

Willem J. Bouma and Leo Radom*

Contribution from the Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia. Received June 11, 1984

Abstract: Ab initio molecular orbital theory has been used to study the hydrazinium radical cation (NH3NH3+·, **5**) and dication (NH3NH3 2+, **6**) as prototypes for the ionized forms of medium-ring bicyclic compounds. The radical cation **5** is characterized by a long N···N bond (2.164 Å) but is nevertheless bound by 134 kJ mol^{-1} with respect to NH3 + NH3+·. In the dication **6**, the N–N bond is markedly reduced (to 1.442 Å). Although dissociation of **6** to 2NH3+· is exothermic by 249 kJ mol^{-1}, this process involves a large activation barrier (194 kJ mol^{-1}). The results suggest that suitably constructed propellane analogues of **6** involving appropriate-sized bridges might exhibit bond-stretch isomerism.

The chemistry of medium-ring bicyclic compounds has flourished recently in the hands of Alder and co-workers.[1-5] In particular, they have been able to synthesize a variety of bicyclic diamines (**1**) and the corresponding radical cations (**2**) and dications (**3**). These systems are of theoretical interest since they
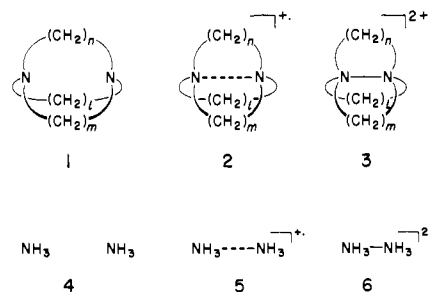
(1) Alder, R. W. *Acc. Chem. Res.* **1983**, *16*, 321 and references therein.
(2) (a) Alder, R. W.; Moss, R. E.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 997. (b) Alder, R. W.; Orpen, A. G.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 999. (c) Alder, R. W.; Moss, R. E.; Sessions, R. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1000. (d) Alder, R. W.; Sessions, R. B.; Gmünder, J. O.; Grob, C. A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 411.
(3) (a) Alder, R. W.; Sessions, R. B.; Mellor, J. M.; Rawlins, M. F. *J. Chem. Soc., Chem. Commun.* **1977**, 747. (b) Alder, R. W.; Sessions, R. B.; Bennet, A. J.; Moss, R. E. *J. Chem. Soc., Perkin Trans. 1* **1982**, 603.
(4) Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651.
(5) Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

include constrained interbridgehead interactions involving four, three, and two electrons, respectively. The characterization of the resulting rather unusual bonds is a tempting target for theoretical investigation. The medium-ring bicyclic systems themselves (**1-3**) are rather too large to lend themselves to reliable ab

Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol⁻¹)[a]

	3-21G[b]	6-31G*	6-31G**	MP3/6-31G*	ZPVE[b]
$NH_3NH_3^{+\cdot}$, **5**	-111.499 52	-112.096 13	-112.118 21	-112.443 89	206.7
$NH_4NH_2^{+\cdot}$, **7**	-111.529 89	-122.124 09	-112.146 00	-112.457 27	200.9
NH_3	-55.872 20	-56.184 36	-56.195 53	-56.365 44	94.6
$NH_3^{+\cdot}$	-55.576 26	-55.873 24	-55.884 89	-56.019 18	89.5
NH_4^+	-56.233 86	-56.530 77	-56.545 52	-56.712 90	138.1
$NH_2^{\cdot}$	-55.245 38	-55.557 70	-55.564 82	-55.705 47	51.4
$NH_3NH_3^{2+}$, **6**	-111.016 23	-111.613 30	-111.635 71	-112.010 79[d]	223.2
TS(**6** → $2NH_3^{+\cdot}$),[c] **8**	-110.973 81	-111.560 67	-111.583 43	-111.929 05[d]	199.8
TS(**6** → $NH_3NH_2^+ + H^+$), **9**	-110.812 58	-111.419 55	-111.437 23	-111.811 57[d]	192.3
$NH_3^{+\cdot}$	-55.576 26	-55.873 24	-55.884 89	-56.045 14[d]	89.5
$NH_3NH_2^+$	-110.910 20	-111.518 33	-111.536 32	-111.909 07[d]	187.7

[a] 6-31G*-optimized structures unless otherwise noted. [b] 3-21G-optimized structures. [c] UHF solution. [d] MP3/6-31G** values.

initio calculations with currently available resources. However, the prototype systems **4–6** may be studied. In the case of the neutral system **4**, nitrogen-to-nitrogen approach of the two ammonia molecules is repulsive, and so **4** cannot serve as a structural model for **1**; the latter is held together by the bicyclic backbone. On the other hand, the hydrazinium radical cation (**5**) and dication (**6**) are well bound and can serve as useful models for **2** and **3** with appropriate bridges. Accordingly, and as part of our continuing interest in radical cations and dications,[6] we report results in this paper of a study of the structures and stabilities of the hydrazinium radical cation (**5**) and dication (**6**).

Method and Results

Standard ab initio molecular orbital calculations were carried out by using a modified version[7] of the GAUSSIAN 80 system of programs.[8] Optimized structures were obtained with the split-valence 3-21G[9] and split-valence-plus d polarization 6-31G*[10] basis sets. Improved relative energies were obtained for the 6-31G*-optimized structures with the split-valence-plus dp polarization 6-31G** basis set[10] and with electron correlation incorporated via Møller-Plesset perturbation theory terminated at third order (MP3).[11] Harmonic vibrational frequencies were calculated[12] at the 3-21G//3-21G level in order to characterize stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point vibrational energies. For some of the species investigated, frequencies were also evaluated at the 6-31G*//6-31G* level. The frequencies were scaled by 0.9 to account for their overestimation by ~10% at these levels of theory.[13] The spin-unrestricted formalism (UHF, UMP) was used for odd-electron species and for transition structures linking even- and odd-electron species.

Optimized structures for $NH_3NH_3^{+\cdot}$ (**5**), $NH_3NH_3^{2+}$ (**6**), and related transition structures and fragmentation products are displayed in Figure 1 (bond lengths in angstroms, bond angles in degrees). Corresponding total energies and zero-point vibrational energies are listed in Table I, while relative energies are shown in Table II. Calculated (6-31G*//6-31G*) frequencies for $NH_3NH_3^{+\cdot}$ and $NH_3NH_3^{2+}$ are listed in Table III. A schematic energy profile showing possible fragmentation reactions of $NH_3NH_3^{2+}$ (**6**) is presented in Figure 2.

Discussion

Hydrazinium Radical Cation ($NH_3NH_3^{+\cdot}$, 5). We are not aware of any experimental studies reported to date involving the hy-

(6) For leading references, see: Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484.

(7) Farnell, L.; Nobes, R. H.; Poppinger, D., unpublished results.

(8) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Khan, L. R.; Pople, J. A. *QPCE* **1981**, *13*, 406.

(9) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(10) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(11) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Symp.* **1976**, *10*, 1.

(12) Using a program written by Dr L. Farnell.

(13) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Symp.* **1981**, *15*, 269.

Table II. Calculated Relative Energies (kJ mol⁻¹)[a]

	3-21G[b]	6-31G*	6-31G**	MP3/6-31G**	MP3/6-31G**[c]
$NH_3NH_3^{+\cdot}$, **5**	0	0	0	0	0
$NH_4NH_2^{+\cdot}$, **7**	-80	-73	-73	-35[d]	-40
$NH_3 + NH_3^{+\cdot}$	134	101	99	154[d]	134
$NH_4^+ + NH_2^{\cdot}$	53	20	21	68[d]	53
$NH_3NH_3^{2+}$, **6**	0	0	0	0	0
TS(**6** → $2NH_3^{+\cdot}$),[e] **8**	111	138	137	215	194
TS(**6** → $NH_3NH_2^+ + H^+$), **9**	535	509	521	523	495
$NH_3^{+\cdot} + NH_3^{+\cdot}$	-358	-350	-352	-209	-249
$NH_3NH_2^+ + H^+$	278	249	261	267	235

[a] 6-31G*-optimized structures unless otherwise noted. [b] 3-21G-optimized structures. [c] Including zero-point vibrational contribution. [d] Evaluated using the additivity relationship $\Delta E(MP3/6-31G^{**}) = \Delta E(MP3/6-31G^*) + \Delta E(HF/6-31G^{**}) - \Delta E(HF/6-31G^*)$ (cf.: Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497). [e] UHF solution.

Table III. Calculated[a] and Experimental[b] Vibrational Frequencies (cm⁻¹) for $NH_3NH_3^{+\cdot}$ (**5**) and $NH_3NH_3^{2+}$ (**6**)

| | | $NH_3NH_3^{+\cdot}$ | $NH_3NH_3^{2+}$ | |
		calcd	calcd	exptl
a_{1u}	torsion	79	272	<260[c]
a_{1g}	ν_{NN}	426	996	1027
e_u	ρ_{NH_3}	508	1036	1096
e_g	ρ_{NH_3}	544	1315	1105
a_{2u}	δ_{NH_3}	446	1558	1485
e_u	δ_{NH_3}	1594	1578	1613
a_{1g}	δ_{NH_3}	1098	1609	1524
e_g	δ_{NH_3}	1607	1629	1599
a_{2u}	ν_{NH}	3310	3092	2600
a_{1g}	ν_{NH}	3327	3127	2650
e_g	ν_{NH}	3475	3183	2745
e_u	ν_{NH}	3475	3188	2739

[a] 6-31G*//6-31G* values, scaled by 0.9. [b] From ref 17a,b unless otherwise noted. [c] Estimated value for free ion, taken from ref 17c.

drazinium radical cation ($NH_3NH_3^{+\cdot}$, **5**). Our calculations indicate a preferred staggered conformation for **5** with D_{3d} symmetry. The most striking feature of the structure of the hydrazinium radical cation (Figure 1) is the very long N⋯N bond: 2.164 Å with 6-31G*. This corresponds formally to a three-electron (two σ plus one σ*) σ bond. A similarly long bond (2.16 Å) was obtained for the 4-31G optimized structure for **5**.[14] The parameters within the NH_3 groups have values intermediate between those in NH_3 and $NH_3^{+\cdot}$, as might have been expected. No crystal structural data, either for **5** or for any of the bicyclic compounds **2**, are currently available.

Despite the long N⋯N bond in **5**, the calculated binding energy with respect to dissociation to $NH_3 + NH_3^{+\cdot}$ is quite large at 134

(14) Reference 10 of ref 4.

Hydrazinium Radical Cation and Dication

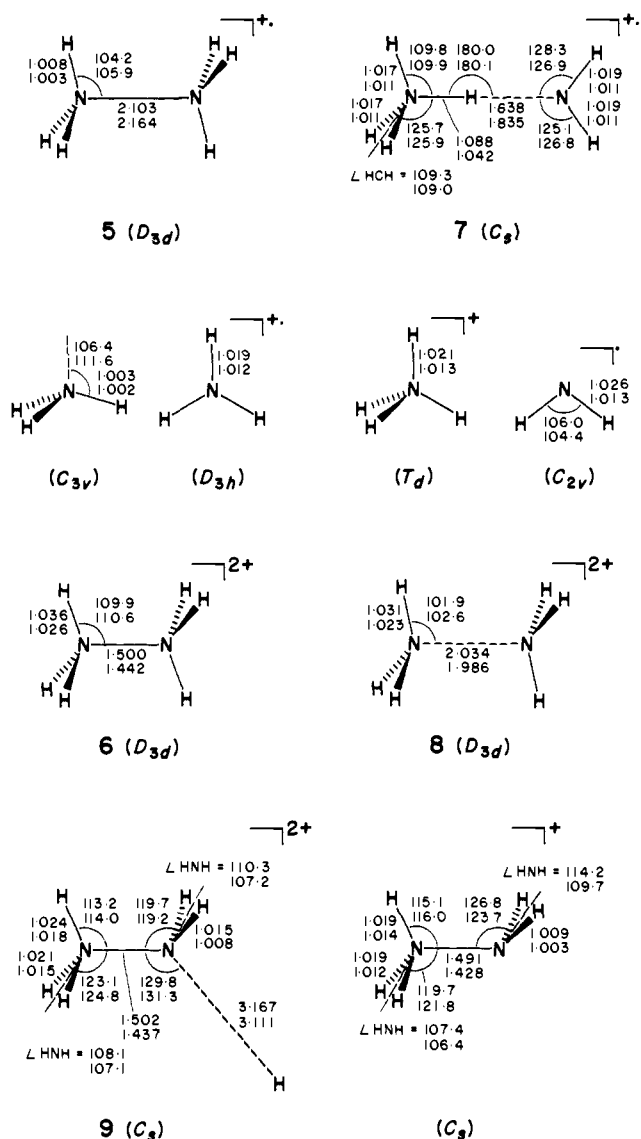*J. Am. Chem. Soc., Vol. 107, No. 2, 1985* 347

Figure 1. Optimized structural parameters (in the order 3-21G, 6-31G*) for the hydrazinium radical cation (**5**), dication (**6**), and related systems.
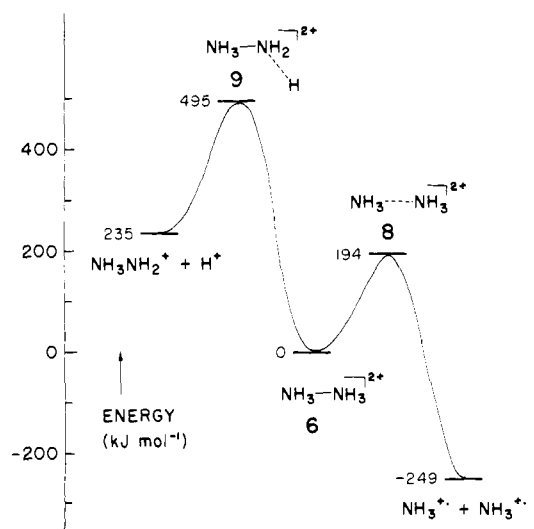

Figure 2. Schematic potential energy profile (MP3/6-31G**//6-31G* including zero-period vibrational contribution) for possible dissociation processes of the hydrazinium dication (**6**).

kJ mol⁻¹. Indirect experimental estimates[5] of the strength of the three-electron σ N⋯N bond in the ring systems **2** are somewhat lower: 61 kJ mol⁻¹ from the free energy of activation for disso-

ciation of **10** and 45-90 kJ mol⁻¹ from gas-phase proton affinity and ionization energy measurements for **11**.
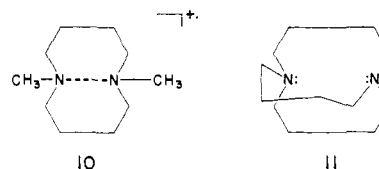
Although formation of $NH_3NH_3^+\cdot$ (**5**) from NH_3 and $NH_3^+\cdot$ is exothermic by 134 kJ mol⁻¹, the gas-phase ion–molecule reaction of $NH_3^+\cdot$ with NH_3 is unlikely to produce **5**. Instead, the hydrogen-bonded complex $NH_4\cdots NH_2^+\cdot$ (**7**), lying 40 kJ mol⁻¹ below **5**, is likely to be formed.[15] The binding energy of **7** with respect to $NH_4^+ + NH_2\cdot$ is 93 kJ mol⁻¹.

Hydrazinium Dication ($NH_3NH_3^{2+}$, 6). The hydrazinium dication (**6**), as well as serving as a model for the propellane **3**, has also attracted considerable previous attention in its own right. Of particular relevance to the present study are X-ray and neutron diffraction studies of the crystal structures of a number of hydrazinium salts (e.g., $N_2H_6F_2$).[16] In addition, infrared spectra and normal coordinate analyses have been reported,[17] and both experimental[18] and theoretical[19] aspects of the NMR spectrum have been investigated.

Our own calculations show that removal of an electron from the hydrazinium radical cation (**5**) to give the dication (**6**) leads to a dramatic reduction in the N–N bond length from 2.164 to 1.442 Å. This is associated with the change from a three-electron σ bond in **5** to a two-electron σ bond in **6**. The available crystal structures for a number of hydrazinium salts[16] show N–N bond lengths of 1.41–1.44 Å, in close agreement with our calculated value. A previous 4-31G calculation[14] yielded 1.46 Å.

Alder[1,5] has noted that diamines of the type **1** are among the most easily ionized of all saturated compounds and that in solution they are also readily oxidized, producing dications (**3**) via very long-lived radical cations (**2**). Our calculations are consistent with such observations. Thus, adiabatic ionization from a pair of NH_3 molecules to give $NH_3\cdots NH_3^+\cdot$ (**5**) requires 7.8 eV (MP3/6-31G*//6-31G*), somewhat less than the corresponding IE_a for $NH_3 \rightarrow NH_3^+\cdot$ (9.4 eV). Subsequent ionization to give the dication requires 13.2 eV in the case of $NH_3\cdots NH_3^+\cdot$ (**5**) $\rightarrow$ $NH_3-NH_3^{2+}$ (**6**), which is considerably lower than the 23.1 eV calculated[20] for the process $NH_3^+\cdot \rightarrow NH_3^{2+}$. Ionization of **4** and **5** formally involves removal of σ* electrons from the N–N bond, and it is not surprising, therefore, that it is relatively facile.

Harmonic vibrational frequencies calculated (6-31G*//6-31G* scaled by 0.9) for $NH_3NH_3^{2+}$ (**6**) are compared with experimental values (for $NH_3NH_3Cl_2$)[17a,b] in Table III. The discrepancy between the theoretical and experimental values (see, for example,

(15) For studies of the analogous $H_3O\cdots OH^+\cdot$ system, see: (a) Sato, K.; Tomoda, S.; Kimura, K.; Iwata, S. *Chem. Phys. Lett.* **1983**, *95*, 579. (b) Curtiss, L. A. *Chem. Phys. Lett.* **1983**, *96*, 442.

(16) See, for example: (a) Kronberg, M. L.; Harker, D. *J. Chem. Phys.* **1942**, *10*, 309. (b) Donohue, J.; Lipscomb, W. N. *J. Chem. Phys.* **1947**, *15*, 115. (c) Liminga, R. *Acta Chem. Scand.* **1966**, *20*, 2483. (d) Jonsson, P. G.; Hamilton, W. C. *Acta Crystallogr., Sect. B* **1970**, *B26*, 536. (e) Kojic-Prodic, B.; Scavnicar, S.; Matkovic, B. *Acta Crystallogr., Sect. B* **1971**, *B27*, 638. (f) Anderson, M. R.; Vilminot, S.; Brown, I. D. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2961. (g) Power, L. F.; Turner, K. E.; King, J. A.; Moore, F. H. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2470. (h) Frlec, B.; Gantar, D.; Golic, L.; Leban, I. *Acta Crystallogr., Sect. B* **1981**, *B37*, 666.

(17) (a) Snyder, R. G.; Decius, J. C. *Spectrochim. Acta* **1959**, *13*, 280. (b) Mielke, Z.; Ratajczak, H. *J. Mol. Struct.* **1973**, *19*, 751. (c) Ludman, C. J.; Ratcliffe, C. I.; Waddington, T. C. *J. Chem. Soc., Faraday Trans 2* **1976**, *72*, 1741.

(18) (a) Deeley, C. M.; Lewis, P.; Richards, R. E. *Trans. Faraday Soc.* **1954**, *50*, 556. (b) Deeley, C. M.; Richards, R. E. *Trans. Faraday Soc.* **1954**, *50*, 560. (c) Morton, T. P.; Howell, F. L. *Mol. Phys.* **1971**, *20*, 1147. (d) Harrell, J. W.; Howell, F. L. *J. Magn. Reson.* **1972**, *8*, 311. (e) Harrell, J. W.; Peterson, E. M. *J. Chem. Phys.* **1975**, *63*, 3609.

(19) (a) Schulman, J. M.; Ruggio, J.; Venanzi, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2045. (b) Schulman, J. M.; Lee, W. S. *J. Magn. Reson.* **1982**, *50*, 142.

(20) Relevant calculated total energies (MP3/6-31G*//6-31G*) not included in Table I are NH_3^{2+}, -55.168 48, and $NH_3NH_3^{2+}$, -111.960 42 hartrees.

the N–H stretching frequencies) is larger than normally found at this level of theory and suggests the likelihood of intermolecular association, contributing to the experimental frequencies. Intermolecular hydrogen bonding weakens the N–H bonds, leading to a reduction in the observed vibrational frequencies. Yamaguchi and Schaefer[21] have noted a similar poor agreement between calculated and experimental (solid state) N–H frequencies for the NH_4^+ ion. The immediate environment of the NH_3^+ groups in $NH_3NH_3Cl_2$ is quite similar to that of the NH_4^+ in NH_4F, the acceptor ions being placed so as to maintain local symmetry.[22] Accordingly, the experimental[23] N–H stretching frequencies in NH_4F of 2870 (a_1) and 2815 (t_2) cm^{-1} are again considerably lower than (and in the reverse order of) our scaled 6-31G* values of 3214 and 3343 cm^{-1}, respectively.[24] Better agreement (and the correct ordering) is found[21] between calculated and experimental frequencies in less strongly hydrogen-bonding environments.[25] Recently, a gas-phase value (3335 cm^{-1}) has been determined[26] for the t_2 vibration of NH_4^+ and this is close to our calculated value (3343 cm^{-1}).

Dissociation of **6** to two molecules of $NH_3^+\cdot$ is exothermic by 249 kJ mol^{-1}. However, the activation energy for this process, which proceeds via transition structure **8**, is also large at 194 kJ mol^{-1}. These results suggest the intriguing possibility that for appropriate-sized rings, it may be possible to generate not only the closed propellane dications of the type **3** but also the isomeric open ions **3'**. This would represent an elegant example of

3'
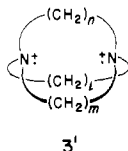
bond-stretch isomerism.[27] The ring sizes (i.e., values of *l*, *m*, and *n* in **3'**) would need to be sufficiently large to accommodate an N···N distance which exceeds the value in transition structure **8** (1.986 Å) by a comfortable margin. Bond-stretch isomerism generally involves the subtle interplay of through-space (favoring the closed isomer) and through-bond (favoring the open isomer)

interactions.[27] It has been found, however, that in the bicyclic compounds with trimethylene and tetramethylene bridges, through-bond interaction is unimportant.[5] Accordingly, an alternative driving force is necessary to create the preconditions for bond-stretch isomerism in such systems. The driving force for formation in our case of the open isomer **3'** is the desire, once the N···N bond is broken, for the nitrogen-centered radical cation moieties to separate as far as possible (cf. Figure 2).

An additional point of interest from Figure 2 is the formation of $NH_3NH_3^{2+}$ (**6**) by protonation of protonated hydrazine ($NH_3NH_2^+$).[28] This process is exothermic by 235 kJ mol^{-1}, but it needs to overcome a barrier, presumably electrostatic in origin, of 260 kJ mol^{-1}. We note in passing that the calculated N–N length in $NH_3NH_2^+$ (1.428 Å) compares favorably with values obtained (1.42–1.44 Å)[29] for crystalline salts.

Dications have recently become accessible in the gas phase through charge-stripping mass spectrometry experiments.[30] Can $NH_3NH_3^{2+}$ be generated in this way? Our calculations predict that this is not likely to be the case. Vertical ionization from $NH_3NH_3^+\cdot$ with its long N···N bond (2.164 Å) will yield the dication with an N···N bond longer than that in the transition structure for dissociation (1.986 Å in **8**). Charge stripping from $NH_3NH_3^+\cdot$ is thus likely to be accompanied by dissociation of the resulting dication.

Conclusions

Several important points emerge from this study.

(i) The hydrazinium radical cation ($NH_3NH_3^+\cdot$, **5**) and dication ($NH_3NH_3^{2+}$, **6**) provide information which may prove useful in studies of corresponding medium-ring bicyclic and propellane structures **2** and **3**.

(ii) The hydrazinium radical cation ($NH_3NH_3^+\cdot$, **5**) has a long N···N bond (2.164 Å) but is well bound (by 134 kJ mol^{-1}) with respect to $NH_3 + NH_3^+\cdot$.

(iii) The hydrazinium dication ($NH_3NH_3^{2+}$, **6**) has a much shorter N–N bond (1.442 Å).

(iv) Dissociation of **6** to $2NH_3^+\cdot$ is strongly exothermic (by 249 kJ mol^{-1}) but requires a large barrier (194 kJ mol^{-1}). These results suggest the possibility of bond-stretch isomerism in propellane analogues of **6** with appropriate-sized bridges.

(21) Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* **1980**, *73*, 2310.
(22) Knop, O.; Oxton, I. A.; Falk, M. *Can. J. Chem.* **1979**, *57*, 404.
(23) Plumb, R. C.; Hornig, D. F. *J. Chem. Phys.* **1955**, *23*, 947.
(24) Other calculated values are 1478 (t_2) and 1687 (e) cm^{-1} compared with the experimental 1494 (t_2) and 1754 (e) cm^{-1}.
(25) (a) Mathieu, J. P.; Poulet, H. *Spectrochim. Acta* **1960**, *16*, 696. (b) Fredrickson, L. R.; Decius, J. C. *J. Chem. Phys.* **1977**, *66*, 2297.
(26) Schwarz, H. A. *J. Chem. Phys.* **1980**, *72*, 284.
(27) (a) Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661. (b) Gleiter, R.; Stohrer, W. D.; Hoffmann, R. *Helv. Chim. Acta* **1972**, *55*, 893. (c) Gregory, A. R.; Paddon-Row, M. N.; Radom, L.; Stohrer, W. D. *Aust. J. Chem.* **1977**, *30*, 473.

(28) For previous calculations on $NH_3NH_2^+$, see also: Del Bene, J. A.; Frisch, M. J.; Raghavachari, K.; Pople, J. A. *J. Phys. Chem.* **1982**, *86*, 1529.
(29) See, for example: (a) Padmanabhan, V. M.; Balasubramanian, R. *Acta Crystallogr.* **1967**, *22*, 532. (b) Nilsson, A.; Liminga, R.; Olovsson, I. *Acta Chem. Scand.* **1968**, *22*, 719. (c) Thomas, J. O. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1767. (d) Chiglien, P. G.; Etienne, J.; Jaulmes, S.; Laruelle, P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2229. (e) Lazarini, F.; Vardjan-Jarec, M. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2355. (f) Bukovec, P.; Golic, L. *Acta Crystallogr., Sect. B* **1976**, *B32*, 948.
(30) See, for example: (a) Cooks, R. G.; Ast, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 490. (b) Ast, T. *Adv. Mass Spectrom.* **1980**, *8*, 555.