Structure and Relative Energies of Some Nitrogen-containing Radical Cations by MNDO Calculation†

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MNDO calculations have been performed on the energy surfaces of four nitrogen-containing radical cations: $[CH_3N]^{\cdot+}$, $[CH_5N]^{\cdot+}$, $[N_2H_4]^{\cdot+}$, and $[N_2H_2]^{\cdot+}$. In general, the calculated structures and relative energies compare well with *ab initio* calculations and experiment (when available). The MNDO method overestimates the stabilities of non-classical isomers and consequently underestimates the energy barriers of 1,2-hydrogen shifts connecting both classical and non-classical species. The energy barriers for the loss of H atoms from X atoms (H–X–N–) are overestimated while those from N atoms (–X–N–H) are underestimated. Specific fragmentations or isomerization within each radical cation are also commented on. The results on the whole suggest that MNDO is a suitable method in this area.

Knowledge of the structures and relative stabilities of cation and radical cation isomers is of prime importance in interpreting data from mass spectroscopy[1] and astrochemistry.[2] Since these species exist in the gas phase, they constitute the ideal, and also one of the greatest challenges for quantum-mechanical methods. For this reason, theoretical studies on small cations and radical cations have long attracted the attention of a number of authors.[3] In many cases the most stable structure of a cation or a radical cation cannot simply be derived from the most stable neutral structure (for example, HNC^+ is of lower energy than HCN^+ [4]), so it is imperative to explore the whole energy surface of the ion or radical ion. This implies that, even for a small species containing, for example, three heavy atoms, the energy surface already shows a number of stationary points to be located and characterized, together with the saddle points connecting different isomers or relating to fragmentation pathways. Accordingly, the study of such a species by employing an *ab initio* method at an appropriate level, *e.g.* including both polarization functions and electron-correlation energies in the wavefunctions, requires very extensive computer time. The field of application is thus consequently limited.

Our current interest in the interpretation of mass spectra [5,6] and chemical processes of interstellar molecules [7] by means of quantum-mechanical calculations prompts us to investigate the MNDO method as an alternative to the expensive *ab initio* studies for larger systems. Several systematic MNDO studies have been reported on closed-shell cations [8] which mainly concerned the evaluation of the proton affinities. On the contrary, there exist only a few MNDO calculations on open-shell radical cations.[9] These latter however do not bear directly on the suitability of the method in this area.

The main purpose of the present paper is to provide a primary test concerning the limit of MNDO predictions on structures and relative stabilities of radical cations. As test cases, we examine four nitrogen-containing radical cations for which data obtained partly from experiment (collisional activation mass spectra) [10] and systematic extensive *ab initio* calculation (MP4/6-31G**) [11] have recently been reported.

In general, for each system of stoicheiometric formula $[H_{m+n}\text{-}X\text{-}N]^{\cdot+}$ (where X is C or N and $m + n = 2$—5) we consider two stable isomers (local minima) $[H_mX-NH_n]^{\cdot+}$ and $[H_{m-1}X-NH_{n+1}]^{\cdot+}$ or $[H_{m+1}X-NH_{n-1}]^{\cdot+}$ together with the 1,2-hydrogen shift transition structure connecting them. Further, for each isomer, the hydrogen-elimination reaction (1)

$$[H_{m+n}X\text{-}N]^{\cdot+} \longrightarrow H^{\cdot} + [H_{m+n-1}X\text{-}N]^+ \qquad (1)$$

and other specific fragmentations or isomerizations are also examined.

Calculations

All calculations were carried out making use of the standard MNDO method [12] implemented on a VAX 11/780 computer with RHF (restricted Hartree–Fock) open-shell wavefunctions. The classic Davidon–Fletcher–Powell algorithm [13] was used to optimize the geometries of minima or to minimize the total energy with respect to internal co-ordinates. For locating the saddle points, we obtained rather unsatisfactory results with the procedure recently proposed by Dewar *et al.*[14] For this purpose, we used instead the distinguished reaction co-ordinate approach. For simple reactions such as 1,2-hydrogen shifts or hydrogen eliminations examined in this work, the corresponding transition structures are obtained unambiguously by this procedure.[15]

The MNDO-optimized geometries of the radical cations considered are collected in Table 1. The calculated and experimental (when available) heats of formation of small cations, radicals, and radical cations resulting from the fragmentations of $[H_{m+n}XN]^{\cdot+}$ species are summarized in Table 2.

In comparing the MNDO geometric parameters with *ab initio* results, we used the HF/6-31G* geometries available in ref. 16. For the isomerization energies, we employed the values reported by Frisch and co-workers [11] at the MP4SDTQ/6-31G**//6-31G* level and corrected for zero-point vibrational energies. For simplicity, they will be denoted as MP4.

Results and Discussion

(*a*) $[CH_3N]^{\cdot+}$.—Table 3 summarizes the calculated and experimental heats of formation and relative energies of six $[CH_3N]^{\cdot+}$ species including: two minima, the ionized formaldimine (**1**) and the ionized aminocarbene (**2**); three

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† *Non-S.I. units employed:* cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J.

Table 1. MNDO geometric parameters for radical cation systems. Bond lengths in Å, bond angles in °

(*a*) $[CH_3N]^{\cdot +}$

(1) (C_s) CN 1.258, CH 1.108, CH^1 1.107, NH 1.001; HCN 122.2, H^{1}CN 120.4, HNC 157.7
(2) (C_s) CN 1.273, CH 1.070, NH 1.015, NH^1 1.017; HCN 155.4, HNC 123.9, H^{1}NC 120.8
(3) (C_s) CN 1.242, CH 1.077, NH 1.007, CH^1 1.381; NH^1 1.311, HCN 155.6, HNC 148.6, H^{1}CN, 59.7
(4) (C_s) CN 1.160, CH 1.076, NH 1.000, CH^1 1.775; HCN 170.4, HNC 177.7, H^{1}CN 106.8
(5) (C_1) CN 1.162, CH 1.072, NH 1.006, NH^1 1.651; HCN 176.2, HNC 167.7, H^{1}NCH 9.0

(*b*) $[CH_5N]^{\cdot +}$

(7) (C_s) CN 1.446, CH^1 1.121, CH 1.014($\times$2), NH 1.012($\times$2); H^{1}CN 106.7, HCN 110.3($\times$2), HNC 122.0, HCNH^1 ±118.5, HNCH^1 ±89
(8) (C_s) CN 1.466, CH 1.086($\times$2), NH^1 1.028, NH 1.027($\times$2); HCN 117.7, H^{1}NC 110.2, HNC 111.5($\times$2), HCNH^1 ±88.5, HNCH^1 ±119.8
(9) (C_s) CN 1.426, CH^1 1.380, NH^1 1.314, CH 1.098($\times$2), NH 1.015($\times$2); H^{1}CN 55.8, HCN 119.0($\times$2), HNC 119.9($\times$2), HCNH^1 ±101.8, HNCH^1 ±102.5
(10) (C_s) CN 1.315, CH^1 1.855, CH 1.103($\times$2), NH 1.011($\times$2); H^{1}CN 104.6, HCN 120.8($\times$2), HNC 122.8($\times$2), HCNH^1 ±94.1, HNCH^1 ±89.0
(11) (C_s) CN 1.314, CH 1.103($\times$2), NH^1 1.665, NH 1.014($\times$2); HCN 121.5($\times$2), H^{1}NC 113.3; HNC 122.9($\times$2), HCNH^1 ±90.2, HNCH^1 ±93.2

(*c*) $[N_2H_4]^{\cdot +}$

(13) (C_{2h}) NN 1.300, NH 1.021($\times$4); HNN 118.6($\times$4), H^{1}NNH 15.0($\times$2), HNNH 165.0($\times$2)
(14) (C_s) NN 1.402, NH 1.019, NH$_a$ 1.036($\times$2), NH^1 1.041; HNN 110.9, H$_a$NN 113.1($\times$2), H^{1}NN 107.7, H$_a$NNH^1 118.2($\times$2)
(15) (C_s) NN 1.370, NH 1.017, N^{1}H$_a$ 1.025($\times$2), N^{1}H^1 1.396; HN^{2}N^1 125.4, H$_a$NN 115.4($\times$2), H^{1}N^{1}N^2 55.7, H$_a$NNH^1 116.5($\times$2)
(16) (C_1) NN 1.232, NH$_a$ 1.034, NH$_b$ 1.032, NH 1.031, N^{2}H^1 2.051; H$_a$NN 118.2, H$_b$NN 127.3, HNN 115.7, H^{1}NN 114.3, H^{1}NNH$_a$ 5.1
(17) (C_1) NN 1.241, NH$_a$ 1.037, NH$_b$ 1.033, NH 1.029, N^{1}H^1 1.752; H$_a$NN 117.3, H$_b$NN 126.6, H^{1}NN 116.0, HNN 106.6, HNNH$_b$ −5.8, H^{1}NNH 92.8

(*d*) $[N_2H_2]^{\cdot +}$

(19) (C_{2h}) NN 1.165, NH 1.032($\times$2); HNN 130.9
(20) (C_{2v}) NN 1.142, NH 1.030($\times$2); HNN 146.6
(21) (C_{2v}) NN 1.210, NH 1.038($\times$2); HNN 122.8
(22) (C_s) NN 1.146, N^{1}H 1.039, N^{2}H 1.021; HN^{1}N^2 131.0, HN^{2}N^1 175.9
(23) (C_c) NN 1.180, N^{2}H^1, 1.390, N^{1}H^1 1.343, N^{1}H 1.028; H^{1}N^{2}N^1 66.5, HN^{1}N^2 140.3
(24) (C_1) NN 1.106, N^{2}H^1 1.898, N^{1}H 1.027; H^{1}N^{2}N^1 124.3, HN^{1}N^2 178.8, H^{1}N^{2}N^{1}H 3.0
(25) (C_s) NN 1.118, H^{1}N^1 1.662, HN^1 1.030; HN^{1}N^2 162.9, H^{1}N^{1}N^2 110.1, H^{1}N^{1}N^{2}H 4.6

Table 2. Calculated and experimental heats of formation (kcal mol^{-1}) of fragments

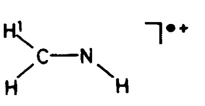
	ΔH_f	
Species	MNDO	Exptl.*
$H^{\cdot}$	52.1	52
$[HCNH]^+$	227.0	226
$[CH_3]^+$	243.9	261
$NH_2^{\cdot}$	37.3	41
$[CH_2]^{\cdot +}$	299.9	334
NH_3	−6.0	−11
$[H_2CNH_2]^+$	187.0	178
$[H_2NNH]^+$	231.8	–
$[HNN]^+$	244.7	

* H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**, Suppl. 1.

Table 3. Energy characteristics (kcal mol^{-1}) of $[CH_3N]^{\cdot +}$ isomers

	ΔH_f		Relative energies		
Species[a]	MNDO	Exptl.[b]	MNDO	MP4[c]	Exptl.[b]
(1) (min.)	251.6	252	0.0	0.0	0
(2) (min.)	239.4	258	−12.2	−6.2	6
(3) (t.s./1,2-H)	300.9	>317	49.3	—	>65
(4) (t.s./addition at C)	289.9	–	38.3	—	—
(5) (t.s./addition at N)	299.8	313	48.2	—	61
(6) $H^{\cdot}$ + $HCNH^+$ (min.)	279.1	278[d]	27.5	—	26[d]

[a] min. = Local minimum; t.s. = transition state. [b] From ref. 10. [c] From ref. 11. [d] See Table 2.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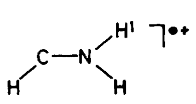
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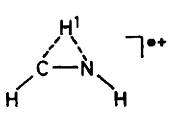
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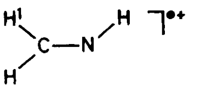
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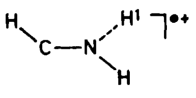
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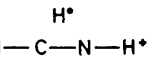

(6)

transition states, (**3**) related to the 1,2-hydrogen shift connecting (**1**) and (**2**) and (**4**) and (**5**) corresponding to the $H^{\cdot}$ loss from (**1**) and (**2**) respectively, leading in both cases to the system $H^{\cdot}$ + $HCNH^+$ (**6**).

The CN bond lengths of 1.258 and 1.273 Å in both species (**1**) and (**2**), respectively (Table 1) are slightly larger than the 6-31G* values of 1.243 and 1.251 Å. Both methods predict however that the CN distance in (**1**) is shorter than that in (**2**). In contrast, the bond angles HNC 157.7° in (**1**) and HCN 155.4° in (**2**) are both overestimated with respect to the 6-31G* ones of 148.6 and 131.8°, respectively. In line with the MP4 results, MNDO predicts a reversal of the relative stabilities within both $[CH_3N]^{\cdot +}$ isomers compared with those of neutral species. The non-classical cation (**2**) is for instance 12 kcal mol^{-1} (6 kcal mol^{-1} by MP4) *lower* in energy than the classical isomer (**1**). This theoretical finding is however in disagreement with experiment[10] where the heat of formation of species (**2**) was measured [by CA (collisional activation) mass spectroscopy] to be of 6 kcal mol^{-1} *higher* than that of (**1**). Since the reversed stability ordering of the radical cations is of general interest, further investigations are desirable to clarify this discrepancy.

The 1,2-hydrogen shift transition structure (**3**) connecting both minima (**1**) and (**2**) has a planar geometry with a bond

Table 4. Comparison between characteristics of the additions $H^\bullet + HCNH^+$ and $H^\bullet + HCO^+$

		$H^\bullet + HCNH^+$		$H^\bullet + HCO^+$		
		MNDO[a]	Exptl.[b]	MNDO[c]	*ab initio*	Exptl.[d]
$\Delta E^{\ddagger}$ [e]	addition at C	10.8	—	8.6	8.3	<5
	addition at N or O	20.7	35 ± 2	18.9	29.3	25
l.u.m.o.[f]	ε	−6.1		−7.6		
	C(C atom)	0.80		0.83		
	C(N or O atom)	0.60		0.56		

[a] This work. [b] From ref. 10. [c] From ref. 18; *ab initio* results at MP2/6-31G** level. [d] From P. C. Burgers, A. A. Mommers, and J. L. Holmes, *J. Am. Chem. Soc.*, 1983, **105**, 5976. [e] In kcal mol^{-1}. [f] Energies (eV) and coefficients of the l.u.m.o. in $HCNH^+$ and HCO^+, respectively.

angle H^1CN of 59.7° and lies *ca.* 61 kcal mol^{-1} above (**2**). This energy barrier compares well with the experimental values of >59 kcal mol^{-1} found for the isomerization (**2**) $\longrightarrow$ (**1**).[10] It should be noted that the 1,2-hydrogen shift in neutral CH_3N has been shown to result in a non-planar structure, of 47 kcal mol^{-1} (MP4) above the corresponding aminomethylene.[17]

The transition structures (**4**) and (**5**) are related to hydrogen loss from (**1**) and (**2**), respectively, or in the reverse direction to the addition of $H^\bullet$ to the nitrilium cation $HCNH^+$ at both carbon [equation (2)] and nitrogen [equation (3)] positions.

$$H^\bullet + HCNH^+ \xrightarrow{\text{addition at C}} (\mathbf{1}) \qquad (2)$$

$$H^\bullet + HCNH^+ \xrightarrow{\text{addition at N}} (\mathbf{2}) \qquad (3)$$

Examining the geometries of (**4**) and (**5**) we note that the intermolecular CH^1 distance of 1.775 Å in (**4**), is calculated to be larger than the NH^1 distance of 1.651 Å in (**5**) (proportional to the difference between normal CH and NH bond lengths).

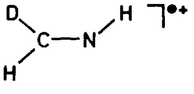
In a recent MNDO study on the similar addition of $H^\bullet$ to HCO^+ cation yielding both $[H_2CO]^{\bullet +}$ and $[HCOH]^{\bullet +}$ radical cations, Frenking *et al.*[18] reported values of 2.108 (CH) and 1.713 Å (OH) for the intermolecular distances in the corresponding transition structures. These distances are of course markedly longer than ones found for the $H^\bullet + HCNH^+$ system. Nevertheless, this difference between reaction co-ordinate lengths implies that the addition of $H^\bullet$ to HCO^+ occurs in a much earlier stage and is reflected in the slightly smaller energy barriers found in the $H^\bullet + HCO^+$ system (see Table 4). In both systems the addition at C is always favoured over addition to the heteroatom by about 10 kcal mol^{-1}. Compared with experimental and *ab initio* results, it appears that MNDO underestimated both energy barriers for addition at N and O, while it overestimated the ones for addition at C. Accordingly, the energy barrier for the addition (at C) $H^\bullet + HCNH^+ \longrightarrow H_2CNH^{\bullet +}$ can be predicted to be small (<5 kcal mol^{-1}), also (see, for instance, ref. 10).

In their earlier work on the $H^\bullet + HCO^+$ addition, Frenking *et al.*[18] showed that the difference in the energy barrier for the $H^\bullet$ addition to C and O atoms can simply be explained using frontier-orbital arguments. The addition is of nucleophilic type and controlled by the interaction between the singly occupied molecular orbital (s.o.m.o.) of $H^\bullet$ and the lowest unoccupied molecular orbital (l.u.m.o.) of the cation. Our results concur. As seen in Table 4, both cations $HCNH^+$ and HCO^+ have similar l.u.m.o. coefficients and in each cation the largest l.u.m.o. coefficient is for the carbon atom. Moreover, the higher energy barriers for $H^\bullet + HCNH^+$ at both carbon and nitrogen centres can be correlated with the higher-lying l.u.m.o. in $HCNH^+$ in comparison with HCO^+ (see Table 4).

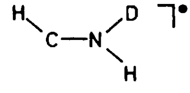
Table 5. MNDO and experimental heats of formation (kcal mol^{-1}) for different structures of $[CH_5N]^{\bullet +}$

Species	MNDO	Exptl.
(**7**) (min.)	211.5	201[a]
(**8**) (min.)	196.2	–
(**9**) (t.s./1,2-H)	248.6	–
(**10**) (t.s./addition at C)	249.8	–
(**11**) (t.s./addition at N)	259.9	–
(**12**) $H^\bullet + H_2CNH_2^+$ (min.)	239.1	230[b]

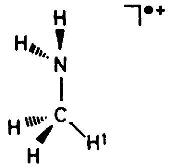
[a] See footnote *d* of Table 4. [b] See Table 2.



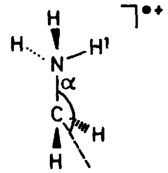
(**1a**)



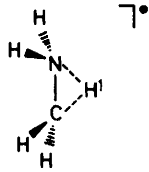
(**2a**)



(**7**)



(**8**)



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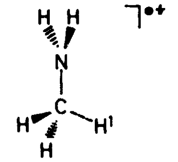
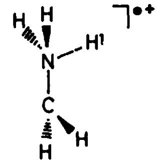
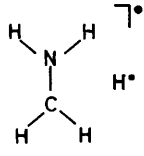


(**10**)



(**11**)



(**12**)

This energy-barrier difference can also be regarded as a result of the higher energy required for nuclear deformation of the $HCNH^+$ cation in the transition states (**4**) and (**5**). It is interesting that the addition of $H^\bullet + HCNH^+$ at both electrophilic centres is stereospecific. Of course, the H–C–N–H skeletons in both (**4**) and (**5**), have, as expected, a *trans*-bent configuration. The nitrilium cation $HCNH^+$, like fulminic acid CNOH,[19] prefers a *trans* deformation. As a consequence, in the reaction $D^\bullet + HCNH^+$, for example, only the *cis* isomers (**1a**) and (**2a**) will be formed in the first kinetic steps. Conversely, $D^\bullet$ loss from the $[CH_2DN]^{\bullet +}$ radical cations will take place from the *cis* isomers (**1a**) and (**2a**).

From the energy data shown in Table 3 it can be emphasized furthermore that the interconversion between both forms (**1**) and (**2**) can also occur *via* a dissociation–recombination path [involving (**4**) and (**5**)]. Both direct 1,2-hydrogen shift and dissociation–recombination paths are in some respects in competition for the isomerization (**1**) $\rightleftharpoons$ (**2**).

(*b*) $[CH_5N]^{\bullet +}$.—Although the existence of both the methylamine radical cation (**7**) and the methyleneammonium radical cation (**8**) as distinguishable isomers has been positively identified,[20] only the heat of formation of (**7**) (201 kcal mol^{-1}) has been reported as yet.

The $[CH_5N]^{\bullet +}$ system has also been previously studied by MINDO/3,[21] as well as by *ab initio* methods at different levels.[11,22,23] One of the recent *ab initio* studies was by Bouma *et al.*[23] who carried out an extensive exploration of the energy surface at the MP3/6-31G**//6-31G* level with correction for zero-point vibrational energies. Here, we mainly compare the MNDO results with these MP3 data.

Table 6. Calculated and experimental energy characteristics (kcal mol^{-1}) of the $[CH_5N]^{\cdot +}$ system

Thermodynamic quantity		MNDO[a]	*Ab initio*		Exptl.[d]
			MP3[b]	MP4[c]	
Isomerization energy (**7**) ⟶ (**8**)	ΔH_1	−15.3	−1.9	−1.0	—
1,2-H-shift energy barrier (**7**) ⟶ (**8**) [*via* (**9**)]	$\Delta E_1^{\ddagger}$	37.1	40.1	—	—
Heat of reaction $H^{\cdot} + H_2CNH_2^+ \longrightarrow$ (**7**)	ΔH_2	−27.6	−27.0	—	−29
Energy barrier for addition at C [*via* (**10**)]	$\Delta E_2^{\ddagger}$	10.7	6.5	—	—
Heat of reaction $H^{\cdot} + H_2CNH_2^+ \longrightarrow$ (**8**)	ΔH_3	−42.9	−28.9	—	—
Energy barrier for addition at N [*via* (**11**)]	$\Delta E_3^{\ddagger}$	20.8	19.4	—	—
Dissociation energy (**7**) $\longrightarrow CH_3^+ + NH_2^{\cdot}$	D_1	69.7	98.5	—	101
Dissociation energy (**8**) $\longrightarrow CH_2^+ + NH_3$	D_2	97.7	119.3	—	—

[a] This work. [b] From ref. 23 at the MP3/6-31G** level with correction for zero-point vibration. [c] From ref. 11, see text. [d] From P. C. Burgers, A. A. Mommers, and J. L. Holmes, *J. Am. Chem. Soc.*, 1983, **105**, 5976; see Table 2.

Besides ions (**7**) and (**8**), three transition structures are located, (**9**) [related to the 1,2-hydrogen shift connecting (**7**) and (**8**)], (**10**) and (**11**) [resulting from the hydrogen-elimination reactions of (**7**) and (**8**), both leading to $H^{\cdot} + H_2C{=}NH_2^+$]. Also considered are the dissociations of (**2**) to $NH_2^{\cdot} + CH_3^+$ and (**8**) to $NH_3 + CH_2^{\cdot +}$. The calculated and experimental energy characteristics of the $[CH_5N]^{\cdot +}$ system are summarized in Tables 5 and 6.

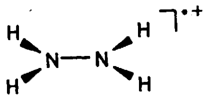
First, we note that like 6-31G* calculations, MNDO also predicts a staggered conformation with C_s symmetry for both species (**7**) and (**8**). In contrast to the previous $[CH_3N]^{\cdot +}$ case, MNDO values for the C–N bond lengths of 1.446 Å in (**7**) and 1.466 Å in (**8**) (Table 1) are both slightly smaller than the 6-31G* ones of 1.458 and 1.470 Å, respectively. The CH_2 moiety in (**8**) is found to be only slightly out-of-plane by MNDO (α = 177°) while significantly pyramidal by 6-31G* (α = 158.3°).

The calculated heats of formation (Table 5) are, as expected, higher than the MNDO-UHF (unrestricted Hartree–Fock) values of 206.1 kcal mol^{-1} for (**7**) and 194.2 kcal mol^{-1} for (**8**) previously reported by Dewar and Rzepa.[21] Nevertheless, in comparison with *ab initio* results where the energy difference between species (**7**) and (**8**) was predicted to be 1—2 kcal mol^{-1} in favour of (**8**) (Table 6), both MNDO-RHF and MNDO-UHF strongly favour the non-classical form (**8**) by 12—15 kcal mol^{-1} over the classical form (**7**). It should be noted that for neutral systems like carbenes or nitrenes the MNDO method is often criticized as disfavouring the non-classical structures.[24] The interconversion (**7**) $\rightleftharpoons$ (**8**) involving the 1,2-hydrogen shift transition structure (**9**) has an energy barrier of $\Delta E_1^{\ddagger}$ = 37.1 kcal mol^{-1} (Table 6). This barrier height is larger than the MINDO/3 value of 25.4 kcal mol^{-1},[21] but reasonably comparable with the MP3 value of 40.1 kcal mol^{-1}.

Concerning geometrical parameters, both bridge distances CH^1 1.38 Å and NH^1 1.314 Å calculated by MNDO for species (**9**) (Table 1) are larger than those obtained by MINDO/3 (1.306 and 1.211 Å[21]) and by 6-31G* (1.309 and 1.263 Å[23]).

Loss of a hydrogen atom from species (**7**) and (**8**) is computed to be endothermic. In the reverse direction, addition of $H^{\cdot}$ to $H_2CNH_2^+$ at both carbon and nitrogen is moderately exothermic. The heat of reaction for the addition at C yielding (**7**) (ΔH_2 = −27.6 kcal mol^{-1}) compares favourably with those of −27 kcal mol^{-1} by MP3 and of −29 kcal mol^{-1} by experiment (Table 6). The heat of reaction, ΔH_3, for addition at N should be overestimated as a consequence of the overestimation of the ΔH_f of (**8**).

The energy barrier for addition at N, $\Delta E_3^{\ddagger}$ = 20.8 kcal mol^{-1}, is similar to the MP3 value of 19.4 kcal mol^{-1}, but the energy barrier for addition at C ($\Delta E_2^{\ddagger}$ = 10.7 kcal mol^{-1}) is again overestimated. Within the frontier-orbital framework, this difference between energy barriers in favour of addition at C can be correlated with the l.u.m.o. coefficients in the $H_2C{=}NH_2^+$ cation. For instance, the coefficients are calculated as 0.85 on carbon and 0.53 on nitrogen [ε(l.u.m.o.) = −8.01 eV].



(**13a**)

The intermolecular distances in the transition states, CH^1 1.855 Å in (**10**) and NH^1 1.665 Å in (**11**) (Table 1), are somewhat longer than the relative 6.31G* ones of 1.776 and 1.638 Å.[23] However, the bond-length ratio CH^1/NH^1 in both cases is similar. The MNDO distances seem also to be reasonable by comparison with the values CH^1 1.775 Å and NH^1 1.651 Å reported above for the $H^{\cdot} + HCNH^+$ addition. As would be expected, the addition to a C≡N triple bond should involve a tighter transition state. In line with 6-31G* calculations, the H_2CNH_2 groups in both transition states (**10**) and (**11**) also possess a *trans*-bent configuration.

It is also interesting to note that MNDO, in agreement with MP3 data, suggests an alternative lower-energy pathway for converting species (**7**) into (**8**) *via* an initial loss of a hydrogen atom. For instance, the pathway (**7**) ⟶ (**10**) ⟶ (**12**) ⟶ (**11**) ⟶ (**8**) has an energy barrier of *ca.* 10 kcal mol^{-1} lower than that involving a direct 1,2-hydrogen shift (**7**) ⟶ (**9**) ⟶ (**8**).

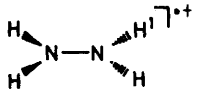
Finally, the dissociation energies D_1 and D_2 of (**7**) and (**8**) for breaking C–N bonds are both underestimated by about 20—30 kcal mol^{-1} with respect to experimental and/or *ab initio* results (Table 6). It is noteworthy that MNDO, in contrast, markedly overestimated the dissociation energies for bond-breaking processes of neutral molecules which result in radical formation.[25]

(*c*) $[N_2H_4]^{\cdot +}$.—Experimentally, the hydrazine radical cation (**13**) has been identified in an e.s.r. study[26] which indicated a slightly non-planar C_{2h} structure. Like 6-31G* calculations, MNDO correctly reproduces this geometry. The ammonio-amide radical cation (**14**) has a staggered (C_s) conformation. The N–N bond lengths of 1.300 Å in (**13**) and 1.402 Å in (**14**) (Table 1) can be compared with the values of 1.290 and 1.437 Å, respectively, obtained from 6-31G*. The non-planar C_s structure (**13a**) is a saddle point (with one imaginary frequency) and has an energy of 215.8 kcal mol^{-1} thus giving a barrier to rotation of 1 kcal mol^{-1} for the NH_2 group. In agreement with *ab initio* results, the non-classical radical cation (**14**) is found to

Table 7. Heats of formation and relative energies (kcal mol^{-1}) of the $[N_2H_4]^{\cdot+}$ system

Species	MNDO ΔH_f	MNDO $\Delta(\Delta H_f)$	MP4*
(13) (min.)	214.8	0.0	0.0
(14) (min.)	236.3	21.5	28.1
(15) (t.s./1,2-H)	299.9	85.1	—
(16) (t.s./addition at N^2)	296.8	82.0	—
(17) (t.s./addition at N^1)	304.0	89.2	—
(18) $H^{\cdot}$ + H_2NNH^+ (min.)	283.9	69.1	—

* From ref. 11.



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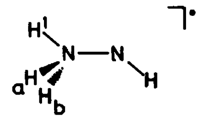

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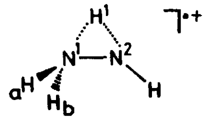

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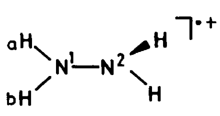

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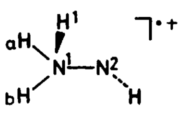

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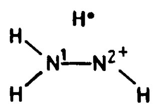


(18)

be higher in energy than **(13)**. The MNDO energy difference of 21.5 kcal mol^{-1} can be compared with that of 28.1 kcal mol^{-1} obtained by MP4 (see Table 7).

The transition state **(15)** (C_s symmetry) lies about 85.1 and 63.6 kcal mol^{-1} above **(13)** and **(14)** respectively. The bridge parameters in **(15)** (N^1H^1 1.396 Å, N^2H^1 1.292 Å, $H^1N^1N^2$ 55.7°) seem to be reasonable compared with the relative geometrical parameters in transition structures **(3)** and **(9)** (see Table 1). Thus, the 1,2-hydrogen shift in $[N_2H_4]^{\cdot+}$ shows a much larger energy barrier than the cases discussed above.

Loss of a hydrogen atom from species **(13)** and **(14)** *via* transition structures **(16)** and **(17)**, respectively, has a rather high energy barrier, too. The $H^{\cdot}$ elimination in **(14)** with an energy barrier of 67.7 kcal mol^{-1} [*via* **(17)**] is however easier than the similar process in **(13)** [82 kcal mol^{-1} *via* **(16)**].

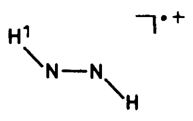
Considering the reverse reactions, namely the $H^{\cdot}$ addition to the trivalent nitrogen N^1 and bivalent nitrogen N^2 of the H_2NNH^+ cation, it is found that the latter has a smaller energy barrier [12.9 kcal mol^{-1}, **(18)** → **(16)** → **(13)**] than the former [20.1 kcal mol^{-1}, **(18)** → **(17)** → **(14)**]. These computed values are of the same order of magnitude as in the previous cases. This implies that the energy barrier for addition at N^2 (6—7 kcal mol^{-1}) is somewhat overestimated by MNDO. With the available data (Tables 3 and 6) it is difficult, on the contrary, to say whether the energy barrier for addition at N^1 is underestimated or not. The value of 20.1 kcal mol^{-1} can thus be considered as its lower limit.

The difference between the energy barriers for additions at N^1 and N^2 are reflected by a longer intermolecular distance N^2H^1 2.051 Å in **(16)** compared with that of N^1H^1 1.752 Å in **(17)**, as well as a larger l.u.m.o. coefficient at N^2 (0.78) than that at N^1 (0.62) in the H_2NNH^+ cation. Also worthy of note is that in both transition states **(16)** and **(17)** the H_2NNH moiety remains almost planar. The $H^{\cdot}$ attack at N^2 and N^1 occurs almost exactly in the molecular and perpendicular planes, respectively. In **(17)**, the group $H^1N^1N^2H$ had a *trans* configuration thus foreshadowing the resulting structure **(14)**.

Table 8. Heats of formation and relative energies (kcal mol^{-1}) of the $[N_2H_2]^{\cdot+}$ system

Species	MNDO ΔH_f	MNDO $\Delta(\Delta H_f)$	MP4*
(19) (min.)	261.7	0.0	0.0
(20) (min.)	266.3	4.6	9.0
(21) (min.)	266.6	4.9	4.6
(22) (t.s./*Z*-*E*)	270.3	8.6	—
(23) (t.s./1,2-H)	327.9	66.2	—
(24) (t.s./addition at N^2)	309.8	48.1	—
(25) (t.s./addition at N^1)	318.0	56.3	—
(26) $H^{\cdot}$ + HNN^+ (min.)	296.8	35.1	—

* From ref. 11.



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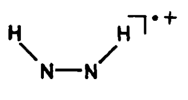

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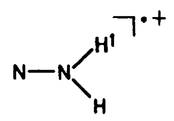

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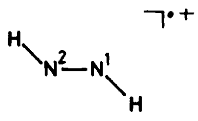

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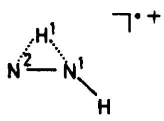

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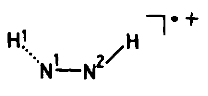

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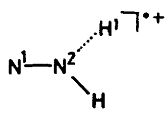

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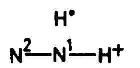

(26)

The pathway **(13)** → **(16)** → **(18)** → **(17)** → **(14)** appears, from MNDO data, likely to be favoured over the direct conversion **(13)** → **(17)** → **(14)**. Nevertheless, the high energy barriers predicted by MNDO for both pathways indicate that the non-classical ammonioamide radical cation **(14)**, although higher in energy than **(13)**, could kinetically be stable and hence be a good candidate for experimental investigation.

(*d*) $[N_2H_2]^{\cdot+}$.—To our knowledge, there is as yet no experimental information on the $[N_2H_2]^{\cdot+}$ system but some *ab initio* calculations have been reported.[17,27] The *trans*-di-imide radical cation **(19)** is also predicted by MNDO to be the most stable structure and is about 4.9 kcal mol^{-1} (4.6 kcal mol^{-1} by MP4) below the aminonitrene radical cation **(21)**. The discrepancy between the MNDO and *ab initio* results concerns the stability ordering relative to the *cis* form **(20)** and the non-classical form **(21)**. Thus MNDO predicts (Table 8) nearly the same energy for both isomers **(20)** and **(21)** while an energy difference of 4.4 kcal mol^{-1} was calculated by MP4 in favour of **(21)**.

Employing the MNDO-UHF method, we found a variation in the stability ordering of the $[N_2H_2]^{\cdot+}$ system, namely: **(19)** (261.0 kcal mol^{-1}) > **(21)** (263.6) > **(20)** (264.3). Although this ordering is comparable with the MP4 one, the energies of the isomers are much closer. Moreover, MNDO gives on the one hand very short N–N bond lengths (1.14—1.17 Å) for both di-imide forms **(10)** and **(20)**, and on the other hand, C_{2h} symmetry for **(19)** and C_{2v} for **(20)**. This finding contrasts with 6-31G* results which show a C_s symmetry for both **(19)** and **(20)** isomers with non-equivalent nitrogens.[11] We note that MNDO also give similar results for the $[P_2H_2]^{\cdot +}$ system.[16]

The *Z–E* isomerization between species **(19)** and **(20)** has a small energy barrier [4 kcal mol^{-1} for **(20)** ⟶ **(22)** ⟶ **(19)**]. Like the $[N_2H_4]^{\cdot +}$ system, the 1,2-hydrogen shift interconverting **(19)** and **(21)** shows a significantly high energy barrier, 66.2 kcal mol^{-1} for the pathway **(19)** ⟶ **(23)** ⟶ **(20)**. Unlike $[N_2H_4]^{\cdot +}$, ions **(20)** and **(21)** lie *ca.* 30.5 and 30.2 kcal mol^{-1} below the fragmented system $H^{\cdot} + HNN^{+}$, respectively. Between them, there exist sizeable energy barriers of 43.5 kcal mol^{-1} [for **(20)** ⟶ **(24)** ⟶ **(26)**] and 51.4 kcal mol^{-1} [for **(21)** ⟶ **(25)** ⟶ **(26)**]. These are however substantially lower than the value of 71.6 kcal mol^{-1} (MP4) for converting the neutral di-imide into the neutral aminonitrene.[17]

With regard to the $H^{\cdot} + HNN^{+}$ additions, it appears that the addition of $H^{\cdot}$ to the terminal nitrogen N^2 of the HNN^{+} cations *via* transition structure **(24)** requires a lower activation energy [13.1 kcal mol^{-1} for **(26)** ⟶ **(24)** ⟶ **(19)**] with respect to the addition to the central nitrogen N^1 [21.2 kcal mol^{-1} for **(26)** ⟶ **(25)** ⟶ **(21)**]. So, this order of magnitude is once again similar in all three systems studied. The related values of the intermolecular distances in the transition structures [N^2H^1 1.898 Å in **(24)** and N^1H^1 1.662 Å in **(25)**] as well as the l.u.m.o. coefficients of HNN^{+} [0.75 at N^2 and 0.63 at N^1, ε(l.u.m.o.) = 7.50 eV] are also in harmony with the general trend.

We emphasize here the stereospecific character of the addition at N^2. For instance, the transition structure **(24)** has a *cis* conformation. Consequently, addition at N^2 leads to the formation of the *cis* isomer **(20)** in the first kinetic step. In a recent *ab initio* study[28] on a similar addition $H^{-} + HNC$ it was shown that this anionic addition takes place stereospecifically by giving first the *cis* isomer of the resulting anion which will be converted into the more stable *trans* isomer by means of a *Z–E* isomerization. This stereoelectronic effect was explicable in terms of the movement of electron pairs accompanying the nuclear deformation of the reactant HNC and the approach of the nucleophile in the earlier stage of the reaction. From these results, it is clear that MNDO also correctly predicts the stereospecific course of nucleophilic additions and $H^{\cdot} + HNN^{+}$. The main difference between radical addition ($H^{\cdot} + HNN^{+}$) and anionic addition ($H^{-} + HNC$) is thus the fact that there is a small energy barrier in the former while the latter occurs without an energy barrier.

As a consequence of this stereoelectronic effect, the loss of hydrogen atom in the di-imide radical cation occurs only from the *cis* isomer **(20)**. So, the corresponding pathway should be: **(19)** ⟶ **(22)** ⟶ **(20)** ⟶ **(24)** ⟶ **(26)** with an associated energy of 48.1 kcal mol^{-1} [*via* **(24)**]. So, the process dissociation–recombination appears to be again favoured over the 1,2-hydrogen shift for the interconversion of isomers **(19)** and **(21)**.

Conclusions

The structures and relative energies provided by MNDO calculations on four nitrogen-containing radical cations, $[CH_3N]^{\cdot +}$, $[CH_5N]^{\cdot +}$, $[N_2H_4]^{\cdot +}$ and $[N_2H_2]^{\cdot +}$, compare well with those from *ab initio* calculations and available experimental data. The MNDO method overestimates the stabilities of non-classical isomers and consequently underestimates the activation energies for 1,2-hydrogen shifts connecting both classical and non-classical forms. The loss of H atoms from X atoms (H–X–N–) is disfavoured, while that from N atoms (–X–N–H) is favoured in comparison with *ab initio* or experimental results.

The number of considered species might be too limited to make generalizations at this point, but it seems tempting to suggest that MNDO is a suitable method in this area. It would be useful in interpreting mass spectroscopic data involving large molecules.

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References

1 For leading references, see: T. A. Lehman and M. M. Bursey, 'Ion Cyclotron Resonance Spectrometry,' Wiley-Interscience, New York, 1976; K. Levsen, *Prog. Mass Spectrosc.*, 1978, **4**, 1.

2 See, for example, G. Berthier, F. Pauzat, and T. Yuanqi, *J. Mol. Struct.*, 1984, **107**, 39; L. R. Thorne, V. G. Anicich, S. S. Prasad, and W. T. Huntress, jun., *Astrophys. J.*, 1984, **280**, 139.

3 R. H. Nobes, W. J. Bouma, and L. Radom: *J. Am. Chem. Soc.*, 1984, **106**, 2774 and refs. therein; M. H. Lien and A. C. Hopkinson, *Can. J. Chem.*, 1984, **62**, 922 and refs. therein; D. J. Swanton, G. B. Bacskay, G. D. Willett, and N. S. Hush: *J. Mol. Struct.*, 1983, **91**, 313 and refs. therein; T. J. Zielinski, M. R. Peterson, I. G. Csizmadia, and R. Rein, *J. Comput. Chem.*, 1982, **3**, 62 and refs. therein.

4 F. W. McLafferty and D. C. McGilvery, *J. Am. Chem. Soc.*, 1980, **102**, 6189.

5 D. Power, P. Brint, and T. Spalding, *J. Mol. Struct.*, 1984, **108**, 81.

6 M. T. Nguyen and T. K. Ha, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1401; *J. Phys. Chem.*, 1984, **88**, 4295.

7 T. K. Ha and M. T. Nguyen, *Chem. Phys. Lett.*, 1983, **97**, 503; *Z. Naturforsch., Teil A*, 1983, **38**, 855.

8 G. P. Ford and J. D. Scribner, *J. Comput. Chem.*, 1983, **4**, 594; R. L. Decock and G. P. Jasperse, *Inorg. Chem.*, 1983, **22**, 3839, 3843; S. Olivella, F. Urpi, and J. Vilarra, *J. Comput. Chem.*, 1984, **5**, 230; G. Frenking and H. Schwarz, *ibid.*, 1982, **3**, 251.

9 C. Glidewell, *J. Chem. Res.*, 1982, (*S*) 22; *Inorg. Chim. Acta*, 1984, **81**, 187; *J. Chem. Soc., Perkin Trans. 2*, 1984, 1175; J. R. Bews and G. Glidewell, *J. Organomet. Chem.*, 1983, **255**, 49; *J. Mol. Struct.*, 1983, **94**, 305.

10 P. C. Burgers, J. L. Holmes, and J. K. Terlouw, *J. Am. Chem. Soc.*, 1984, **106**, 2762.

11 M. J. Frisch, K. Raghavachari, J. A. Pople, W. J. Bouma, and L. Radom, *Chem. Phys.*, 1983, **75**, 323.

12 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4889, 4907.

13 R. Fletcher and M. J. D. Powell, *Comput. J.*, 1963, **6**, 163; W. C. Davidon, *ibid.*, 1968, **10**, 406.

14 M. J. S. Dewar, E. F. Healy, and J. J. P. Stewart, *J. Chem. Soc., Faraday Trans. 2*, 1984, 227.

15 T. K. Ha, M. T. Nguyen, M. Hendricx, and L. G. Vanquickenborne, *Chem. Phys. Lett.*, 1983, **96**, 267.

16 R. A. Whiteside, M. J. Frisch, J. S. Binkley, D. J. DeFrees, J. B. Schlegel, K. Raghavachari, and J. A. Pople, *Carnegie-Mellon Quantum Chemistry Archive*, 1981.

17 J. A. Pople, K. Raghavachari, M. J. Frisch, J. S. Binkley, and P. V. R. Schleyer, *J. Am. Chem. Soc.*, 1983, **105**, 6389.

18 G. Frenking, N. Heinrich, W. Koch, and H. Schwarz, *Chem. Phys. Lett.*, 1984, **105**, 490.

19 M. T. Nguyen, M. Sana, G. Leroy, K. J. Dignam, and A. F. Hegarty, *J. Am. Chem. Soc.*, 1980, **102**, 573.

20 J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *J. Am. Chem. Soc.*, 1982, **104**, 2931.

21 M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, 1977, **99**, 7432.

22 L. Bonazzola, N. Leray, and Y. Ellinger, *Chem. Phys.*, 1982, **73**, 145.

23 W. J. Bouma, J. M. Dawes, and L. Radom, *Org. Mass Spectrom.*, 1983, **18**, 12.

24 G. Frenking and J. Schmidt, *Tetrahedron*, 1984, **40**, 2123.
25 R. Engelke, *Chem. Phys. Lett.*, 1981, **83**, 151.
26 M. H. Reilly and C. L. Marquardt, *J. Chem. Phys.*, 1970, **53**, 3257 and refs. therein.
27 N. C. Baird and D. A. Wernette, *Can. J. Chem.*, 1977, **55**, 350.
28 M. T. Nguyen, A. F. Hegarty, M. Sana, and G. Leroy, *J. Am. Chem. Soc.*, in the press.

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