An *Ab Initio* Study of the Hydrogen Addition to Methyl Isocyanide (CH₃N≡C) and Methanediazonium Ion (CH₃N≡N⁺): a Case of a Bifurcating Point on the Potential Energy Surface

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Results of *ab initio* calculations on the reaction pathways for the hydrogen addition to methanediazonium ion (CH₃N≡N⁺) and methyl isocyanide (CH₃N≡C) at both central and terminal atoms as well as for the stereomutation of α-adducts are reported. Structures of points on the energy surfaces were determined at the UHF/3-21G level while their relative energies were estimated at UMP4SDQ/6-31G**. Thermochemical properties were also computed. The α-addition of H˙ either to the terminal nitrogen of CH₃N≡N⁺ or to the carbon atom of CH₃N≡C is not stereospecific. Only a single transition structure can be located in each case. At the transition state, the substrate is only marginally bent. Soon after the transition state is passed, a bifurcation of the addition pathway occurs leading to the formation of both *cis*- and *trans*-isomers of the adduct. In both cases, the *trans*-adduct is more stable than the *cis*; the *cis–trans* stereomutation takes place *via* nitrogen inversion of the methyl group and requires only 5—6 kcal mol⁻¹ therefore the *trans*-isomer should be the major adduct. The β-addition to central nitrogen exhibits, in both cases, an appreciably larger energy barrier which precludes the formation of the β-adduct.

Recently, new synthetic routes to isocyanides (1) have resulted in increased interest in the use of this functional group in synthesis and further study of the often facile rearrangement to cyanides (2).[1]

Aliphatic diazonium ions (3), which are isoelectronic with cyanides and isocyanides, are less stable but are formed as intermediates in a number of reactions.[2,3] Owing to the extremely good leaving ability of N₂, they usually undergo rapid dediazoniation to give the corresponding carbocations R⁺. In some cases however, the diazonium ions can be trapped by nucleophiles in a diazo-coupling reaction giving an azo compound (4).[3c,4]

Nucleophilic addition to diazonium ions[4] and to isocyanides[5] has been shown to be stereospecific in both cases. The initially formed product is, in most cases, a *cis*-isomer (5a) even though the corresponding *trans*-isomer (5b) is thermodynamically more stable. In this regard, the stereochemistry of the radical addition to these compounds is of particular interest.

R—N≡C   R—C≡N   R—N≡N⁺

(1)   (2)   (3)

R—N≡N—Nu   [N≡C]⁻ with R, Nu   [N≡C with R, Nu]⁻

(4)   (5a)   (5b)
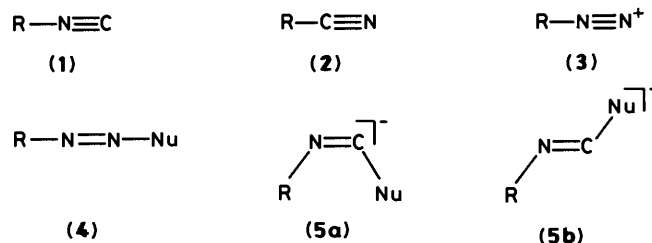
A variety of radicals have been found to add to the terminal carbon of alkyl isocyanides (1), forming the imidoyl radical (6) which goes on to react further in a number of ways[1b,6] [equation (1)]. The mechanism of radical addition to alkyl isocyanides as well as structures of the adducts were investigated by Blum and Roberts[6] using e.s.r. spectroscopy. They found the radicals (6) have σ-character and the *trans*-configuration, according to INDO calculations, was the more stable.

The addition of a radical to a diazonium ion could produce
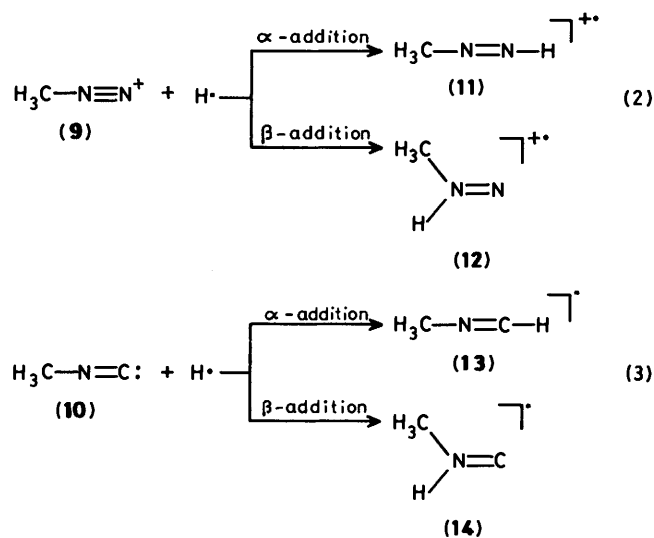
R—N≡C: + R˙ ⟶ R—N≡C—R˙

(6)
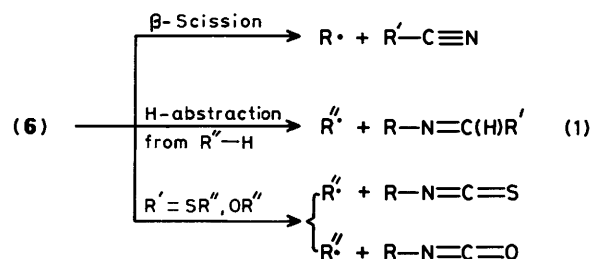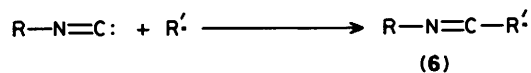
either an azo radical cation (7) or an aminonitrene ion (8). This reaction has been proposed as an intermediate step in a radiation-induced chain reaction between arenediazonium ions

[R—N≡N—R']⁺˙   [R,R'>N≡N]⁺˙

(7)   (8)
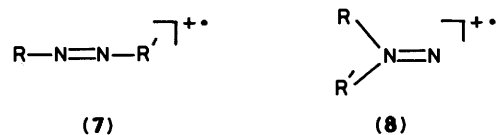
and reducing agents.[7] Packer and his co-workers[7] postulated that the radicals (formed during the chain reaction) add to the terminal nitrogen of diazonium ions [giving (7)]. MNDO calculations[8] on the hydrogen addition to the parent ion H–N≡N⁺ showed in fact that the latter requires the smallest energy barrier within the two processes.

In this paper, we report results of *ab initio* calculations on the reaction pathways for the addition of atomic hydrogen to methanediazonium (9) [equation (2)] and to methyl isocyanide (10) [equation (3)], yielding the radical cations (11)—(12) and (13)—(14), respectively. In particular, we are interested in the possible specificity of the α-additions. The data which we report show that on each of the two potential energy surfaces there is a

$$H_3C-N\equiv N^+ + H\cdot \longrightarrow \begin{array}{c} \overset{\alpha\text{-addition}}{\longrightarrow} H_3C-N=N-H \\ (11) \end{array} \qquad (2)$$

(9)

$$\overset{\beta\text{-addition}}{\longrightarrow} \begin{array}{c} H_3C \\ N=N \\ H \end{array}^{+\cdot}$$

(12)

$$H_3C-N\equiv C: + H\cdot \longrightarrow \begin{array}{c} \overset{\alpha\text{-addition}}{\longrightarrow} H_3C-N=C-H \\ (13) \end{array} \qquad (3)$$

(10)

$$\overset{\beta\text{-addition}}{\longrightarrow} \begin{array}{c} H_3C \\ N=C \\ H \end{array}$$

(14)

bifurcating point in the region of the α-addition, leading to the formation of both *cis-* and *trans-*isomers of (11) or (13).

Calculations

Geometrical parameters of the stationary points considered were determined from analytically computed gradients and numerical second derivatives (by finite gradient difference) of energy and the 3-21G[9] basis set. Harmonic vibrational frequencies were calculated at the HF/3-21G level in order to characterize stationary points as minima or transition structures and to calculate zero-point vibrational contributions to relative energies. The latter were obtained from single-point calculations at the SCF and fourth-order Møller–Plesset perturbation theory[10] (neglecting the triple substitutions) employing the 3-21G-optimized geometries and the 6-31G* and 6-31G**[11] basis sets. The spin-unrestricted formalism (UHF, UMP) was used for open-shell species. Our best relative energies correspond to UMP4/6-31G**/UHF/3-21G values, with zero-point correction, estimated by using the additivity approximation.[12] $\Delta E(\text{MP4}/6\text{-}31G^{**}) \approx \Delta E(\text{MP4}/6\text{-}31G^{*}) + \Delta E(\text{HF}/6\text{-}31G^{**}) - \Delta E(\text{HF}/6\text{-}31G^{*})$. Calculations were carried out using the MONSTERGAUSS[13] and GAUSSIAN 82[14] programs.

Results and Discussion

(a) *Addition of* H⋅ *to* $CH_3N\equiv N^+$.—Figure 1 displays the optimized geometries of $CH_3-N\equiv N^+$ (9) and the stationary points on the addition pathways including the Z-form (11a) and E-form (11b) of the methylazo ion, the methylaminonitrene ion (12a), and four transition structures (11c—e) and (12b).

In order to follow the course of the α-addition, the two internal parameters R and α as defined in (11f) have been

$$\begin{array}{c} H_3C \\ \overset{\alpha}{\diagdown} \\ N-X \qquad (X = N,C) \\ \overset{R}{\diagdown} \\ H \end{array}$$

(11f)
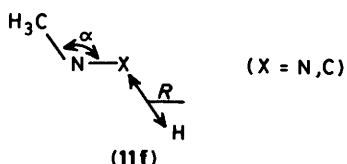
selected as independent co-ordinates. For each couple of fixed (R, α) values, the remaining parameters were optimized at the UHF-3-21G level. The two-dimensional energy surface for the
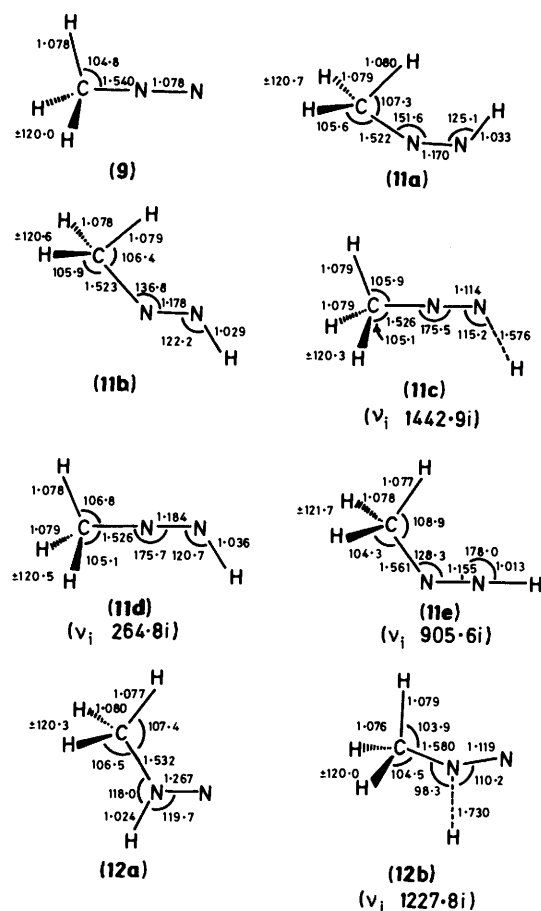
Figure 1. UHF/3-21G-optimized geometries of stationary points on the $H_4CN_2^{+\cdot}$ energy surface considered. Bond lengths are given in Å and bond angles in degrees. v_i are imaginary frequencies in cm^{-1}

α-addition of H⋅ to $CH_3N\equiv N^+$ with respect to R and α is displayed in Figure 2. The total and relative energies along with some thermochemical data are listed in Table 1. Some thermochemical properties of the reactions considered are recorded in Table 2. In the following discussion, we always use the $\Delta H(298\text{ K})$ value, unless otherwise mentioned.

Structure and unimolecular dissociation of methane-diazonium ion (9) have recently been studied by both semiempirical and *ab initio* methods;[15] it therefore warrants no further comment.

The N–N distance in both radical ions (11a and b) is quite short (1.17—1.18 Å): it is even shorter than that in the neutral counterparts (1.25 Å). This is due to the fact that the HOMO in the neutral azo compound is an anti-bonding combination of nitrogen lone pairs. Removal of an electron from such an orbital obviously favours the delocalization and consequently strengthens the bond. In contrast, removal of an electron from the terminal nitrogen lone pair in the neutral methylamino-nitrene giving the radical ion (12a) does not, as expected, significantly affect the adjacent N–N bond. The value of 1.267 Å in (12a) is in fact comparable with that of the corresponding bond (1.25—1.26 Å) in the neutral molecule.

Among the four minima considered, the *trans-*azo cation (11b) is found to be the most stable. It lies 6.9, 7.3, and 12.5 kcal mol^{-1} below the nitrene (12a), the *cis-*isomer (11a), and the separated system (9), respectively. For a comparison, the relative order of energies in the parent $H_2N=N^+$ system is: *trans-*HN=NH$^+$ (0.0 kcal mol^{-1}) < nitrene $H_2N=N^+$ (4.6) <

Table 1. Total (a.u.), relative (kcal mol^{-1} in parentheses), and zero-point vibrational [ZPE, (kcal mol^{-1})] energies, entropies (S cal mol^{-1} K^{-1}), and specific heat capacities (C_p cal mol^{-1} K^{-1}) of stationary points on the H$^{\cdot}$ + CH$_3$N≡N^{+} pathways

Species[a]	N.I.[b]	UHF/3-21G	UHF/6-31G*	<S^2>	UHF/6-31G**	UMP4SDQ/6-31G*	Estimated[c]	ZPE[d]	S^e	C_p^e
(9) + H$^{\cdot}$	0	−147.863 51 (0.0)	−148.713 94 (0.0)		−148.719 15 (0.0)	−149.163 99 (0.0)	(0.0)	27.4	60.5	12.5
(11a)	0	−147.884 25 (−13.0)	−148.729 25 (−9.6)	0.9120	−148.738 54 (−12.2)	−149.175 85 (−7.5)	(−10.1)	31.6	66.1	14.7
(11b)	0	−147.893 81 (−19.0)	−148.739 24 (−15.9)	0.9153	−148.748 41 (−18.4)	−149.187 39 (−14.7)	(−17.2)	32.0	65.5	14.2
(11c)	1	−147.844 55 (11.9)	−148.688 04 (16.2)	0.9113	−148.694 36 (15.5)	−149.139 32 (15.5)	(14.8)	27.3	68.0	15.5
(11d)	1	−147.882 68 (−12.0)	−148.723 87 (−6.3)	0.9743	−148.733 00 (−8.7)	−149.165 07 (−1.1)	(−3.5)	30.8	65.4	13.6
(11e)	1	−147.873 12 (−6.0)	−148.712 10 (1.2)	0.8535	−148.721 85 (−1.7)	−149.163 92 (0.0)	(−0.5)	31.1	65.3	13.8
(12a)	0	−147.921 15 (−36.2)	−148.754 76 (−25.6)	1.162	−148.763 57 (−27.9)	−149.177 80 (−8.7)	(−11.0)	32.5	65.1	13.6
(12b)	1	−147.841 26 (14.0)	−148.686 17 (17.4)	1.0003	−148.691 85 (17.1)	−149.129 93 (21.4)	(21.1)	27.5	65.4	15.0

[a] Using 3-21G geometries given in Figure 1. [b] Number of imaginary frequencies. [c] At UMP4 SDQ/6-31G** using the additivity relationship, see text. [d] Scaled by a factor of 0.9. [e] At 298 K.

Table 2. Some thermochemical properties for chemical processes of the H$_4$CN$_2^{+}$ system

	H$^{\cdot}$ + CH$_3$N≡N^{+} ⟶ (11b)	H$^{\cdot}$ + CH$_3$N≡N^{+} ⟶ (12a)	cis–trans Isomerization (11a) ⟶ (11b)	
Property[a]	[α-addition via (11c)]	[β-addition via (12b)]	methyl inversion (11d)	hydrogen inversion (11e)
ΔH(0 K)	−13.1	−5.9	−7.2	
ΔH(298 K)	−12.5	−5.6	−7.3	
ΔS(298 K)	5.0	4.6	−0.6	
ΔG(298 K)	−14.0	−7.0	−7.1	
$\Delta H^{\ddagger}$(0 K)	14.7	21.2	5.8	9.1
$\Delta H^{\ddagger}$(298 K)	15.6	21.9	5.5	8.8
$\Delta S^{\ddagger}$(298 K)	7.5	4.9	−0.7	−0.8
$\Delta G^{\ddagger}$(298 K)	13.4	20.4	5.7	9.0

[a] From data given in Table 1. ΔH(0 K) = ΔE(MP4SDQ/6-31G**) + Δ(ZPE); ΔH(298 K) = ΔH(0 K) + $\Delta C_p dT$; $\Delta S = S_2 - S_1$; $\Delta G = \Delta H - T\Delta S$; ΔH, ΔG in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1}.

cis-HN=NH (9.0); [ΔH(0 K) at similar level of calculations].[16]

Hence, the methyl substituent seems to disfavour the aminonitrene ion. We note that, at the UHF level, the latter is lower in energy than the trans-azo ion (11b), but the order of energy is reversed after incorporation of the correlation energy. Previous calculations[8] showed that the azo–aminonitrene interconversion via a 1,2-shift in the ionic state is a rather difficult process requiring an energy barrier of >60 kcal mol^{-1}. It can thus be expected that the aminonitrene radical cation (12a) is also a stable low-energy species with respect to unimolecular rearrangement.

For the cis–trans stereomutation of the azo ion, there are two possible pathways involving either hydrogen or methyl as inverting group. In the cis–trans direction, the energy barrier for methyl inversion through the transition structure (11d) is 5.5 kcal mol^{-1} whereas the barrier for hydrogen inversion amounts to 8.8 kcal mol^{-1}. Then, methyl group inversion is slightly favoured. These processes are thus by far easier than those which occur in the neutral species (ca. 55 kcal mol^{-1}).

As seen in Figure 2, at large values of the intermolecular distance R (⩾ 1.8 Å), the C–N–N skeleton of the ion (9) does not bend at all (α ca. 180°) when H$^{\cdot}$ attacks the terminal nitrogen. In the transition state (11c), the supermolecule adopts a slight cis-conformation for CH$_3$ and H$^{\cdot}$ with respect to the N=N bond, the α angle being 184.5°. Along the addition pathway, the hydrogen atom approaches the cation at an NNH angle of ca. 115—120°.

At the transition state (11c), the N–H distance is R 1.576 Å. This structure is rather reactant-like.

In the region immediately after the transition state (11c), the cis-conformation of the supermolecule still prevails. Hence, it appears that there is a geometric driving force which makes the supersystem go 'downhill' to the cis-adduct (11a). On the other hand, because the trans-(11b) is lower in energy (see above), a thermodynamic driving force is likely to occur leading to its formation. Accordingly, there should exist a point on this region of the energy surface where the reaction pathway bifurcates into two separate valleys. A possible bifurcating point is noted as (11g) in Figure 2. In this context, the α-addition of H$^{\cdot}$ to CH$_3$N≡N^{+} is not stereospecific. Both isomers, cis and trans, could be formed. However, as the cis–trans isomerization of the azo ion via methyl inversion is rather facile, the equilibrium should strongly shift in favour of the trans-ion.

In an earlier experimental study on the reaction of diazonium ions with nucleophiles [equation (4)] Zollinger[3a] proposed that if the transition state is reactant-like, the cis-product is favoured (as is the case of small anions) while if the transition state is product-like, the trans-product is favoured (as is the case of molecules or anions whose negative charge is highly delocalized). Schematic representation for these situations is displayed in the Scheme. These two are in clear contrast with the profile for the hydrogen addition found in this work (Figure 3). The fact that the H$^{\cdot}$ addition follows the α ca. 180° valley is quite typical (see Figure 2). Indeed, in the addition of H^{-} to H–N≡C,[5]
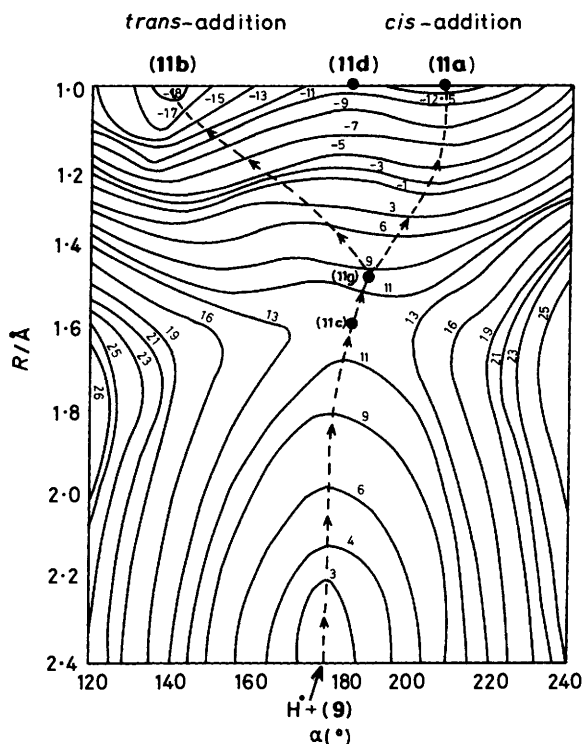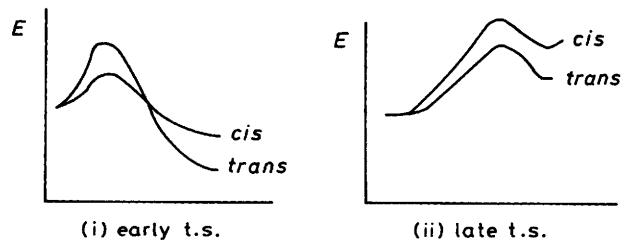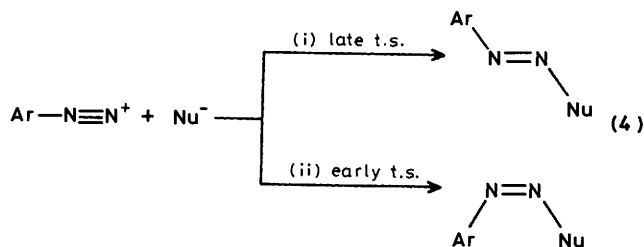
Figure 2. Energy map for the α-addition of H· to $CH_3-N\equiv N^+$ (9). See (11f) for the definition of R and α. Isocontour values are given in kcal mol^{-1}. Zero energy level is the separated H· + $CH_3N\equiv N^+$ system. (11g) is the assumed bifurcating point

Scheme.

it was shown that even at large distances R, the nucleophile already induces strong bending of isocyanide (α *ca.* 120°). This difference of behaviour could be understood in a simple way: the H· addition is essentially controlled by the interaction between the SOMO of H· and LUMO of the substrate.[17] In this regard, the disposition of the central nitrogen lone pair is not a matter of importance. As a consequence, the H· addition is not stereospecific. On the contrary, the addition of H⁻ occurs with
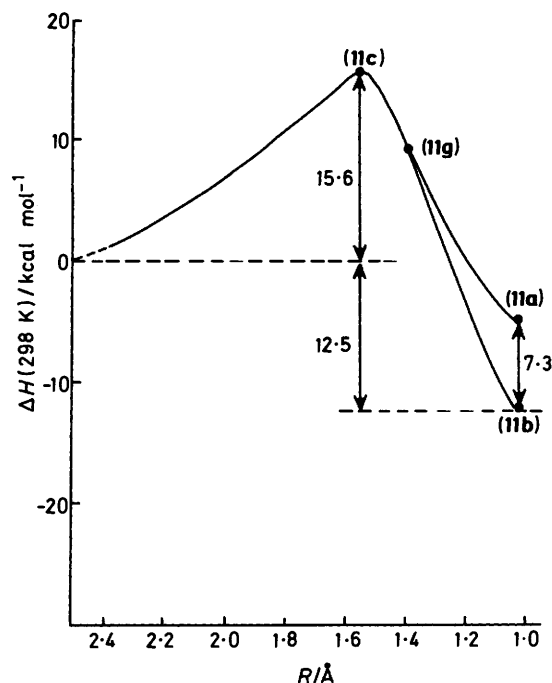

Figure 3. Schematic energy profile for the α-addition of H· to $CH_3N\equiv N^+$. Values of ΔH (298 K) are given in kcal mol^{-1}

a movement of two electron pairs (those of nucleophile and central nitrogen lone pair); the best disposition for the two electron pairs corresponds to a *trans*-configuration yielding consequently a *cis*-adduct (5a) in the first kinetic step. The anionic addition is therefore stereospecific.

Proceeding in the opposite direction, *i.e.* the H· loss from the azo ion, it seems that the direct dissociation from each of the two isomers (11a and b) and the pathway (11b) ⟶ *cis*-(11a) ⟶ dissociation are equally probable. Indeed both must necessarily go through the common transition state (11c). This point is at variance with an earlier conclusion[8] which was based only on the structure of the transition state. The energy barrier for the fragmentation of (11b) is calculated as 28.1 kcal mol^{-1} (Table 2).

We now consider the β-addition of H· to the central nitrogen of $CH_3N\equiv N^+$ (9). The transition state (12b) was located. Although the N-H intermolecular distance in this structure (1.73 Å) is surprisingly longer than that in (11c) (a reverse situation was found for H· + $HN=N^{+}$ [8]), it actually lies higher in energy than the transition state (11c). This is in line with a previous MNDO study for the H· addition to $HN\equiv N^{+}$ [8] which reported that the α-addition is favoured over the β-addition by *ca.* 8 kcal mol^{-1}. As mentioned above, this H· addition is determined by the SOMO(H·)–LUMO(ion) interaction. Bearing a large LUMO coefficient, the terminal nitrogen carries consequently a more favourable interaction with H·, implying a smaller energy barrier for the addition.

Looking in the opposite direction, it is noted that the energy barrier for the H· loss from (12a) amounts to 27.5 kcal mol^{-1}. This is again much smaller than the barrier of *ca.* 60 kcal mol^{-1} for the 1,2-shift connecting (12a) to (11b) (see above). Accordingly, the interconversion between these two low-energy species is likely to occur, if experimental conditions permit, *via* a dissociation–recombination mechanism rather than through a direct substituent migration.

(b) *Addition of* H· *to* $CH_3-N\equiv C$.—Figure 4 shows the optimized geometries of stationary points determined at the
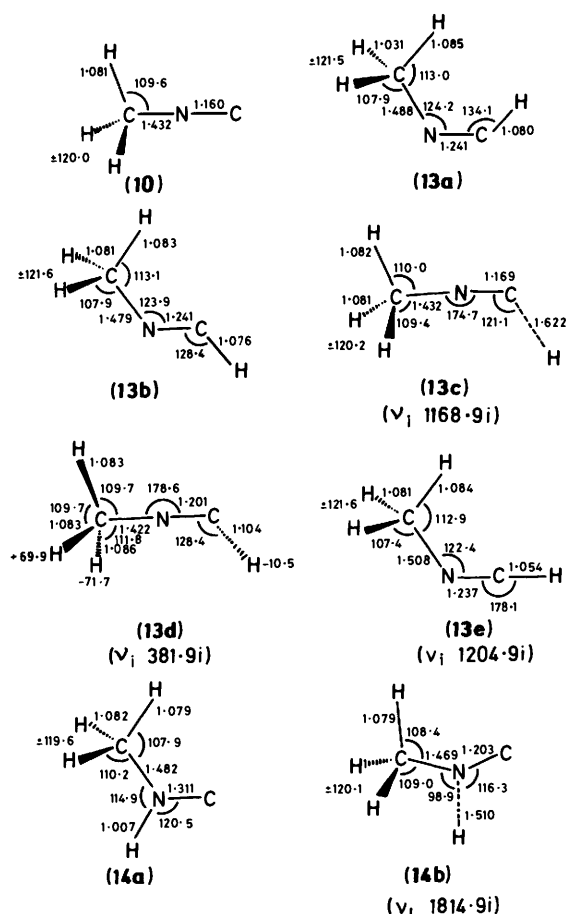
Figure 4. UHF/3-21G-optimized geometries of stationary points on the $H_4C_2N^{\cdot}$ energy surface. Bond lengths are given in Å and bond angles in degrees. v_i are imaginary frequencies in cm^{-1}
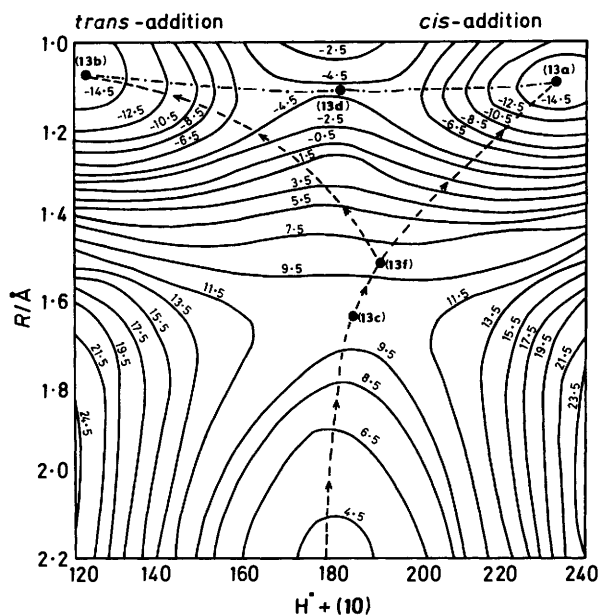

Figure 5. Energy map for the α-addition of H$^{\cdot}$ to $CH_3N{\equiv}C$ (10). See (11f) for the definition of R and α. Isocontour values are given in kcal mol^{-1}. Zero energy level is the H$^{\cdot}$ + (10) system; (13f) is the bifurcating point

UHF/3-21G level. They include the methyl isocyanide (10), the cis-form (13a), and trans-form (13b) of the α-adducts, the β-adduct (14a) and four relevant transition structures (13c—e) and (14b). The two-dimensional energy surface (R, α) for the α-addition of H$^{\cdot}$ to the carbon end of $CH_3N{\equiv}C$ was constructed in the same way as that for the diazonium ion [see (11f)] and is displayed in Figure 5.

Energetic and thermochemical data are recorded in Tables 3 and 4. As in the previous section, we always use the $\Delta H(298$ K) values for the discussion unless otherwise noted. From these calculated results, the following points are noteworthy.

(i) The C–N distance of 1.24 Å in the imidoyl radicals (13a and b) is slightly shorter than that of the imine $H_2C{=}NH$ (1.25—1.26 Å) whereas the CNC angle is significantly larger (ca. 14°). A recent ab initio study[18] compared in some detail the geometries of the parent radical HC=NH obtained by various methods of computation.

(ii) Inference from e.s.r. data previously suggested[6] that structures like (13a and b) are σ-type radicals. Our computed results concur. The unpaired electron is in fact essentially localized on the carbon atom.

(iii) Amongst the four minima examined, the trans-(13b) is again calculated to be the lowest in energy. It is more stable than the cis-(13a) by 4.9 kcal mol^{-1}, the aminocarbyne radical (14a) by 18.1 kcal mol^{-1}, and the separated H$^{\cdot}$ + $CH_3N{\equiv}C$ by 18.2 kcal mol^{-1}. Hence the carbyne radical is much less stable than the nitrene radical cation analogue (see above).

(iv) cis-$CH_3N{=}CH$ (13a) can be converted into trans-(13b) either by a nitrogen or by a carbon inversion via the transition states (13d and e), respectively. The isomerization process is predicted to occur by a nitrogen inversion (having methyl as the inverting group) with an energy barrier of 6.2 kcal mol^{-1}. The carbon inversion requires an additional energy of ca. 5.5 kcal mol^{-1}. The barrier to nitrogen inversion is comparable with the value found above for the azo ion.

(v) The main features of the α-addition of H$^{\cdot}$ to $CH_3N{\equiv}C$ are similar to the previous case. In brief, the transition state (11c) exhibits a slight cis-conformation with a C–N–C frame only marginally bent ($<5°$). The intermolecular distance at the saddle point (R 1.622 Å) is comparable to the N–H value in (11d) (1.576 Å) if we take into account the ratio of those in normal bonds. The attack angle is also ca. 115—122°. The most interesting aspect is that of the bifurcating point [noted as (13f) in Figure 5] again exists on the energy surface so that production of both isomers, cis and trans, is possible. The reaction is thus also non-stereospecific. As mentioned above, this non-stereospecificity is in contrast to the addition of H$^-$ to H–N=C[5] but, to some extent, close to the neutral addition involving $NH_3{\cdot}H_2O$, etc. as nucleophiles to isocyanide.[19] In the latter, the key point which determines the stereochemistry of the transformation is the non-participation of the central nitrogen lone pair to the electronic reorganization along the addition pathway. A similar phenomenon appears to exist in the present case. It is worth noting that addition of H$^{\cdot}$ to the nitrogen end of hydrogen cyanide H–C≡N forms a transition structure also having a cis-conformation but the HCN frame becomes in this case strongly bent.[18]

With regard to the β-addition at the central nitrogen of $CH_3N{\equiv}C$, it can be seen from data listed in Tables 3 and 4 that the energy barrier for this reaction via transition state (14b) (23.8 kcal mol^{-1}) is much higher than that for reaction at the carbon end [7.0 kcal mol^{-1} via (13c)]. This is again in line with the diazonium case.

In the reverse transformation, the energy barriers for the H$^{\cdot}$ loss are as follows: from trans-(13b), 25.2; from cis-(13a), 20.3; from (14a), 23.9 kcal mol^{-1}. These are comparable to the values obtained above for the radical cations $H_4CN_2^+$.

Table 3. Total (a.u.), relative (kcal mol⁻¹, in parentheses), and zero-point vibrational [ZPE (kcal mol⁻¹)] energies, entropies (S, cal mol⁻¹ K⁻¹) and specific heat capacities (C_p, cal mol⁻¹ K⁻¹) of stationary points on the H˙ + CH_3–N≡C pathways

Species[a]	N.I.[b]	UHF/3-21G	UHF/6-31G*	$<S^2>$	UHF/6-31G**	UMP4SDQ/6-31G*	Estimated[c]	ZPE[d]	S^e	C_p^e
(10) + H˙	0	−131.655 36 (0.0)	−132.392 41 (0.0)		−132.397 07 (0.0)	−132.814 05 (0.0)	(0.0)	27.5	58.0	12.0
(13a)	0	−131.681 62 (−16.5)	−132.424 52 (−20.1)	0.9114	−132.431 23 (−21.5)	−132.841 83 (−17.4)	(−18.8)	32.6	63.7	13.2
(13b)	0	−131.684 78 (−18.5)	−132.429 28 (−23.1)	0.8799	−132.435 90 (−24.4)	−132.850 27 (−22.7)	(−24.0)	32.9	63.6	13.2
(13c)	1	−131.640 14 (9.5)	−132.377 04 (9.7)	0.8020	−132.382 86 (8.9)	−132.804 11 (6.3)	(5.5)	28.0	67.6	15.3
(13d)	1	−131.662 92 (−4.8)	−132.402 32 (−6.2)	0.7638	−132.408 96 (−7.5)	−132.830 70 (−10.4)	(−11.7)	31.8	65.2	12.7
(13e)	1	−131.660 26 (−3.1)	−132.399 05 (−4.1)	0.9059	−132.406 24 (−5.8)	−132.820 56 (−4.1)	(−5.8)	31.3	63.8	13.2
(14a)	0	−131.676 18 (−13.1)	−132.407 39 (−9.4)	0.7672	−132.415 86 (−11.8)	−132.820 89 (−4.3)	(−6.7)	33.9	63.5	12.8
(14b)	1	−131.618 55 (23.1)	−132.352 71 (24.9)	0.8736	−132.358 55 (24.2)	−132.777 71 (22.8)	(22.1)	28.7	64.1	13.8

[a] Using 3-31G geometries given in Figure 4. [b] Number of imaginary frequencies. [c] At UMP4SDQ/6-31G** using the additivity relationship, see text. [d] Scaled by a factor of 0.9. [e] At 298 K.

Table 4. Some thermochemical properties for chemical processes of the $H_4C_2N˙$ system

	H˙ + CH₃N≡C ⟶ (13b) [α-addition via (13c)]	H˙ + CH₃N≡C ⟶ (14a) [β-addition via (14b)]	cis–trans Isomerization (13a) ⟶ (13b)	
Property[a]			by methyl N-inversion (13d)	by hydrogen C-inversion (13e)
ΔH(0 K)	−18.6	−0.3	−4.9	
ΔH(298 K)	−18.2	−0.1	−4.9	
ΔS(298 K)	5.6	5.5	−0.1	
ΔG(298 K)	−19.9	−1.7	−4.9	
$\Delta H^{\ddagger}$(0 K)	6.0	23.3	6.3	11.7
$\Delta H^{\ddagger}$(298 K)	7.0	23.8	6.2	11.7
$\Delta S^{\ddagger}$(298 K)	9.6	6.0	1.5	0.1
$\Delta G^{\ddagger}$(298 K)	4.1	22.0	5.8	11.7

[a] From data given in Table 3. See footnotes of Table 2 for definition of properties.

(c) *Conclusions.*—In summary, the α-addition of H˙ either to the nitrogen end of methanediazonium ion or to the carbon end of methyl isocyanide appears to be non-stereospecific. Only a single transition structure exists in each case. The approach of the radical does not induce any significant bending of the substrate. Soon after the transition structure point is passed along the intermolecular distance, a bifurcation of the reaction pathway occurs leading to the formation of both *cis*- and *trans*-isomers of the adduct. It is not yet clear whether the corresponding points empirically located on the energy surfaces belong to a more general class of bifurcating points[20] or not.

In both cases the *trans*-adduct is more stable than the *cis*-adduct and the *cis–trans* stereomutation is, through β-nitrogen inversion, rather easy to achieve. Therefore, the *trans*-isomer can be expected to be the major adduct formed under normal experimental conditions.

Finally, the β-addition at the central nitrogen of both starting compounds is predicted to have an energy barrier higher than that of the α-addition. An energy difference of 7—17 kcal mol⁻¹ seems enough to preclude the formation of a significant amount of the β-adduct.

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