A Theoretical Investigation of the Energy and Structure of Ion–Molecule Pairs in Polar Solvents. Part 2.† Methanediazonium Cation in Water

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MO theory at the CNDO/2 level of approximation was used to investigate the dissociation process of methanediazonium ion *in vacuo* and in water. The dissociation *in vacuo* has also been studied by means of *ab initio* calculations. $CH_3N_2^+$ in solution dissociates without formation of intermediates, unlike $C_6H_5N_2^+$, which forms stable ion–molecule pairs. For both ion–molecules the dissociation energy is drastically reduced on going from gas phase to solution. *Ab initio* calculations for methanediazonium ion, in which polarization functions are included in the basis set, show that the open structure is still significantly more stable than the bridged ones.

DIAZONIUM ions, RN_2^+ have been the object of intense experimental research. In particular, they have frequently been used in the generation of carbonium ions in the liquid phase. However the reaction mechanism is not always completely defined: for example, the nature of the species, R^+ or RN_2^+, which is subject to nucleophilic attack in solution is still a matter of debate.[1] Another problem is the nature of the transition state in the $N_\alpha N_\beta$ rearrangement of benzenediazonium ion.[2,3] To obtain information on these points Vincent and Radom [4] performed *ab initio* MO calculations with minimal (STO-3G) and split-valence (4-31G) basis sets on the open and bridged structures of methane- and benzenediazonium ions.

Since previous theoretical work on diazonium ions [4,5] has generally been limited to the study of isolated ions *in vacuo*, while most experimental work is carried on in solution, it seemed to us appropriate to extend the theoretical study to dissociation in presence of solvent molecules. As a first step the role of the solvent in the dissociation mechanism has been investigated in the case of benzenediazonium ion, by performing MO calculations at the CNDO/2 approximation level [6] on a model cluster formed by the ion and six or seven water molecules simulating the first shell of solvation. The dissociative reaction path revealed the existence of stable ion–molecule pairs, giving significant support to the mechanism proposed by Szele and Zollinger, on the basis of kinetic data,[2,3] for the dediazoniation of 2,4,6-trimethylbenzenediazonium ion in 2,2,2-trifluoroethanol.

As a second step the reaction path for the dissociation of methanediazonium ion was studied both *in vacuo* and in solution. For the reaction *in vacuo* the calculations were performed both by *ab initio* and semiempirical methods. The aim of the *ab initio* calculation was to obtain an energy curve of quantitative significance for the dissociation process in the gas phase and to check the influence of the basis set and of the method of calculation on the results. For the reaction in solution only semiempirical calculations were feasible and the aim of this qualitative approach was to explore the possible formation of intermediates, stabilized by the surrounding solvent molecules. We now report our results.

The first shell of solvation of $CH_3N_2^+$ is simulated by nine water molecules. The assumption of the model and its validity and limits were discussed in our previous paper.[6] In particular we want to stress again that only qualitative significance can be assigned to semiempirical results. Furthermore the results of these calculations allow a comparison with the corresponding ones for benzenediazonium ions,[6] and can provide further support in favour of the reliability of the proposed model for investigating the dissociation of ion–molecules in solution. Particular attention has to be paid to the danger that the existence of intermediates in the reaction path may be an artifact of the approximations included in the model.

CALCULATIONS

(a) Ab initio.—*Ab initio* calculations for the open and bridged structures (I)—(III) (Figure 1) of $CH_3N_2^+$, CH_3^+, and N_2 were performed by the IBMOL program, using double zeta quality basis sets. A first basis set, to which we refer as (9/5), was built up by (9*s*5*p*) Gaussian functions,[7] contracted [8] to [4*s*2*p*] for the C and N atoms, and by (4*s*), contracted [9] to [2*s*], for the H atoms. A more extended basis set, which we refer to as (9/5/1), was obtained by adding to the first a polarization function [10] of *d* symmetry on the C and N atoms, and of *p* symmetry on the H atoms, respectively.

The open and bridged structures (I)—(III) of $CH_3N_2^+$, CH_3^+, and N_2 were fully optimized with the (9/5) basis set, subject only to symmetry constraints. When the extended basis was employed, CH_3^+ and N_2 were fully optimized. For the bridged structures (II) and (III) of $CH_3N_2^+$, C–H and N–N bond lengths were kept fixed (C–H 1.08, N–N 1.10 Å). Previous calculations by Vincent and Radom [4] justify the assumption of a fixed N–N bond length. In the case of the open structure (I) the total energy and charge distribution were computed with the (9/5/1) basis set, the geometry being that optimized with the reduced (9.5) basis.

(b) *Semiempirical.*—The energies and the charge densities of the isolated $CH_3N_2^+$, structures (I)—(III), and the cluster $CH_3N_2^+(H_2O)_9$, structure (VI), have been computed by the CNDO/2 method with standard parametrization.

For each system, isolated or surrounded by water mole-

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† Part 1, see ref. 6.

cules, an energy minimization process,[12] which iteratively optimizes the geometrical parameters through a quadratic interpolation until a self-consistent set of values is obtained, was carried out.

TABLE 1

Ab initio energies (a.u.) for the open (I) and bridged (II) and (III) structures of $CH_3N_2^+$, CH_3^+, and N_2, calculated by different computing techniques and basis sets

	STO-3G [a]	4-31G [a]	(9/5) [b]	(9/5/1) [b]
$CH_3N_2^+$ (I)	−146.362 38	−147.974 76	−148.111 05	−148.218 41 [c]
$CH_3N_2^+$ (II)	−146.287 87	−147.929 93	Unstable	−148.189 63
$CH_3N_2^+$ (III)	−146.287 87	−147.929 93	Unstable	−148.189 63
CH_3^+	−38.779 48	−39.175 12	−39.210 21	−39.233 69
N_2	−107.500 65	−108.754 22	−108.860 23	−108.955 39

[a] Vincent and Radom's calculations.[4] [b] Present calculations. [c] Geometry optimized with the (9/5) basis set.

Both for the ions $CH_3N_2^+$ and CH_3^+ and the molecules N_2 and H_2O fully optimized CNDO/2 geometries were assumed throughout the calculations. For the clusters simulating the first shell of solvation the number of optimizing geometrical parameters was limited to those that proved to be the most relevant in the reaction under study.

RESULTS AND DISCUSSION

(a) Ab initio.—$CH_3N_2^+$ in vacuo. With the basis set (9/5) only the open structure corresponds to a stable conformation, unlike the bridged ones which are unstable. The total energy of $CH_3N_2^+$, together with those of the component fragments CH_3^+ and N_2, calculated with the same basis set, are reported in Table 1. In Table 1 the corresponding energies obtained by different computing techniques and basis sets are also included for reference.

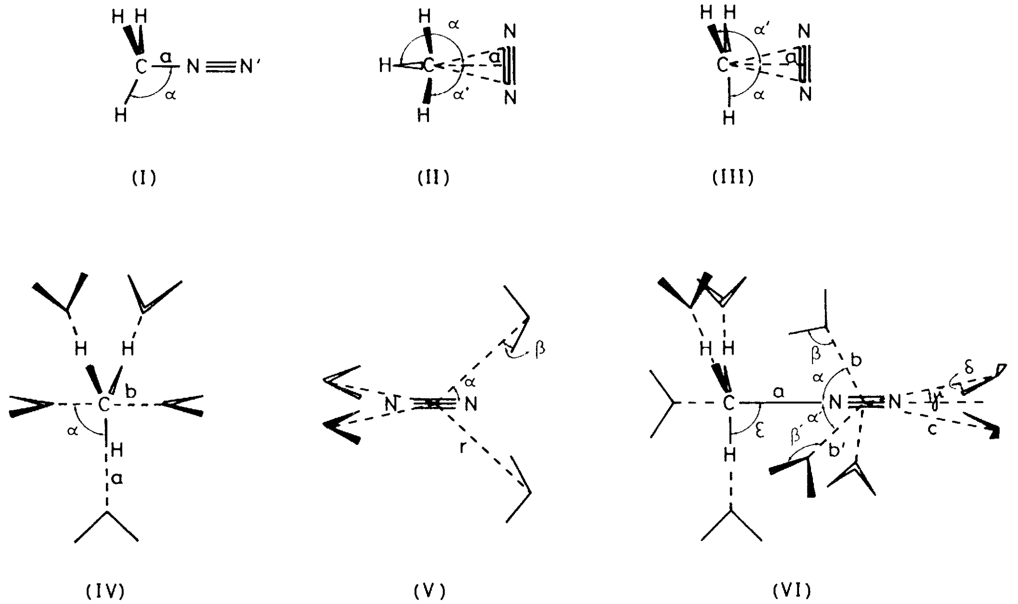

FIGURE 1 Geometrical parameters for $CH_3N_2^+$ [(I)—(III)], $CH_3^+(H_2O)_5$ (IV), $N_2(H_2O)_4$ (V), and $CH_3N_2^+(H_2O)$ (VI)

The dissociation energy calculated at 0 K, without zero point energy correction, is 25.5 kcal mol^{-1}. This value is in line with a theoretical result (28.5 kcal mol^{-1}) previously obtained by using a different basis set and computing technique,[4] and can be compared with the value of 38 kcal mol^{-1} estimated from ion cyclotron resonance spectroscopy.[13]

When the carbon–nitrogen distance was increased from the value at the energy minimum, the curve shown in Figure 2 was obtained. The geometry, charges, and total energy at each point of the reaction co-ordinate (*a*) are collected in Table 3, where the corresponding values for the dissociated moieties are also included. The regular trend of the energy and of the charge distribution from the minimum to dissociation are noteworthy.

TABLE 2

Ab initio binding energies (kcal mol^{-1}) and geometrical parameters of the open structure (I) of $CH_3N_2^+$

Method	$-\Delta E$	C–N (Å)	C–H (Å)	N–N (Å)	$\widehat{HCN}$ (°)
STO-3G [a]	51.6	1.56	1.10	1.14	104.7
4-31G [a]	28.5	1.51	1.08	1.08	105.6
(9/5) [b]	25.5	1.53	1.08	1.10	105.1
(9/5/1) [b]	18.4	1.53	1.08	1.10	105.1

[a] Vincent and Radom's calculations.[4] [b] Present calculations.

The total energy and the charge distribution for the open structure as well as for the component fragments were also computed with (9/5/1) basis set, which includes polarization functions. The energies and geometries are given in Tables 1 and 2, the charge distributions are displayed in Figure 3. With this extended basis set an energy minimum was found also for the bridged structures (II) and (III), which turned out to have practically the same energy and the same value (2.75 Å) for the geometrical parameter *a* (see Figure 1). For both structures, due to the distance between the two fragments in the minimum, the methyl cation was found to be planar, carrying a positive charge of 0.96 e. The rotation of the methyl group occurs without energy barrier. The dissociation energy is extremely low, <1 kcal mol^{-1}.

TABLE 3

Ab initio [a] total energy, geometry, and charges for $CH_3N_2^+$, structure (I), at several points of the reaction path

	a(Å)	$-E$(a.u.)	α(°)	q_C	q_H	q_N	$q_{N'}$
$CH_3N_2^+$ (I)	1.53	148.1111	105.1	−0.59	+0.43	−0.02	+0.32
	2.06	148.1002	94.4	−0.40	+0.42	−0.09	+0.22
	2.32	148.0940	92.0	−0.35	+0.43	−0.11	+0.18
	3.00	148.0818	90.0	−0.30	+0.43	−0.10	+0.11
	3.50	148.0772	90.0	−0.30	+0.43	−0.08	+0.08
	4.00	148.0748	90.0	−0.30	+0.43	−0.06	+0.06
	5.00	148.0727	90.0	−0.31	+0.44	−0.04	+0.04
	6.00	148.0717	90.0	−0.31	+0.44	−0.03	+0.03
CH_3^+		39.210 21		−0.31	+0.44		
N_2		108.860 23				0	0

[a] (9/5) Basis set.

From the previous[4] and present results some points emerge. First the geometries computed by different methods and basis sets are very similar and no significant improvement could probably be obtained by more sophisticated calculations. On the contrary, the charge distributions are basis dependent. In particular, while the charge spread on methyl moiety is *ca.* 0.6—0.7 e for the linear structure, the charge polarization on CH bonds strongly depends on basis set (see Figure 3, Table 3, and ref. 4). For the bridged structures 0.78 and 0.96 e are predicted on methyl moiety by the STO 3G and (9/5/1) basis sets, respectively. The same effects on charge distribution of CH bonds observed in the open structure are found in the bridged ones.

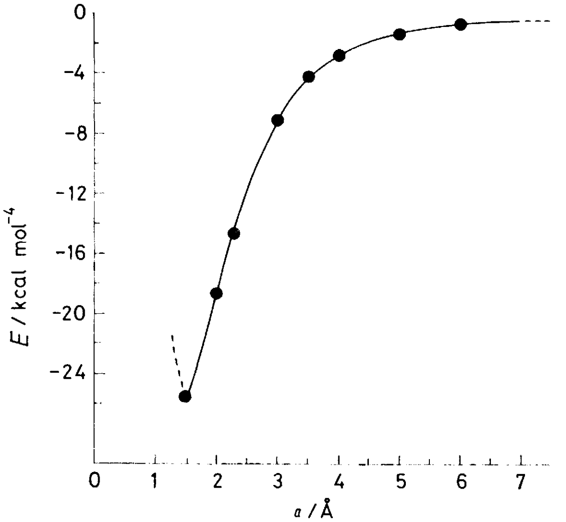

FIGURE 2 *Ab initio* binding energy *versus* C–N distance *a* for the dissociation of $CH_3N_2^+$ *in vacuo* for the open structure (I)

The inclusion of polarization functions in the basis set does not modify significantly the relative stability of the open and bridged structures. Moreover the low binding energy, the large interfragment distance, and the sharp charge separation demonstrate the rather low stability of the bridged structures in the gas phase.

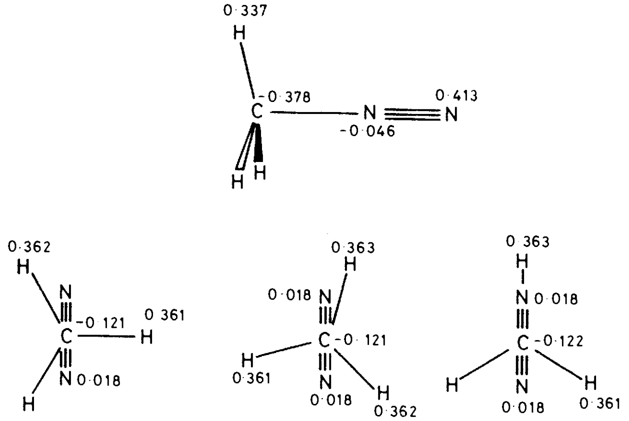

FIGURE 3 Charges (in a.u.) for the open and bridged structures of $CH_3N_2^+$, as computed by the *ab initio* method [(9/5/1) basis set]

(b) *Semiempirical*.—$CH_3N_2^+$ in vacuo. The structures of the open (I) and bridged forms (II) and (III) of methanediazonium ion shown in Figure 1, for which there are no experimental data, have been fully optimized by the CNDO/2 method. The most important data are collected in Tables 4 and 5. The main results from the CNDO calculations are the order of stability of the structures and the instability of structure (II). Unlike the *ab initio* results, structure (III) is the most stable. Furthermore no barrier was found in the interconversion between structures (III) and (II) simply connected by a methyl rotation, so that structure (II) is associated with an unstable conformer. The fact that structure (III) is more stable than (I) is easily explained by the consideration that CNDO/2 systematically overestimates bonding properties. The same inversion of stability of open and bridged structures was found by CNDO in the case of the benzenediazonium cation,[6] again in contrast with the *ab initio* calculations.[4] In Figure 4 it appears that the energy dissociation curve of the ion molecule (I) *in vacuo* shows the expected Morse-like behaviour. It emerges from Table 4, where total energy, geometry, and atomic charges for the open structure, at several points along the reaction path of $CH_3N_2^+$ are reported, that the positive charge, which at the minimum is spread between $CH_3^{+\delta}$ (δ 0.423) and $N_2^{+\delta'}$ (δ' 0.577) moieties after the reaction co-ordinate reaches *a* 2.45, is practically localized on the methyl ion (δ 0.88), which is nearly planar.

TABLE 4

CNDO/2 Total energy, geometry, and charges for $CH_3N_2^+$, structure (I), at several points of the reaction path[a]

	a(Å)	$-E$(a.u.)	α(°)	q_C	q_H	q_N	$q_{N'}$
$CH_3N_2^+$ (I)	1.39	32.2299	108.5	+0.020	+0.135	+0.320	+0.255
	1.70	32.1127	105	+0.124	+0.130	+0.215	+0.272
	2.00	31.9517	98	+0.232	+0.146	+0.102	+0.227
	2.45	31.8139	92	+0.349	+0.176	−0.018	+0.139
	2.90	31.7728	90	+0.399	+0.191	−0.057	+0.084
	4.00	31.7623	90	+0.412	+0.196	−0.043	+0.043
	5.00	31.7619	90	+0.412	+0.196	−0.029	+0.029
CH_3^+		8.6711	90	+0.412	+0.196		
N_2		23.0905				0.000	0.000

[a] C–H bond length was kept fixed (1.13 Å); N–N bond length was practically unchanged along the reaction path (1.043 Å).

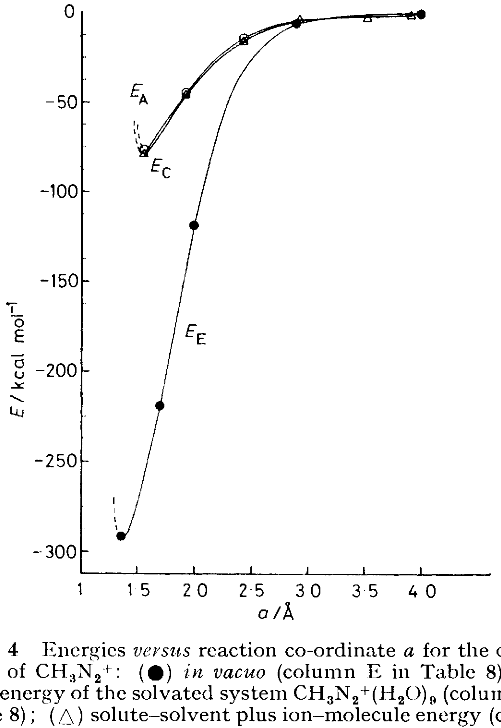

FIGURE 4 Energies *versus* reaction co-ordinate *a* for the dissociation of $CH_3N_2^+$: (●) *in vacuo* (column E in Table 8); (○) total energy of the solvated system $CH_3N_2^+(H_2O)_9$ (column A in Table 8); (△) solute–solvent plus ion–molecule energy (column C in Table 8). In all cases it is assumed $E(\infty) = 0$

$CH_3^+(H_2O)_n$, n = 5. According to CNDO/2 calculations, the methyl cation *in vacuo* has planar geometry (D_{3h} symmetry) with bond lengths of 1.118 Å. The first shell of solvation of the ion was simulated by five water molecules at the apices of a trigonal bipyramid, with water oxygens pointing towards the central cation. The optimized geometrical parameters shown in (IV) were taken from ref. 14 and the relevant data are collected in Table 6.

$N_2(H_2O)_n$, n = 4. An analysis, of the solvation of N_2 is available in ref. 15. To keep the required amount of computing time for hydrated $CH_3N_2^+$ at a reasonable level, four water molecules were used to describe the first shell of solvation of N_2. For this system the calculated energy *E* is −102.7160 a.u. and the geometry is given by *r* 2.90 Å, α 50°, β 10° [see (V)]. The water molecules at the two ends of N_2 lie in perpendicular planes.

$CH_3N_2^+(H_2O)_n$, n = 9. The cage representation of the first shell of solvation of $CH_3N_2^+$ was built up by nine water molecules, as a consequence of the five and four solvent units used to describe the first shell of solvation of CH_3^+ and N_2, respectively. The reaction co-ordinate for the dissociative reaction path of $CH_3N_2^+$ [structure (VI)] in solution is the same as *in vacuo, i.e.* N_2 moves along the symmetry axis (C_3) of the methyl cation.

TABLE 5

CNDO/2 Total energy, binding energy, and geometry for structures (I)—(III) of $CH_3N_2^+$ *in vacuo*

$CH_3N_2^+$	E (a.u.)	$-\Delta E$[a]	C–N (Å)	N–N (Å)	C–H (Å)	α (°)	α' (°)
(I)	32.2299	293.6	1.39	1.143	1.13	108.5	
(II)	32.2757	322.0	1.50	1.243	1.13	114.0	108
(III)	32.2849	328.0	1.50	1.243	1.13	90.0	116

[a] $\Delta E = E[CH_3N_2^+] - E[CH_3^+] - E[N_2]$ in kcal mol^{-1}.

TABLE 6

CNDO/2 energy and geometrical parameters of $CH_3^+(H_2O)_n$ (n = 0–5)

	$-E$ (a.u.)	$-\Delta E$[a]	C–H (Å)	a (Å)[b]	b (Å)[b]	α (°)[b]
CH_3^+	8.6711		1.118			
$CH_3^+(H_2O)_5$	108.6364	320	1.118	1.647	1.529	90.0

[a] $\Delta E = E[CH_3^+(H_2O)_5] - E[CH_3^+] - 5E\ [(H_2O)]$ in kcal mol^{-1}. [b] Geometrical parameters shown in (IV).

The geometrical parameters taken into consideration at each point of the reaction co-ordinate are shown in Table 7, where the optimized values are also collected. The trend of the total energy *versus* the reaction co-ordinate is shown in Figure 4 (E_A). The values of the energies shown here have no quantitative significance as can easily be recognized by comparison of the curve E_E in Figure 4 with the corresponding one of Figure 2. The structures of the clusters corresponding to the minimum (*a* 1.526 Å) and to other two points of the reaction co-ordinate, *a* 2.43 and 3.93 Å respectively, are shown in Figures 5—7. As *in vacuo*, just only one minimum is found at *a* 1.526 A; thus, the covalent C–N bond in solution is considerably stretched with respect to the same bond in the gas phase. No local minima are found between the solvated $CH_3N_2^+$ and the solvated products of dissociation, in sharp contrast with our finding for benzenediazonium cation[6] and methyl fluoride.[14] For the minimum in solution, unlike *in vacuo*, the $\widehat{HCH}$ bond angle is nearly 120°, so that the methyl moiety is practically planar. Moreover the charge is now partially spread on the surrounding solvent molecules. The positive charge on the methyl ion is practically unchanged (δ 0.423 *in vacuo* and 0.404 in solution), unlike the N_2 moiety which in solution is significantly different (δ′ 0.577 *in vacuo* and 0.194 in solution). Starting from *a* 2.5 Å the positive charge is almost completely smeared over the methyl moiety and its surrounding water molecules. The charge distributions in Figures 5—7 show that a significant charge separation between solute and solvent is always present. However this effect is probably overestimated by the method of calculation employed.

TABLE 7

CNDO/2 Optimized geometry for $CH_2N_2^+(H_2O)_9$ [a]

a(Å)	b(Å)	α(°)	β(°)	c(Å)	γ(°)	δ(°)	ε(°)	b'(Å)	α′(°)	β′(°)	θ(°)
1.526	1.76	63.9	95.8	2.90	50.0	10.0	90.0				
1.9285	1.79	55.3	89.4	2.90	50.0	10.0	90.0	1.79	57.4	89.9	120.0
2.4285	1.79	56.0	89.5	2.90	50.0	10.0	90.0	1.79	56.0	89.5	118.0
2.9285	1.79	56.0	89.5	2.90	50.0	10.0	90.0	1.79	56.0	89.5	120.0
3.4285	1.79	56.0	89.5	2.90	50.0	10.0	90.0	1.79	56.0	89.5	120.0
3.9285	1.79	56.0	89.5	2.90	50.0	10.0	90.0	1.79	56.0	89.5	120.0

[a] Geometrical parameters shown in (VI). [b] θ is the dihedral angle defined by ($a \times b$) and ($a \times b'$).

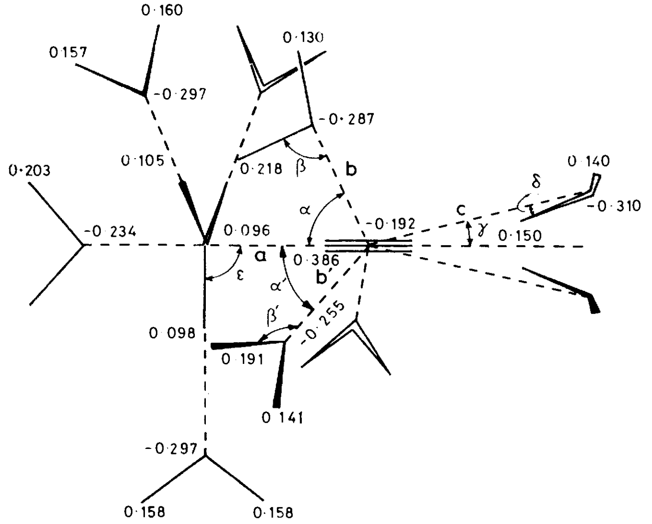

FIGURE 5 Geometries and charges (in a.u.) for the solvated $CH_3N_2^+$ (I), at the energy minimum (*a* 1.526 Å). The values of the optimized parameters are reported in Table 7

To investigate the role of the different contributions to the energy of the cluster, the energies of the solvent molecules alone, fixed at the position optimized at the different values of the reaction co-ordinate, have been computed. The results are summarized in Table 8, where in columns A and B the total energy of solvated methanediazonium ion and the energy of the cor-

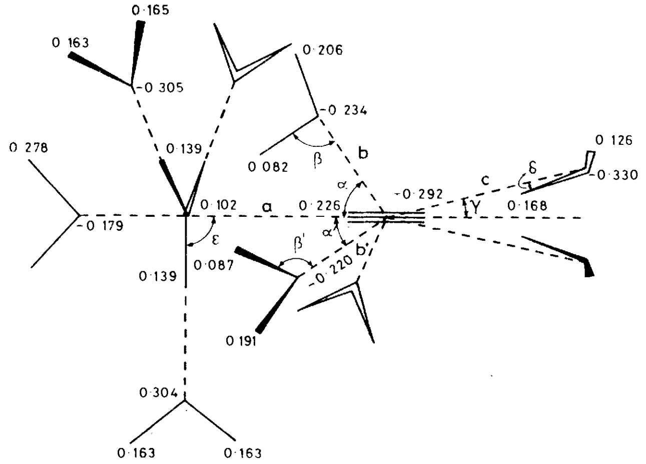

FIGURE 6 Geometries and charges (in a.u.) for the dissociation process of the solvated $CH_3N_2^+$ at *a* 2.43 Å. The values of the optimized parameters are reported in Table 7

TABLE 8

Total energy, solvent cage energy, and different contributions to solvation energy for $CH_3N_2^+(H_2O)_9$ (VI) [a]

a(Å)	A	B	C	D	E	F
1.56	−211.4681	−179.0184	−32.4497	+0.0024	−32.1827	−0.2670
1.93	−211.4108	−179.0199	−32.3909	+0.0009	−31.9552	−0.4357
2.43	−211.3601	−179.0201	−32.3400	+0.0007	−31.8167	−0.5233
2.93	−211.3431	−179.0203	−32.3228	+0.0005	−31.7720	−0.5508
3.43	−211.3386	−179.0205	−32.3181	+0.0003	−31.7640	−0.5541
3.93	−211.3375	−179.0207	−32.3168	+0.0001	−31.7619	−0.5549

[a] A, total energy; B, energy of the solvent cluster; C, $E_C = E_A - E_B$; solute–solvent plus ion–molecule energy; D, $E_B - nE_{H_2O}$; energy difference between water cage and a corresponding number of isolated solvent units; E, energy of the isolated ion–moecule; F, $E_F = E_C - E_E$; this term prepresents the solute–solvent interaction. Energies in a.u.

responding solvent cages are reported. In column C the energy difference between A and B, which represents both the solute–solvent interaction and the methanediazonium ion energy, is reported. In column D the difference between the energy of the water cages and that of a corresponding number of isolated water molecules is given. By substracting the energy of free $CH_3N_2^+$ (reported in column E) from the values of column C, the energy of the solute–solvent interactions at each point of the reaction co-ordinate are obtained (column F).

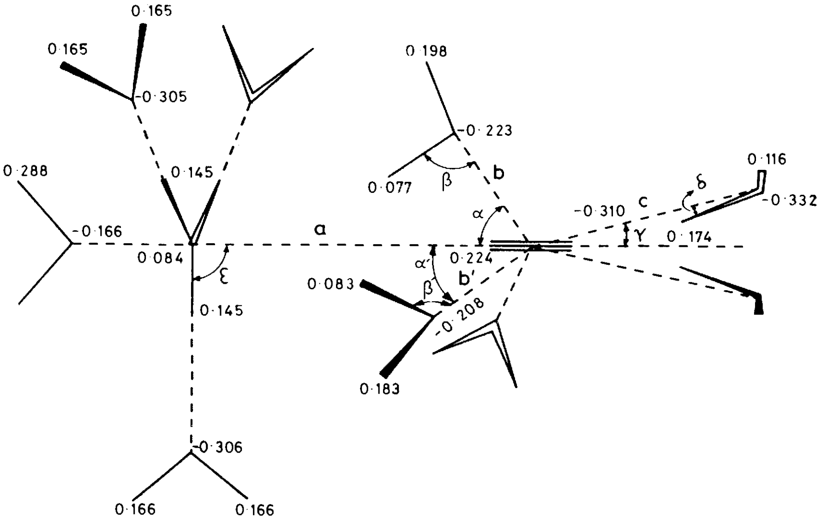

FIGURE 7 Geometries and charges (in a.u.) in the dissociation process of the solvated $CH_3N_2^+$ at *a* 3.93 Å. The values of the optimized parameters are reported in Table 7

The data collected in Table 8 have some interesting features. First, it emerges that the binding energies of the solvent cage (column D) are small, <0.15 kcal mol^{-1} per water unit, and much smaller than the corresponding values for the cluster of benzenediazonium ion (Table 5 in ref. 6). Moreover the curve of E_C (or E_A) shows a trend qualitatively similar to that of E_E as shown in Figure 4. Lastly, starting at *a ca.* 2.5 Å the solute–solvent interactions alone (column F) become independent of the reaction co-ordinate.

This behaviour helps to explain the substantial and interesting differences predicted by CNDO/2 calculations for the dissociative path of methanediazonium and benzenediazonium ion–molecules. While for benzenediazonium cation stable ion–molecule pairs are predicted in solution (Figures 3 and 4 in ref. 6) and assist the dissociative process, in the case of methanediazonium cation dissociation occurs without any formation of intermediates. This finding confirms that the minima present in the curve of total energy *versus* the reaction co-ordinate of $C_6H_5N_2^+$ in solution are mainly due to solute–solvent interactions rather than to the solvent–solvent ones. This suggests that the existence of stable ion–molecule pairs predicted by CNDO/2 for benzenediazonium cation (and not predicted for methanediazonium cation) is not an artifact due to the approximations included both in the model and in the method of calculation employed.

In conclusion, by comparison of the present results with those obtained in the companion study of benzenediazonium cation in water it appears that the two ion–molecules show the common feature that the dissociation energy is drastically reduced on going from the gas phase to solution, while their behaviour is opposite with respect to the formation of stable intermediates. Consequently, $N_\alpha N_\beta$ rearrangement in methanediazonium ion should occur without formation of an intermediate not only in the gas phase but in solution as well.

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