A Theoretical Investigation on the Energy and Structure of Ion–Molecule Pairs in Polar Solvents. Part 1. Benzenediazonium Cation in Water

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Molecular-orbital theory at the CNDO/2 level of approximation has been used to investigate the stability and structure of ion–molecule pairs in polar solvents. Benzenediazonium cation in water was chosen as a model system. The energy of the solute–solvent supermolecule was calculated as a function of the phenyl–nitrogen distance and the position of the water molecule in the first shell of solvation. The results are in favour of the existence of stable ion–molecule pairs and strongly support the mechanism which has been proposed for the dediazoniation of 2,4,6-trimethylbenzenediazonium ion in 2,2,2-trifluoroethanol on the basis of kinetic data.

THE intervention of ion pairs in solvolytic reactions was suggested and demonstrated long ago,[1] while the stability and structure of such ion pairs have recently been investigated in a simple case (CH_3F in water) by means of calculations based on MO theory.[2] In recent papers it has been proposed that dediazoniation reactions may occur through molecule-ion pairs, and kinetic evidence has been presented to support such a claim.[3] In the present work MO calculations have been performed in order to find out if indeed molecule–ion pairs can be stabilized by a surrounding shell of polar molecules. The benzenediazonium cation in water has been chosen as a model system. The structure of the intermediates formed by interaction between the benzenediazonium cation and the water molecules of the first shell of solvation, are of primary interest for interpreting the path by which the dediazoniation reaction can occur.

However the study of that part of the reaction path from the intermediates to the final products is not within the scope of the present investigation. In this work, fixed structures for solvent molecules of the first shell of solvation were assumed, not allowing bond breaking to occur for the solvent molecules.

The benzenediazonium cation was chosen as a large number of experimental data are available in the literature,[4] both for the unsubstituted compound and for its derivatives. The choice of water as solvent is due to the necessity of limiting the complexity of the 'supermolecule' under study. Fluorinated solvents, such as CF_3CH_2OH or $CF_3CHOHCF_3$ are not suitable for the present calculations. On the other hand the choice is justified insofar as the reaction also occurs in water.[5] The most important aspect of our calculations is the trend of total energy *versus* a reaction co-ordinate which was chosen as the phenyl–nitrogen distance.

It must be kept in mind that for each value of the reaction co-ordinate a large number of configurations with nearly the same energy are present at room temperature. However, we followed the usual practice of ignoring entropy effects. The assumption that the existence of deep minima separated by large energy barriers on the potential surface remains in the free-energy hyperspace is well justified by the results obtained for both chemical reactivity[6] and conformational analysis[7,8] in solution.

The energies and charge distributions of the supermolecules formed by benzenediazonium cation and water molecules have been calculated by the CNDO/2 method.[9] The choice of this semiempirical technique seems reasonable as it proved to lead to satisfactory results for a number of problems in which the influence of the solvent was under study.[10-13]

In the case of solvation of the NH_4^+ ion the CNDO/2 results are in even better agreement with experiment than *ab initio* results.[2]

The speed and accuracy of the CNDO/2 method, in comparison with other MO methods, have been critically discussed.[14] The use of more accurate methods for systems of the size of the supermolecules considered in the present work is precluded by economic considerations.

The electronic and geometrical structure of isolated benzenediazonium cation as well as the variation of energy during dissociation *in vacuo* to N_2 and phenyl cation have also been calculated by the same method. Our results can be compared with those of a recent *ab initio* calculation[15] (see Results and Discussion section).

Calculations.—An energy-minimizing process,[16] which iteratively optimizes the geometrical parameters through a quadratic interpolation until a self-consistent set of values is obtained, was carried out for each system considered, isolated, or surrounded by water molecules. The total energy was calculated by the CNDO/2 method with standard parametrization.[9]

For N_2 and H_2O, the optimized CNDO geometries were assumed. For $C_6H_5^+$ the idealized geometry of a regular hexagon was adopted, as in ref. 17 In the case of solvated supermolecules the number of the geometry parameters to be optimized was limited to those that proved to be the most important in the reaction under study. In every case it has been verified that the existence and position of the minimum was independent of the order in which the different parameters were optimized and on the starting geometry.

RESULTS AND DISCUSSION

1. $C_6H_5^+(H_2O)_n$ ($n = 0, 2, 4, 7,$ *or* 8).—The phenyl cation *in vacuo* ($n = 0$) has been assumed as a regular hexagon with C–C and C–H bond lengths equal to 1.397 and 1.100 Å, respectively. This assumption accords well with the mean value of bond angles of the phenyl ring

in benzenediazonium salts, as shown by *X*-ray diffraction data.[18,19] An assumed rather than an optimized geometry is justified by the need for comparison with the solvated systems, where parameters to be optimized had to be much reduced to keep the length of calculations within a reasonable range.

TABLE 1

Total energies, hydration energies, and geometrical parameters for $C_6H_5^+(H_2O)_n$

n [a]	$-E$/a.u.	$-\Delta E$ [b,c]	a [d]	b [d]	θ	α	c [d]	γ	δ	ε
0	45.768									
2 (1), (2)	85.967	260	1.49		83° 12′ [e]	131° [e]				
4 (1)—(4)	125.764	270	1.49	1.73	83° 12′ [f]	131° [f]				
7 (1)—(7)	185.454	281	1.49	1.76	83° 12′ [f]	131° [f]				
8 (1)—(4), (8)—(11)	205.482	366	1.49	1.81	81° 52′ [e]	116° [e]	1.67	128°	95°	91°

[a] For water molecules see Figure 1. [b] $\Delta E = E(C_6H_5^+ \cdot nH_2O) - E(C_6H_5^+) - n \cdot E(H_2O)$ in kcal mol⁻¹. [c] The reported value should be lowered by *ca.* 10 kcal mol⁻¹ if the mean self-interaction energy of the solvent molecules is taken into consideration (see Table 1 of ref. 10). [d] In Å. [e] Optimized. [f] Assumed.

The hydration of the phenyl cation has been studied by taking into consideration 2, 4, 7, and 8 solvent molecules, respectively. The total energy of $C_6H_5^+(H_2O)_2$ was minimized with respect to the geometrical parameters *a*, *b*, α, and θ shown in Figure 1a. The latter parameters α and θ were kept fixed for the supermolecules with $n = 4$ and 7. A more refined calculation, in which the total energy was minimized with respect to the eight independent parameters shown in Figure 1b, has been performed for investigating the role in the solvation process of four more water molecules, two above and two below the phenyl ring.

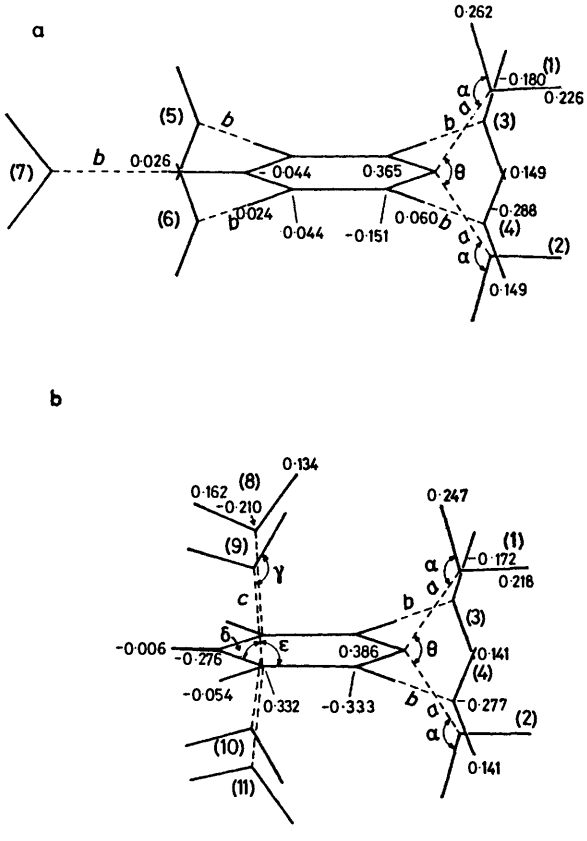

FIGURE 1 Geometry parameters for the $C_6H_5^+(H_2O)_n$ systems: (a) the reported net charges refer to the fully optimized $C_6H_5^+$-$(H_2O)_4$ system: solvent molecules lie in planes perpendicular to the phenyl ring; (b) $C_6H_5^+(H_2O)_8$ fully optimized: in this system the planes containing the water molecules (8)—(11) are bent by *ca.* 50° with respect to the phenyl ring

The most important calculated data, *i.e.* the minimum energy, the hydration energy, and the optimized parameters are collected in Table 1. It must be remarked that the solvent molecules (1)—(7) (Figure 1a) lie in planes perpendicular to the phenyl ring, and displacements from these planes have an insignificant effect on the total energy ot the hydrated systems.

It emerges from column 3 of Table 1 that the main contribution to hydration energy comes from the water molecules identified as (1) and (2) in Figure 1a. In this view water molecules labelled (5)—(7) were not included into the calculation of the reaction path for the solvolysis.

Even if the four molecules (8)—(11) (Figure 1b) give a rather important contribution to the solvation energy (*ca.* 25%), it may be expected that, owing to their location, they do not play an important role in solvolysis. This has been verified in our calculations (see later). Moreover it emerges from Figure 1 that their exclusion affects but slightly the charge distribution of the carbons and the hydrogens close to the reaction site.

2. $C_6H_5N_2^+$ *in vacuo*.—It is well known from *X*-ray crystallographic data[18,19] that the geometry of the benzenediazonium cation in the solid phase is approximately that of structure (I) in Figure 2. However the existence of structures (II) and (III) in Figure 2 has been proposed to explain the solvation mechanism of benzenediazonium salts.[5] The geometries of the three structures have been optimized by the CNDO/2 method and the relevant results are collected in Table 2, together with experimental and *ab initio* values.

TABLE 2

Total energies, stabilization energies, and optimized geometrical parameters for structures (I)—(III) of benzenediazonium cation *in vacuo*

$C_6H_5N_2^+$	$-E$/a.u.	$-\Delta E$ [a]	a [b]	b [b]
(I)	69.257	250	1.400 [c,d]	1.146 [c,d]
(II)	69.314	285	1.375	1.190
(III)	69.331	301	1.370 [e]	1.195 [e]

[a] $\Delta E = E(C_6H_5N_2^+) - E(C_6H_5^+) - E(N_2)$ in kcal mol⁻¹. [b] In Å. [c] Mean experimental values: *a* 1.40 Å, *b* 1.10 Å.[15] [d] *Ab initio* values:[15] *a* 1.469, *b* 1.143 Å. [e] *Ab initio* values:[15] *a* 1.50, *b* 1.22 Å.

The energies along the reaction path for the dissociation process concerning the three structures have been calculated for several values of the reaction co-ordinate *a*, and are illustrated in Figure 2. Total energies, charge densities of the atoms directly involved in the dissociation, and optimized N–N bond distances are collected in Table 3.

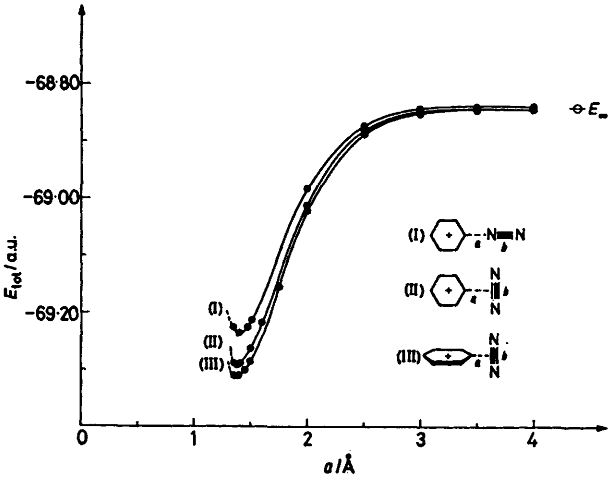

FIGURE 2 Reaction paths for the dissociation of benzenediazonium cation *in vacuo*

Structure (III) is the most stable—contrary to the results in ref. 15. The result is not surprising, keeping in mind that the CNDO/2 method systematically overestimates bonding properties. From Tables 2 and 3 it appears that our results *in vacuo* both for geometries and charge distributions are in reasonable agreement with those of ref. 18. The most striking difference is the charge on N′ for structure (1), but it must be taken into account that these numbers refer to geometries with a significant difference in the C′–N′ distance. The three energy curves in Figure 2 do not show energy barriers between reactants and reaction products.

TABLE 3

Energy, geometry parameters, and charge densities for $C_6H_5N_2^+$ [structures (I)—(III)] *in vacuo* at several values of the reaction co-ordinate

	a	Min [b]	2.0	2.5	3.0	4.0	∞
(I)	*E*/a.u.	−69.257	−69.008	−68.890	−68.863	−68.858	−68.858
	$r(N_2)$/Å	1.15 (1.14)	1.14	1.14	1.14	1.14	1.14
	$q_{C'}$ [a]	0.073 (0.119)	0.228	0.289	0.302	0.303	0.303
	$q_{N'}$	0.215 (0.083)	0.086	−0.015	−0.040	−0.032	0.0
	q_N	0.277 (0.279)	0.164	0.081	0.050	0.032	0.0
(II)	*E*/a.u.	−69.314	−69.033	−68.897	−68.864	−68.858	*c*
	$r(N_2)$/Å	1.19	1.15	1.14	1.14	1.14	
	$q_{C'}$	0.149	0.223	0.282	0.299	0.303	
	q_N	0.212	0.129	0.038	0.006	0.000	
(III)	*E*/a.u.	−69.331	−69.045	−68.906	−68.872	−68.866	*c*
	$r(N_2)$/Å	1.19 (1.22)	1.15	1.15	1.14	1.14	
	$q_{C'}$	0.115 (0.060)	0.213	0.280	0.298	0.301	
	q_N	0.164 (0.110)	0.128	0.039	0.006	0.000	

[a] C′–N′–N. [b] Numbers in parentheses are from ref. 16. [c] See structure (I).

In the case of structure (I), the N–N bond length is independent of the reaction co-ordinate *a*, and, as shown in Table 3, it is nearly coincident with the value calculated for the isolated molecule (1.143 Å).[9] In the case of structure (II) and (III) N–N bond lengths show small and regular variations from 1.195 to 1.143 Å. On the basis of these results, in the following calculations N–N bond lengths were assumed fixed at the values calculated in the minimum of the isolated molecule.

3. $C_6H_5N_2^+(H_2O)_n$ [$n = 7$ *for* (I), 6 *for* (II) *and* (III)].—To keep the amount of computing time reasonable, the solvent molecules which affect the solvation energy only slightly have not been taken into consideration. Accordingly, the solvent cage for the main part of the first solvation shell of the benzenediazonium cation was composed of seven water molecules in the case of structure (I), and six for structures (II) and (III). However it must be observed that the water molecule (7) in Figure 3 does not play any role in the dissociation process, even if it belongs to the first shell of solvation. The geometrical parameters optimized in the three cases represent positions and orientations of the solvent molecules subject to the following constraints: water molecules (1)—(4) and (7) in Figure 3 are in planes perpendicular to the phenyl ring of structure (I), as opposed to water molecules (5) and (6) which lie in the plane of the phenyl ring.

The reaction co-ordinate *a* is the same as that *in vacuo*, *i.e.* N_2 moves along the symmetry axis (C_2) of the phenyl ring. The reaction co-ordinate for structure (I) is identical with the C–N distance; for structures (II) and (III) the reaction co-ordinates are the distances between the carbon atom carrying no hydrogen and the middle point of the N–N bond. The calculated reaction path for structure (I) is shown in Figure 4. As opposed to the same calculation *in vacuo*, two well defined minima are found at 2.3 and 5.0 Å, respectively (from the phenyl ring). The more stable intermediate corresponds to the larger distance. The most interesting point is the disappearance of the minimum found *in vacuo* at a reaction co-ordinate corresponding to the C–N bond length. The optimized geometrical parameters or the reaction intermediates, corresponding to the energy minima, are shown in Table 4. The charge distribution is shown in Figure 3.

TABLE 4

Optimized geometry parameters for the reaction intermediates of $C_6H_5N_2^+(H_2O)$ shown in Figures 3—6

	a/Å	b/Å	α (°)	θ (°)	c/Å	ε (°)	d/Å	β (°)	e/Å [b]	γ (°)	δ (°)
(I)	2.30	1.51	92.0	90.4	1.33	[a]	2.44	28.0	2.66	16.2	76.4
	5.00	1.47	106.5	91.1	1.35	[a]	3.45	6.5	2.58	16.9	36.0
(II)	1.43	1.82	103.4	152.1		56.2	1.76	168.6	2.56	33.5	144.0
	3.43	1.45	122.7	81.5		79.3	1.58	153.5	2.55	20.0	146.5
(III)	1.45	1.88	98.8	158.8		100.2	1.62	186.5	2.86	43.4	127.2
	3.58	1.48	118.4	82.7		120.1	1.48	166.5	2.71	21.4	129.2
	5.01	1.48	122.2	81.0		126.6	1.48	160.0	2.46	20.1	56.6

[a] ε = 180°. [b] f 1.60 Å, was kept fixed.

From these data it appears that solute–solvent distances and their relative locations are reasonable: *e.g.* notice that the shortest distances are in line with those predicted for hydrogen bonds. The comparison between the charge densities of the solvated intermediates and the isolated systems provides evidence that solvation brings about a significant redistribution of charge. In detail the positive charge, equally spread between the phenyl ring and the nitrogen subsystem *in vacuo*, is now located on the phenyl ring and on the water molecules directly involved in the nitrogen bonds, more on water molecules (1) and (2), than on (3) and (4). Nitrogen is practically neutral. For the reaction co-ordinate a = 5 Å the mechanism of expulsion of N_2, carried out by molecules (5) and (6) becomes evident.

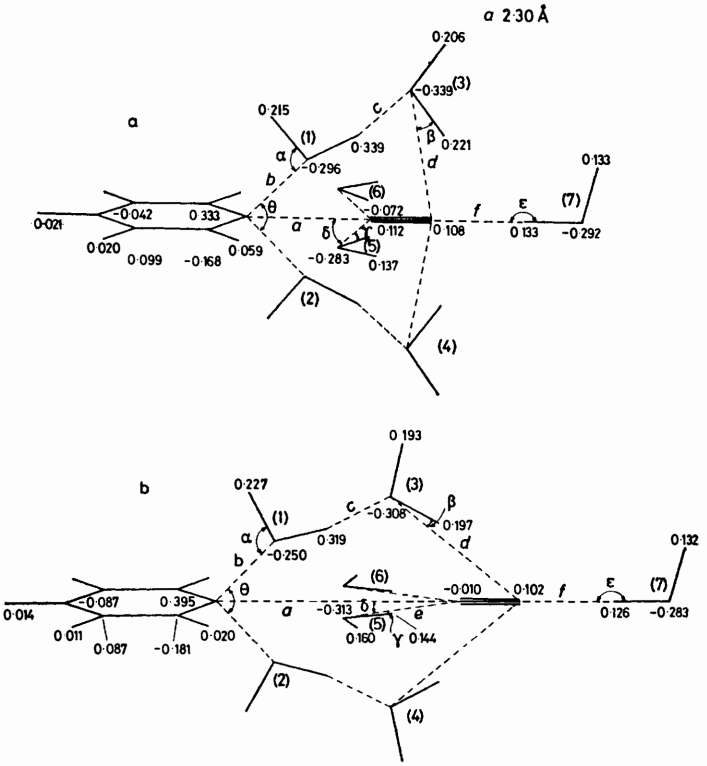

FIGURE 3 Geometries and net charges (in electrons) for the two intermediates (a 2.30 and 5.00 Å, respectively) in the dissociation process of solvated benzenediazonium cation (I). The values of the optimized geometry parameters are reported in Table 4. The solvent molecules identified as (5) and (6) are in the phenyl ring plane, on the opposite sides of the reaction co-ordinate

Also in the case of the reaction path of structure (II), two well defined minima are observed. The relevant data on the two intermediates are available in Table 4 and Figure 5. The more stable intermediate is found at a 1.43 Å, a reaction co-ordinate nearly coincident with that of the only minimum found *in vacuo*. The other intermediate is found at a 3.43 Å, and in this case the nitrogen is moving away together with four molecules of solvent. The charge distribution of the first intermediate is like that found *in vacuo*, whereas the charge distribution of the second intermediate puts in evidence for the presence of an aryl cation not completely solvent-separated from nitrogen. However the N_2 molecule is practically neutral.

The positive charge is spread both on the phenyl ring and on the solvent molecules (1) and (2).

From the shape of the energy curve related to structure (III) three well defined minima at *a* 1.45, 3.58, and 5.01 Å, respectively, can be identified. Their relevant energy and geometry parameters are shown in Table 4 and Figure 6. The intermediates associated with the three minima have comparable stabilities and are separated by barrier heights of chemical significance, even if the absolute values may be questionable. The first intermediate falls at a reaction co-ordinate nearly coincident with that of the only minimum found *in vacuo*, as observed for structure (II). The two intermediates at *a* 3.58 and 5.01 Å are interesting pictures of solvent-separated (or loose) pairs in which the ' free ' (but solvated) phenyl cation is solvent-separated from nitrogen. These intermediates are formed by the following mechanism: during the removal of N_2, the solvent molecules (5) and (6), which at lower reaction co-ordinates are outside the bonding region, insert themselves between the phenyl cation and the leaving nitrogen. Starting from *ca.* 3.5 Å the positive charge is localized on the phenyl cation and its neighbouring solvent molecules.

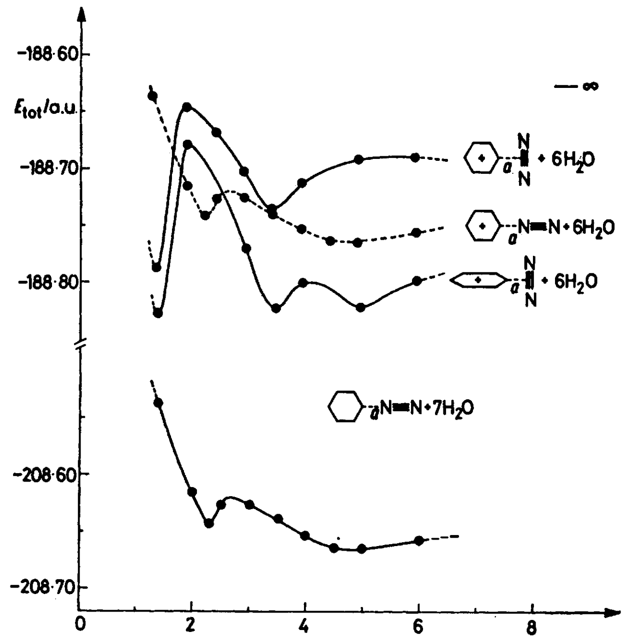

FIGURE 4 Reaction path for the dissociation of solvated benzenediazonium cation. The dotted line in the figure represents the reaction path for structure (I), if the total energy of the system is decreased by the contribution due to the water molecule identified as (7). The level at infinite distance (—∞) corresponds to the energy of $C_6H_5^+,4H_2O$ (from Table 1) and $N_2,2H_2O$ (optimized, E 62.8970 a.u.)

It appears from the present results that stable ion–molecule pairs exist in solution. It is to be noticed from Figure 4 that even at large values of the reaction co-ordinate the energies of the different systems do not converge, contrary to what happens for the solvent-free systems. It might then be questioned whether the minima shown in Figure 4 are mainly due to the interactions between solvent molecules, rather than to solute–solvent interactions; that is the existence of (stable) ion–molecule pairs could be an artefact of the approximations included in the model. To elucidate this point the energies for the solvent molecules alone, fixed at the positions optimized for the supermolecules (see Figures 3—6), at the different values of the reaction co-ordinate, have been calculated for the three structures.

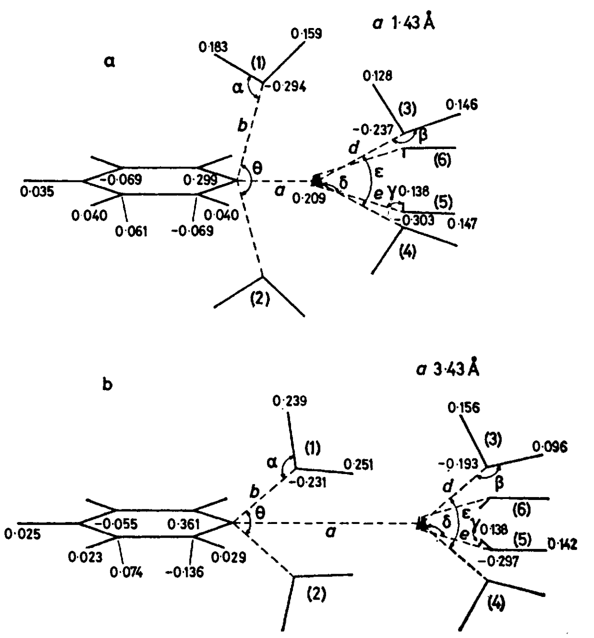

FIGURE 5 Geometries and net charges (in electrons) for the two intermediates (*a* 1.43 and 3.43 Å, respectively) in the dissociation process of solvated benzenediazonium cation (II). The values of the optimized geometry parameters are reported in Table 4. The solvent molecules identified as (5) and (6) are in the phenyl ring plane, on the opposite sides of the reaction co-ordinate

The results are summarized in Table 5 where the total energies of the supermolecules and the corresponding energies of the solvent cages are reported in columns A and B, respectively. In column C the difference between the energies of the first two columns is reported. This energy difference ΔE represents the sum of the solute–solvent and the ion–molecule interactions. The plots of ΔE *versus* the reaction co-ordinate (Figure 7) show that both the number and the position of the energy minima correspond to those calculated for the supermolecules. In column D of Table 5 the difference between the energy of the water cages and that of a corresponding number of isolated water molecules is reported. In column E the energies of the free ion–molecule pair are reported, and when the values of column E are subtracted from the values of column C, the energies for the solute–solvent interactions are obtained. Column F in Table 5 lists these energies.

By examining the data reported in Table 5 it emerges that (a) the binding energies of the solvent clusters are relatively small, (b) the variation of energy for the supermolecules is not determined by the energy variation for the corresponding solvent clusters, and (c) moreover in the case of some minima for the energy of the supermolecules, the cluster of solvent molecules gives a destabilizing contribution. In column F of Table 5 the solute–solvent interactions alone, obtained by subtracting the values in column E from those in column C, are given. It appears that the contribution increases as the reaction co-ordinate increases. The distincton between tight and loose ion pairs, as described in the organic chemistry literature, may be related to the relative importance of solute–solvent and ion–molecule (or ion–counter ion in the case of ion pairs) interaction energy. Furthermore it emerges from Figure 7 that for high values of the reaction co-ordinate, the three curves converge as expected, towards the same point, namely the energy of the separated but solvated ion–molecule pair.

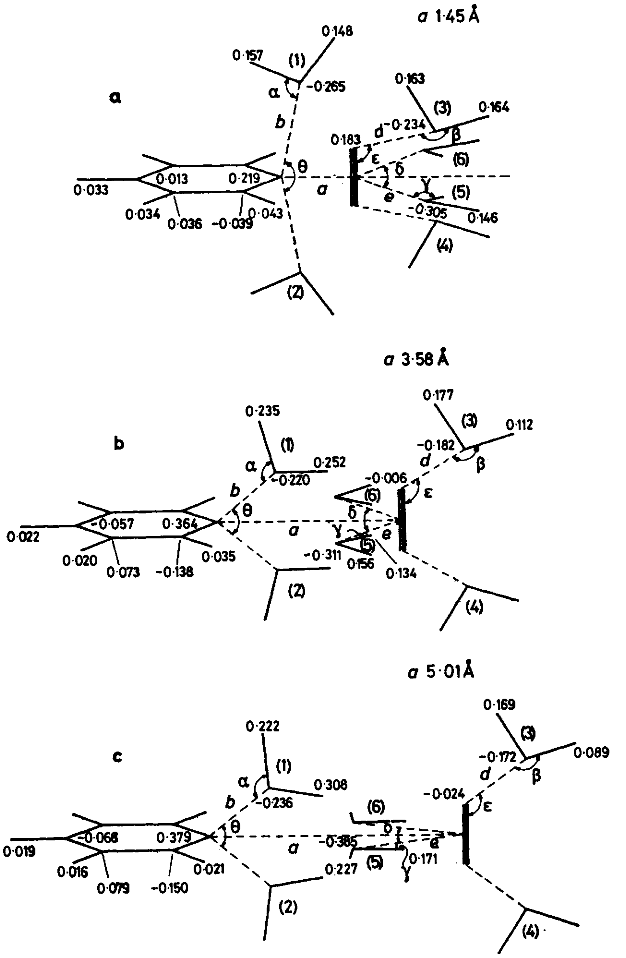

FIGURE 6 Geometries and net charges (in electrons) for the three intermediates (*a* 1.45, 3.58, and 5.01 Å, respectively) in the dissociation process of the solvated benzenediazonium cation (III). The values of the optimized geometry parameters are reported in Table 4. The solvent molecules identified as (5) and (6) are in the phenyl ring plane, on the opposite sides of the reaction co-ordinate

Since the $C_6H_5^+$ ion interacts significantly only with molecules 1, 2, 5, and 6 (see Figure 3) which are situated between the nitrogen molecule and the ion, one might suspect that the maximum at *ca.* 2 Å is an artefact due to the displacement of the only water molecules available for the solvation of the ion. On the other hand it might also be that the solvation energy due to solvent molecules located around the ion but far from the corner where the nitrogen molecule is moving is not significantly affected by the position of nitrogen. To check on this possibility we performed calculations in which four water molecules were added, two above and two below the phenyl ring, at different values of the reaction co-ordinate *a*. Due to the long computing time needed, this calculation was performed only for system (III). The existence and positions of the two minima, as well as the height and positions of the energy barrier between them are almost unaffected, confirming the reliability of our model.

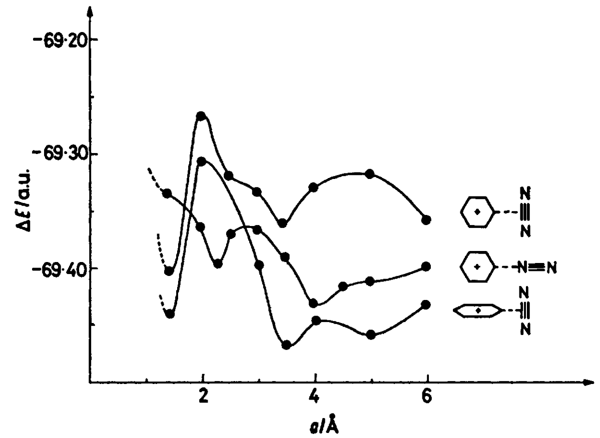

FIGURE 7 Energy along the reaction paths for the dissociation of benzenediazonium cation in water, when solvent–solvent interactions are not included

Conclusions.—(1) The numbers that are obtained in the calculations of the kind presented here have no absolute value; only a comparison of trends in similar situations can be treated with confidence.

(2) The fact that the diazonium cations incorporating a triatomic ring are calculated to be more stable than the so called linear cation is again a consequence of the method of calculation (CNDO overestimates bonding).

(3) A small portion of the potential surface for the reaction in solution has been examined. However it is gratifying that energy minima along all studied reaction paths have been found, and that they are in correspondence with reasonable geometries.

(4) A free phenyl cation is never found; in fact the positive charge on the phenyl group is less than 0.5 electron for the structures corresponding to energy minima. The geometry of the phenyl ring has been taken as rigid. Probably, if the geometry was allowed to relax, different structures could have been found in different situations.

(5) From Figures 2 and 4 it appears that the energy needed to separate the nitrogen molecule is greatly reduced by solvation: from 1/3 [(II) and (III)] to more than one order of magnitude [(I)].

(6) Since we postulated a solvent of zero nucleo-

TABLE 5

Total energy for supermolecules and free ion–molecules, solvent cage energies, and different contribution to solvation energies for $C_6H_5N_2^+$ [structures (I), (II), and (III)] [a]

	a	A	B	C	D	E	F
(I)	1.400	−208.537 12	−139.201 19	−69.335 39	+0.0372	−69.2575	−0.077 89
	2.000	−208.616 00	−139.252 51	−69.363 49	−0.0141	−69.0080	−0.105 99
	2.300	−208.643 37	−139.243 94	−69.396 43	−0.0006	−68.9600	−0.436 43
	2.500	−208.627 14	−139.257 28	−69.369 85	−0.0189	−68.8900	−0.479 65
	3.000	−208.626 25	−139.259 18	−69.367 07	−0.0208	−68.8630	−0.503 77
	3.500	−208.638 82	−139.248 57	−69.390 24	−0.0102	−68.8585	−0.531 04
	4.000	−208.653 20	−139.222 20	−69.431 00	+0.0162	−68.8585	−0.572 50
	5.000	−208.664 72	−139.253 27	−69.411 44	−0.0149	−68.8585	−0.447 05
	6.000	−208.657 39	−139.259 35	−69.398 03	−0.0210	−68.8585	−0.539 53
(II)	1.428	−188.785 82	−119.382 82	−69.403 00	−0.035 62	−69.3140	−0.075 00
	2.000	−188.644 60	−119.378 04	−69.266 56	−0.030 84	−69.0330	−0.221 56
	2.500	−188.659 00	−119.340 55	−69.318 45	−0.006 65	−68.8970	−0.412 75
	3.000	−188.705 00	−119.372 30	−69.332 70	−0.025 10	−68.8640	−0.460 90
	3.430	−188.735 53	−119.375 59	−69.359 97	−0.028 39	−68.8585	−0.493 57
	4.000	−188.710 76	−119.381 88	−69.328 88	−0.034 67	−68.8585	−0.463 08
	5.000	−188.690 81	−119.374 07	−69.316 74	−0.026 87	−68.8585	−0.470 38
	6.000	−188.690 42	−119.331 13	−69.359 29	+0.016 07	−68.8585	−0.500 79
(III)	1.448	−188.825 40	−119.384 35	−69.441 59	−0.037 15	−69.3202	−0.121 39
	2.000	−188.677 72	−119.371 25	−69.306 47	−0.024 05	−69.0450	−0.273 97
	3.000	−188.769 30	−119.371 06	−69.398 24	−0.028 86	−68.8720	−0.534 14
	3.584	−188.821 84	−119.354 63	−69.474 64	−0.007 43	−68.8685	−0.606 14
	4.000	−188.799 75	−119.354 54	−69.442 51	−0.007 34	−68.8660	−0.587 01
	5.011	−188.823 54	−119.364 23	−69.459 31	−0.017 03	−68.8585	−0.600 81
	6.000	−188.799 47	−119.368 46	−69.430 38	−0.021 26	−68.8585	−0.571 88

[a] A, total energy of the supermolecule; B, energy of the solvent cluster; C, $E_C = E_A - E_B$: solute–solvent plus ion–molecule energy; D, $E_B - n \cdot E_{H_2O}$: energy difference between water cage and a corresponding number of isolated molecules; E, energy of the isolated ion–molecule; F, $E_F = E_C - E_E$: this term represents the solute–solvent interaction. Energies are in a.u.

philicity we cannot make any estimate of the life-time of our intermediates, that in our oversimplified model appear as products. As a consequence our results cannot be quantitatively compared with kinetic data.

(7) Both the solute–solvent and ion–molecule interactions are important for stabilizing the tight ion pair in solution; moreover solute–solvent interactions give the main contribution towards stabilizing the loose ion pairs, owing to the insertion of the solvent molecules between ion and molecule.

(8) The existence of the energy minima has been shown not to be an artefact of our model, due to the fact that interactions of the first solvation shell with the bulk of the solvent are not included.

(9) Other intermediates are possible besides the ones we found: for example in the exchange reaction with dissolved nitrogen,[3] intermediates with four nitrogen atoms could be present. It is, however, worth noticing that two intermediates are found along our reaction paths, and that the same number has been proposed following the analysis of kinetic experiments,[4] even though the two studies were done with different solvents, water, and fluorinated alcohols, respectively. It may be said, however, that qualitatively, the characteristics of the reactions in these solvents are the same.

(10) The present results are in good agreement with that previously obtained for ion pairs.[3]

(11) To sum up, though our results do not allow a discussion of the liquid structure, since entropy effects have not been considered, they are in complete agreement with the kinetic findings by Szele and Zollinger,[3] where the existence of energy barriers along the dissociation path of the benzenediazonium cation is suggested.

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