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THEORETICAL STUDY OF SIMPLE PUSH–PULL ETHYLENES IN SOLUTION

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The influence of solvation on the *Z–E* isomerization process of three representative molecules of simple push–pull ethylenes [$H_2N(H)C_1{=}C_2(H)R$, $R = NO_2$, *COH* and *CN*] derived from aminoethylene was investigated by means of RHF-SCF *ab initio* calculations at the 3–21 + G level. Solute–solvent interactions were modelled by a cavity model. The shape of the cavity is based on electronic isodensity surfaces. By using an ellipsoidal cavity very close to the isodensity surface, the perturbation due to the solvent takes an analytical form which is incorporated into the Hartree–Fock equations and leads to efficient quantum chemical computations. The polarization of the solutes under the influence of the solvent is noticeable and was analysed in detail. Similarly, the barriers to internal rotations are substantially modified by the solvent: the barrier around the C=C double bond is appreciably decreased in the thermal mechanism whereas its lowering is less important in the anionic mechanism; in contrast, the barrier around the C-1—N bond is slightly increased. The variation of the barriers with the nature of the acceptor group is fairly well reproduced by the computations. The electronic structure of the push–pull ethylene molecules and the modifications of this structure under the influence of the solvent are analysed in detail.

INTRODUCTION

Isomeric equilibria around a double bond are basic to the concepts of the structural theory of organic chemistry. The simplest molecules having this characteristic are the ethylene derivatives, which show a free-energy barrier of 259–272 kJ mol^{-1}. However, appropriate substitutions on the double bond can reduce the barrier to isomeric interconversion. This is the case with the push–pull ethylenes, where an electron-accepting group replaces a hydrogen atom at one end of the double bond and an electron-withdrawing group is substituted on the other end. This arrangement favours a cooperative effect of both groups to stabilize the charge separation on the C—C fragment, facilitating the breakdown of the double bond during the rotation. For this type of compound the energy barrier is sometimes below the limit of the dynamic nuclear magnetic resonance (DNMR) technique, *ca* 21 kJ mol^{-1}. A strong dependence of the C=C barriers on solvent polarity has been observed since the first DNMR studies and this was interpreted as strong support for a zwitterionic transition state.[2] The literature on the static and dynamic stereochemistry of push–pull and strained ethylenes has been exhaustively reviewed by Sandström.[3]

Different theoretical studies have been carried out on push–pull ethylenes to examine electron distributions on the ground and transition states.[4–11] The theoretical rotational barriers have been found to be systematically overestimated. The absolute error was usually greater than 42 kJ mol^{-1}, which represented relative errors of *ca* 50%. This large discrepancy has been generally ascribed to the neglect of the solute–solvent interactions in the calculations. The influence of the solvation on the barriers has been included in the theoretical calculations as a perturbation by means of the continuum approximation in two previous studies. Olsson and

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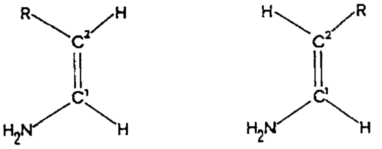
Sandström[12] estimated the rotational barrier of some 6,6-dihetero-substituted fulvenes in solution by using the CNDO/2 method. The results indicated a considerable discrepancy between theoretical and experimental barriers, which was attributed to the failure of this semi-empirical method to describe rotational barriers correctly. More recently, we have shown that the use of the AM1 semi-empirical method gives a more accurate description of the intrinsic barrier and as a consequence a qualitative agreement with experiment may be reached with the inclusion of the solvent effects.[13]

The internal rotation may in any case occur via a thermal mechanism. This is made possible by the presence of the donor and the acceptor groups and is expected to be strongly dependent on the magnitude of the intramolecular charge transfer. With enamines containing a primary or occasionally a secondary amino group, an alternative mechanism which implies a deprotonation of the enamine has been shown to occur.[14] We shall call this the anionic process. Finally, these compounds also display hindered rotation around the C-1—N bond with substantial barriers which have also been determined by DNMR techniques.[15-19]

Regarding the thermal process, the intramolecular charge transfer is known to be strongly solvent dependent and the process indeed undergoes large solvent effects. The aim of this work was to examine the modifications of the electronic structure of the two isomers and of the transition state induced by the solvent and to understand further the effects of the solvent on the isomerization process, from the electronic structure point of view.

For this study we selected three molecules derived from the aminoethylene (Scheme 1), where substituent groups of increasing acceptor capacity were considered. It is worth noting that the nitro derivative **1** is the prototype of the nitroenamines family, which have attracted much experimental attention during recent years for their potential use in organic synthesis[20-23] and also as components of the architecture of molecular electronic switching devices.[24]



	R
1	NO_2
2	COH
3	CN

Scheme 1

THE MODEL OF THE SOLUTION

The solvent is represented as a continuum characterized by its dielectric permittivity ε, and the solute molecule is assumed to be set in a cavity prepared in this continuum.

The key feature of this model is the definition of the cavity.[25] It seems reasonable to define its volume as V/N_A, where V is the partial molar volume of the solute in the solution and N_A is Avogadro's number. When this quantity is not known, it can be approximated by relating it to the van der Waals volume of the solute. This is the case for compounds **1**–**3**, where the molecular volume has been obtained from a correlation[10] between the experimental molecular volume of the pure liquid at room temperature for a set of structurally related compounds and the van der Waals volume [$V(\mathbf{1}) = 135{\cdot}5\,\text{Å}^3$, $V(\mathbf{2}) = 126{\cdot}8\,\text{Å}^3$ and $V(\mathbf{3}) = 125{\cdot}1\,\text{Å}^3$].

The shape of the cavity raises another problem if one strives to establish it on a sound physical basis. Several attempts have been made to do this. Our proposal is to define the boundary between the molecule and the solvent as the surface which encloses the largest fraction of particles belonging to the solute's molecule considered independently of the solvent, i.e. all the nuclei and the largest fraction of the electron cloud compatible with the volume. This surface *appears to be an* isodensity surface (Figure 1). It appears that such a

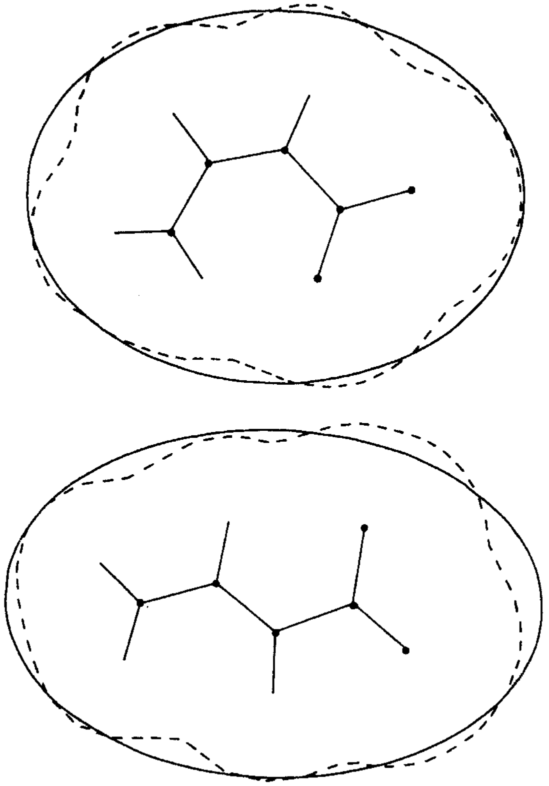


Figure 1. Cross-section of the isodensity surfaces and of the ellipsoidal cavities for the *Z* and *E* isomers of nitroaminoethylene

surface is very close to the surface defined by other workers based on the van der Waals spheres,[26] except that the artificial cusps which appear at the intersection of the spheres are replaced with more regular junction conditions which make this surface qualitatively comparable to the so-called molecular surfaces defined by a rolling sphere[27] or some techniques that consider the surface of the solute exposed to the solvent.[28–30]

The cavity being defined, it then becomes possible to compute the electrostatic part of the free energy of interaction of the solute with the solvent, and to set up a 'liquid state quantum chemistry' scheme[25] by including the perturbation in the Hartree–Fock equations of the solute leading to the so-called self-consistent reaction field (SCRF) methods. Nevertheless, this perturbation can be obtained, in the general cases, by a numerical integration which lengthens the computational time prohibitively for a result which is still limited by the physical crudeness of the model. In previous studies[25,31] we have shown that although the free energy of interaction depends very much on the shape of the cavity, the molecular wavefunction may be considered, to a first order, as independent of small variations in the shape of the cavity. In some favourable cases, it then becomes possible to reduce the cavity to an ellipsoid having the same volume, which allows an analytical expansion of the perturbations giving rise to fast SCF computations.

The Hartree–Fock–Roothaan equations take a very simple form. The (μ, ν) term of the Hartree–Fock matrix is written as[32]

$$F_{\mu\nu} = F^{\circ}_{\mu\nu} + \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} \times f_{ll'}^{mm'} M_{l'}^{m'} \langle \mu | \hat{M}_l^m | \nu \rangle \qquad (1)$$

where $F^{\circ}_{\mu\nu}$ is the corresponding term for the isolated molecule, M_l^m is a component of a multipole moment defined at the centre of the cavity, in spherical tensors notation, $\langle \mu | \hat{M}_l^m | \nu \rangle$ is the corresponding matrix element and $f_{ll'}^{mm'}$ an element of a 'reaction field tensor' which depends on the dielectric constant of the solvent and on the geometry of the cavity. It then becomes possible to study the modifications of the electronic structure of the solute under the influence of the continuum representing the solvent routinely. A more precise evaluation of the free energy of solvation may be obtained by using the isodensity cavity surface and the electrostatic properties of the solute from the SCF computation.

It is worth noting that since the experimental permittivity of the solvent includes orientational and induced polarization effects, and since the polarization of the solute by its surroundings is taken into account in the SCF computation, the free energy of interaction includes both the electrostatic and induction terms. If one considers the contribution of the solute itself, the variation of the molecular energy when passing from the isolated to the solvated state cannot be reduced to the induction term, since it does not include the variation of the induction energy of the solvent. We shall call it the energy of polarization of the solute.

The free energy of solvation does not reduce to the free energy of interaction obtained in this scheme. Two important terms are missing: the dispersion term, which has been shown to play a minor role in the modification of the electronic structure of the solute,[33] and the free energy spent in creating the cavity. Nonetheless, in some chemical processes, such as isomerizations considered in this paper, the free energy changes are usually assumed not to depend strongly on these two omitted contributions.

COMPUTATIONS

As the aim of this study was focused on the electronic structure rather than on the energetics of the internal rotation process, a limited basis set was used. Nevertheless, in order to describe correctly both the anions and the molecules in which a substantial intramolecular charge transfer induces negative charge on some atoms, the use of diffuse orbitals was regarded as important. Hence the standard 3–21 + G basis set[34] was used.

The computations were performed by means of the Gaussian 86 package.[35] A SCRF algorithm based on the above model was written and implemented in the original Gaussian package. It was used to study the modifications of the electronic structure of the species defined in a vacuum. The stable geometries of the free molecules were fully optimized. The potential energy surfaces were inspected by the linear synchronous transit method[36] and the transitions states located on the surfaces by using Schlegel's algorithm.[37] In the case of the solvated molecules, we retained the gas-phase geometries. Although the coordinates of the molecules are expected to be slightly modified by the effect of the reaction field and the energy barriers to be modified slightly, these modifications should not change much the results or the discussion presented here. The geometry optimization of a solvated molecule is a delicate problem which requires further development of the cavity model, in particular to obtain the second derivatives of the reaction field factor with respect to the nuclear coordinates. This restriction, together with the use of the ellipsoidal cavity, limit the use of the energies obtained in this approach to only qualitative conclusions regarding the thermodynamics of the process in solution.

RESULTS

Isolated molecules

Table 1 gives some of the most significant geometrical parameters involved in the rotational processes. All the

Table 1. Main structural parameters C-1=C-2 and C-1—N bonds (distances in Å and angles in degrees)

Compound	Structure	Geometrical parameters			
		Planar isomers			
		C-1—C-2	C-1—N		
1	*Z*	1·352	1·335		
	E	1·341	1·348		
Anion of **1**	*Z*	1·447	1·276		
	E	1·439	1·284		
2	*Z*	1·356	1·344		
	E	1·345	1·356		
Anion of **2**	*Z*	1·435	1·289		
	E	1·425	1·298		
3	*Z*	1·340	1·363		
	E	1·338	1·366		
Anion of **3**	*Z*	1·409	1·305		
	E	1·406	1·308		
		Transition state for C-1=C-2 rotation			
		C-1—C-2	C-1—N	α	β
1	$TS_{C\text{-}1-C\text{-}2}$	1·465	1·287	85·5	103·6
Anion of **1**	$TS_{C\text{-}1-C\text{-}2}$	1·482	1·267	86·2	96·4
2	$TS_{C\text{-}1-C\text{-}2}$	1·457	1·291	91·9	96·1
Anion of **2**	$TS_{C\text{-}1-C\text{-}2}$	1·483	1·275	89·2	94·5
3	$TS_{C\text{-}1-C\text{-}2}$	1·450	1·294	102·6	103·9
Anion of **3**	$TS_{C\text{-}1-C\text{-}2}$	1·486	1·276	97·1	100·6
		Transition states for C-1—N rotation			
		C-1—C-2	C-1—N	C-1—NH	γ
1	$TS_{C\text{-}1-N}$	1·322	1·425	114·7	64·6
2	$TS_{C\text{-}1-N}$	1·328	1·435	114·1	63·3
3	$TS_{C\text{-}1-N}$	1·325	1·427	117·6	71·4

stable isomers are planar. In the three instances considered here the most stable isomer in the gas phase corresponds to the *Z* configuration. In the case of the formyl substituent, the number of isomers is doubled owing to the isomerization around the C-2—R bond. In both the *E* and *Z* isomers the most stable conformation corresponds to the *s-cis* arrangement of the carbonyl group relative to the double bond. All the structures of compound **2** considered in this study correspond to this local arrangement. For this compound, the structural and energetic descriptions of the isomers are fairly close to the 4–31G results reported by Emsley *et al.*[8]

The electron delocalization of these push–pull ethylenes can be observed in their planar isomers, where the C-1—C-2 bond lengths are longer than those corresponding to simple ethylenes (typically 1·34Å), whereas the C-1—N bond lengths are shorter than that of the aminoethylene (1·40Å). When the anions are considered this trend is enhanced: the C-1—C-2 distances become greater than 1·40Å and the C-1—N distance shorter than 1·31Å.

The cleavage of the double bond for rotation around the C-1—C-2 bond is reflected in the values taken by the bond length in the transition structures ($TS_{C\text{-}1—C\text{-}2}$). These values are comparable to but still slightly shorter than those obtained for the twisted singlet and triplet states of ethylene (*ca* 1·46 Å).[38] In the case of push–pull ethylenes, the triplet < singlet energy ordering of simple twisted ethylene[39] is favoured by the fact that the ionic components of the bond are greatly increased by the substituent groups at both sides of the double bond.[11]

The C-1—N distance is shorter in the transition state than in the stable isomers. This observation is consistent with a greater intramolecular charge transfer from the amino group to the acceptor group in the transition state. This electron reorganization is also visible in the atomic rearrangement around the C-2

Figure 2. Definition of the dihedral angles α, β and γ (see Table 1)

atom where the values of the dihedral angles α and β, which are defined in Figure 2, indicate a slight pyramidalization.

The analysis of the transition structures for the rotation around the C-1—N bond confirms the previous interpretation of the role of the amino group. By twisting the C-1—N bond, the conjugation of the nitrogen lone pair with the ethylenic bond is suppressed, leading to a shortening of the C-1—C-2 distance and a substantial lengthening of the C-1—N distance, together with strong pyramidalization of the amino group.

The modification of the rotational barrier to internal rotation around the C-1=C-2 bond with the substituent appears in the first column of Table 2. It is consistent with the acceptor properties of the substituent, which are known to decrease in the sequence $NO_2 > COH > CN$. It is clear that the barrier is lowered more efficiently when the substituent is a better acceptor. This is true for both neutral molecules and deprotonated anions. Nevertheless, the barrier is far lower in the case of the anions.

Table 2. Relative free-energies (kJ mol^{-1}) for the isomerization processes in the gas phase and in solution

Compound	Structure	Gas phase	$\varepsilon = 2·0$	$\varepsilon = 38·8$
1	*Z*	0·00	0·00	0·00
	E	15·70	11·74	6·06
	TS$_{\text{C-1—C-2}}$	174·01	135·06	66·75
	TS$_{\text{C-1—N}}$	91·29	96·73	104·83
Anion of **1**	*Z*	0·00	0·00	7·52
	E	4·51	0·50	0·00
	TS$_{\text{C-1—C-2}}$	58·10	46·52	21·57
2	*Z*	0·00	0·00	0·00
	E	18·89	13·46	3·80
	TS$_{\text{C-1—C-2}}$	196·67	164·44	104·50
	TS$_{\text{C-1—N}}$	84·98	86·82	89·41
Anion of **2**	*Z*	0·00	0·38	3·43
	E	0·29	0·00	0·00
	TS$_{\text{C-1—C-2}}$	66·80	55·22	22·07
3	*Z*	0·00	0·00	0·00
	E	7·94	5·85	3·47
	TS$_{\text{C-1—C-2}}$	236·80	205·82	149·02
	TS$_{\text{C-1—N}}$	53·42	54·34	54·47
Anion of **3**	*Z*	0·00	0·00	0·00
	E	0·54	8·79	17·86
	TS$_{\text{C-1—C-2}}$	89·54	88·62	80·71

The barrier to internal rotation around the C-1—N bond undergoes variations which go the opposite way. This again is perfectly consistent with the intramolecular charge transfer which weakens the C-1=C-2 bond and strengthens the C-1—N and the C-2—R bonds.

Solvent effects

The computations have been performed with the values of the dielectric constant $\varepsilon = 2$, which represents a typical non-polar solvent, and $\varepsilon = 38·8$, which is the dielectric constant of acetonitrile at room temperature. The results are given in Table 2.

Although the energy values obtained with the solvated molecules only have qualitative significance, for the reasons detailed earlier, they clearly show the effect of the solvent on the relative stability of the isomers, leading to closer energies of the *E* and *Z* isomers but without changing the order of stability in the case of the neutral molecules. The quantities corresponding to the TS entries in Table 2 have to be considered as upper limits of the energies of the transition state, since the geometry of the corresponding structure is the gas-phase geometry, without any further optimization in the solvent. The barrier to internal rotation around the C-1=C-2 bond is considerably lowered, by about 100 kJ mol^{-1}, in the neutral molecules and 10–40 kJ mol^{-1} in the deprotonated forms. The barrier to C-1—N rotation is slightly raised (a few kJ mol^{-1}). These observations are consistent with an enhancement of the intramolecular charge transfer under the influence of the solvent, which increases with the solvent polarity for both the stable forms and the transition states, as shown by the variation of the dipole moments given in Table 3.

Table 3. Dipole moments (D) for ground and transition states of neutral molecules in the gas phase and in solution

Compound	Structure	Gas phase	$\varepsilon = 2.0$	$\varepsilon = 38.8$
1	*Z*	7.65	8.47	9.85
	E	8.45	9.35	10.87
	TS$_{\text{C-1—C-2}}$	11.79	13.13	15.30
	TS$_{\text{C-1—N}}$	4.03	4.39	4.97
2	*Z*	4.14	4.57	5.3
	E	5.53	6.15	7.21
	TS$_{\text{C-1—C-2}}$	7.76	8.66	10.32
	TS$_{\text{C-1—N}}$	2.95	3.23	3.71
3	*Z*	5.74	6.37	7.38
	E	6.76	7.50	8.76
	TS$_{\text{C-1—C-2}}$	10.18	11.45	13.78
	TS$_{\text{C-1—N}}$	3.28	3.67	4.37

DISCUSSION

Electronic structure of the transition state in the gas phase

In order to elucidate the modification of the electronic structure of the two rotating groups during the internal rotation, we present in Table 4 the results of a Mulliken population analysis for the π electrons. The values for the transition state correspond to an idealized structure simply deduced from the *Z* isomer by a twist of 90° around the double bond without any other geometric change. In this way, it is possible formally to separate π and σ populations.

The values in Table 4 indicate that the π population in the $C-NH_2$ half of the molecule substantially decreases in the TS structure. Conversely, the π population in the $C-NO_2$ half becomes greater for all the atoms. This is in agreement with the larger electron donation of the nitrogen atom of the amino group in the twisted form and with a net polarization of the whole π electron system towards the nitro group. In fact, this polarization is partially compensated for by a σ retrodonation, but we have not included total net atomic charges in Table 4 because the use of diffuse orbitals here makes the Mulliken analysis fail in describing the σ population.

These results are consistent with an increase of the dipole moment (Table 3) between the planar conformation and the transition state. It also supports the strong coulombic interaction between the two molecular halves in the transition state, which shortens the C-1—C-2 bond.

Solvent effect on the equilibrium

The relative stabilities of the *E* and *Z* isomers in a vacuum and in the two solvents have already been analysed. Our results confirm the possibility of observing a mixture of both isomers in a polar solvent by spectroscopic techniques. This is in agreement with the existing experimental data, which are only available for compounds **1** and **2**.[17–21]

Table 4. π Electron populations of the *Z* isomer and of the structure close to the transition state of nitroaminoethylene

Atom	*Z*	TS	*Z* (solvated molecule, $\varepsilon = 38{\cdot}8$)
N (amino)	1·740	1·573	1·697
C-1	0·769	0·484	0·710
C-2	1·324	1·535	1·328
N (nitro)	1·056	1·081	1·053
O—1	1·504	1·602	1·575
O—2	1·607	1·672	1·638

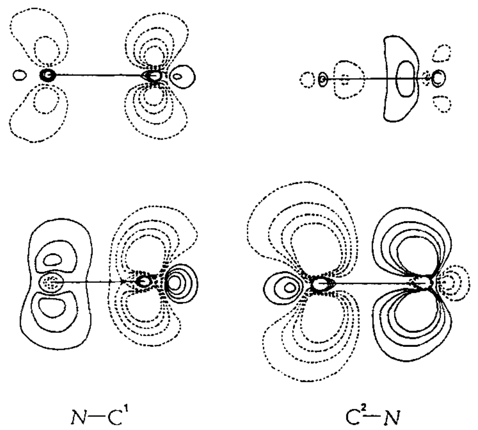
The strong solvent effect on the height of the barrier in the case of the neutral molecules makes the thermal isomerization process possible for some compounds, especially compounds **1** and **2** in acetonitrile solutions. The mechanism of the isomerization process, which is likely to be purely anionic in a basic solvent of low polarity, may therefore be expected to be more complex in a solvent of high dielectric constant. Indeed, the rate-limiting process for the anionic mechanism is the deprotonation, which has been shown to have an activation energy of the order of 80 kJ mol^{-1} in the case of compounds **1** and **2**.[3,19,40] The predicted upper values for the heights of the barrier to internal rotation reach the same order of magnitude for these compounds. Although no experimental data are available for compound **3**, one predicts a more difficult isomerization process, which can occur through the anionic process anyway.

Electronic perturbation of the solute induced by the solvent

The polarization contribution to the solute–solvent interaction, as defined above, is directly related to the electronic perturbation of the solute by the solvent and is consistent with the variations in the dipole moment. As observed in Table 5, this contribution is far from negligible, especially in highly polar solvents, and justifies a separate quantum chemical computation of the solvated molecule. In turn, the wavefunction permits a detailed analysis of the electronic modification induced by the solvent. Figure 3 shows the difference in electronic density between the solvated and the free molecules in the case of the *Z* isomer and of the transition state of compound **1**. The data refer to symmetry planes of the two halves. The solvent effect on the *Z* isomer may be summarized as an increase in the intramolecular electron transfer from the amino group to the nitro group in the π system, partly compensated for by an opposite modification of the σ system. A π electron population analysis (see Table 4) show that the π electron population of the C-2—N(nitro) bond is not modified much by the solvent, so that the whole effect can be represented by a π electron transfer from the C-1—N(amino) bond to the oxygen atoms. In the transition state, the situation is completely different. There is a strong polarization of each individual molecular half, which now behaves as an individual molecule undergoing the reaction field created by its own charge distribution. This always has the effect of increasing the polarity of the molecule so that one observes in both cases a decrease in the electronic density on the carbon atoms and an increase in that on the nitrogen atoms. This is easy to understand since the twisting of the molecule breaks down the conjugation between the two π systems.

Table 5. Decomposition of the free energies of the solvation (kJ mol^{-1}) in electrostatic and polarization contributions

		$\varepsilon = 2 \cdot 0$		$\varepsilon = 38 \cdot 8$	
Compound	Structure	Elec.	Pol.	Elec.	Pol.
1	*Z*	−19·40	−1·92	−44·35	−10·41
	E	−23·16	−1·92	−52·71	−12·08
	$TS_{C\text{-}1-C\text{-}2}$	−54·59	−5·60	−127·87	−34·32
	$TS_{C\text{-}1-N}$	−15·05	−0·71	−36·74	−4·64
Anion of **1**	*Z*	−123·64	−1·63	−249·13	−10·99
	E	−127·11	−2·22	−257·95	−14·21
	$TS_{C\text{-}1-C\text{-}2}$	−133·72	−3·14	−274·38	−22·28
2	*Z*	−13·79	−1·00	−33·40	−6·19
	E	−18·64	−1·55	−44·73	−9·99
	$TS_{C\text{-}1-C\text{-}2}$	−43·05	−3·97	−104·54	−27·25
	$TS_{C\text{-}1-N}$	−12·33	−0·63	−30·85	−4·31
Anion of **2**	*Z*	−127·74	−1·46	−258·62	−9·99
	E	−128·37	−1·50	−261·46	−10·83
	$TS_{C\text{-}1-C\text{-}2}$	−137·52	−3·26	−284·66	−28·67
3	*Z*	−15·84	−1·25	−37·37	−7·57
	E	−17·56	−1·55	−40·80	−8·69
	$TS_{C\text{-}1-C\text{-}2}$	−42·93	−4·97	−99·78	−32·98
	$TS_{C\text{-}1-N}$	−15·05	−1·05	−36·95	−6·98
Anion of **3**	*Z*	−127·03	−1·38	−250·38	−8·02
	E	−119·42	−0·71	−236·60	−4·48
	$TS_{C\text{-}1-C\text{-}2}$	−127·20	−2·13	−252·47	−14·76



igure 3. Differences in electronic density between the olvated ($\varepsilon = 38.8$) and free nitroaminoethylene molecule in he plane of symmetry of the fragment for the *Z* conformation top) and the transition state (bottom). Left, N(amino)—C ond; right, C—N(nitro) bond. The values of the curves orrespond to $|\psi_{\text{solv}}|^2 - |\psi_{\text{free}}|^2 = \pm 0.25$, ± 0.50, ± 0.75 nd $\pm 1.00 \times 10^{-2}$ a.u. (dashed lines correspond to negative values)

CONCLUSION

t has been shown that quantum chemical computations n solvated molecules, which are relatively easy to perform provided that the solute fits an ellipsoidal cavity, give detailed information on the electronic processes involved in a reaction occurring in the liquid state. An analysis of the wavefunction provides a better insight into the modification of the electronic structure induced by the solvent and the mechanism of the chemical process. In the case of push–pull ethylenes it confirms the current interpretation, which assumes that the transition state has a strongly zwitterionic structure which is greatly favoured by the presence of a polar solvent.

Although we do not claim to have reached quantitative conclusions, the computed relative energies and heights of the potential energy barriers are in fair agreement with the known experimental results. This provides a strong inducement to set up a more refined evaluation of the solute–solvent interaction energy[25] based on the molecular structure obtained by means of these self-consistent reaction field computations.

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REFERENCES

1. J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.* **23**, 315 (1955); B. S. Rabinovitch and K.-W. Michel, *J. Am. Chem. Soc.* **81**, 5056 (1959); R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.* **57**, 1936 (1961); M. C. Lin and K. J. Laidler, *Can. J. Chem.* **46**, 973 (1968).
2. I. Belsky, H. Dodiuk and Y. Shvo, *J. Org. Chem.* **42**, 2734 (1977); H.-O. Kalinowski, H. Kessler and A. Walter, *Tetrahedron* **30**, 1137 (1974).
3. J. Sandström, *Top. Stereochem.* **14**, 83 (1983).
4. G. Favini, A. Gamba and R. Todeschini, *J. Chem. Soc., Perkin Trans. 2* 915 (1985).
5. R. Osman, A. Zunger and Y. Shvo, *Tetrahedron* **34**, 2315 (1978).
6. Y. Borisov, K. K. Bavievski, V. I. Bakhmutov, Y. T. Struchko and E. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 123 (1982).
7. A. Mehlhorn, J. Fabian and F. Dietz, *Izv. Khim.* **20**, 569 (1987).
8. J. Emsley, N. J. Freeman, R. J. Parker, R. Kuroda and R. E. Overill, *J. Mol. Struct.* **159**, 173 (1987).
9. E. N. Gate, M. A. Meck, C. H. Schwalbe, M. F. G. Stevens and M. D. Threadgill, *J. Chem. Soc., Perkins Trans. 2* 251 (1985).
10. E. Sanchez Marcos, J. J. Maraver, J. L. Chiara and A. Gomez-Sanchez, *J. Chem. Soc. Perkin Trans. 2* 2059 (1988).
11. E. Sanchez Marcos, P. Karafiloglou and J. Fernandez Sanz, *J. Phys. Chem.* **94**, 2763 (1990).
12. T. Olsson and J. Sandström, *Acta Chem. Scand., Ser. B* **36**, 23 (1982).
13. R. R. Pappalardo and E. Sanchez Marcos, *J. Chem. Res., S.* 290 (1989).
14. V. I. Bakhmutov and E. I. Fedin, *Bull. Magn. Reson.* **6**, 142 (1984).
15. A. Mannschreck and U. Koelle, *Tetrahedron Lett.* 863 (1967).
16. M. L. Blanchard, A. Chevallier and G. J. Martin, *Tetrahedron Lett.* 5057 (1967); M. L. Blanchard, F. Clesse, J. Bignebat and G. J. Martin, *Tetrahedron Lett.* 981 (1969).
17. J.L. Chiara, *PhD Thesis*, University of Seville (1988).
18. J. Dabrowski and L. J. Kozerski, *Org. Magn. Reson.* **4**, 137 (1972).
19. R. F. Hobson and L. W. Reeves, *J. Phys. Chem.* **77**, 419 (1973).
20. S. Rajappa, *Tetrahedron* **37**, 1453 (1981).
21. A. Krowczynski and L. Kozerski, *Synthesis* 489 (1983); *Heterocycles* **24**, 1209 (1986).
22. K. Fuji, M. Node, H. Nagasawa, Y. Naniwa and S. Terada, *J. Am. Chem. Soc.* **108**, 3855 (1986).
23. A. Sanchez-Gomez, F. J. Hidalgo-Garcia and J. L. Chiara, *Carbohydr. Res.* **167**, 55 (1987); *J. Heterocycl. Chem.* **24**, 1757 (1987).
24. K. Tanaka, S. Yamanaka, T. Koike and T. Yamabe, *Phys. Rev. B* **32**, 2731 (1985).
25. J. L. Rivail, B. Terryn, D. Rinaldi and M. F. Ruiz-Lopez, *J. Mol. Struct., Theochem* **120**, 387 (1985),
26. S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.* **55**, 117 (1981); S. Miertus and J. Tomasi, *Chem. Phys.* **65**, 239 (1982).
27. R. B. Hermann, *J. Phys. Chem.* **76**, 2754 (1972).
28. B. K. Lee and F. M. Richards, *J. Mol. Biol.* **55**, 379 (1971).
29. M. H. Zehfus, J. P. Seltzer and G. D. Rose, *Biopolymers* **24**, 2511 (1985).
30. J. L. Pascual-Ahuir, E. Silla, J. Tomasi and R. Bonaccorsi, *J. Comput. Chem.* **8**, 778 (1987).
31. D. Rinaldi, M. F. Ruiz-Lopez and J. L. Rivail, *J. Chem. Phys.* **78**, 834 (1983); D. Rinaldi, *Comput. Chem.* **6**, 155 (1982).
32. J. L. Rivail and D. Rinaldi, *Chem. Phys.* **18**, 233 (1976); B. Terryn and J. L. Rivail, *J. Chim. Phys.* **79**, 1 (1982).
33. D. Rinaldi, B. J. Costa Cabral and J. L. Rivail, *Chem. Phys. Lett.* **125**, 495 (1986).
34. T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. v. R. Schleyer, *J. Comput. Chem.* **4**, 294 (1983).
35. M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder and J. A. Pople, *Gaussian 86*. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA (1984).
36. T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.* **49**, 225 (1977).
37. H. B. Schlegel, *J. Comput. Chem.* **3**, 214 (1982).
38. M. Said, D. Maynau, J. P. Malrieu and M. A. Garcia Bach, *J. Am. Chem. Soc.* **106**, 571 (1984), and references cited therein.
39. H. Kollmar and W. Staemmler, *Theor. Chim. Acta* **48**, 223 (1978).
40. E. Czerwinska, L. Kozerski and J. Boksa, *Org. Magn. Reson.* **8**, 345 (1976).