CROATICA CHEMICA ACTA CCACAA 57 (6) 1395—1409 (1984)

YU ISSN 0011-1643
CCA-1530 UDC 541
Original Scientific Paper

An Evaluation of Solvent Effects on Isomerization Mechanisms in Diimide and Methylenimine

Maurizio Persico and Jacopo Tomasi

Istituto di Chimica Fisica dell'Università di Pisa, Via Risorgimento 35, I-56100 Pisa, Italy

Received February 2, 1984

Inversional and rotational isomerization mechanisms in N_2H_2 and CH_2NH have been studied by an *ab initio* procedure including in the solute hamiltonian the reaction potential of a solvent modelled as a dielectric continuum. The basic computed quantity is a solution free energy parametrically dependent on the solute internal coordinates. The solvent effect, mainly related to the hybridization state of the nitrogens and to the relative orientation of their lone pairs, in N_2H_2 leads to a lowering of both barriers, and to a stabilization of the cis form with respect to trans. In CH_2NH, the inversional barrier is increased, whereas the rotational one remains unchanged.

INTRODUCTION

In this paper we report some results of an investigation into the effect of the solvent on the thermal isomerization barriers in diimide (diazene) HN=NH, and methylenimine (methanimine) CH_2=NH, supplemented with some information on the effect of the solvent on the electronic distribution of the solute. The introductory section attempts to set the present study in the appropriate context.

Isomerization processes involving a change of conformation at a double bond have been the object of several theoretical investigations, performed with *ab initio* methods, and a description of these processes in the gas phase is now available for quite a large number of representative compounds (the pertinent literature for N_2H_2 and CH_2NH is summarized in Refs. 1—18). At present it seems possible to provide general interpretations of the intrinsic molecular factors governing these stereomutations, including also substitution effects.[10,18,19]

Less advanced is the theoretical investigation on the solvent effects on such processes. In principle different approaches are available.

The so called cluster approach reduces the dilute solution to a molecular aggregation composed of the solute M and a limited number of solvent molecules $S_1 \ldots S_n$. In the supermolecule version[20] the cluster is considered as a unique entity, to be treated with the usual methods of quantum chemistry, in other versions the interactions between the cluster components are schematized and treated accordingly[21,22]. In all cases the optimization of the molecular isomerization paths includes also the solvent coordinates. This approach is able to give information on the effect of the solvent on the internal characteristics of M which govern the conformational change (*e. g.* changes in bond polarities, in the relative weight of different electronic structures when excited states are involved, *etc.*), making thus possible a comparison with the interpretation of the mechanism for isolated molecules. The isomerization coordinate obtained by this approach is rather detailed, because it includes changes in the position and orientation of $S_1 \ldots S_n$, bringing out, thus, cooperative effects of the solvent in favouring (or disfavouring) the isomerization process. There are good reasons to suspect that these effectes may in particular cases be of some importance, as has been recently advocated for other reactions in solution[23,24]. However, the information obtained in this way must be used with great caution because the limitations on the dimension of the cluster, imposed by the complexity of the many-variable optimization procedure, emphasize the importance of direct M—S interactions with respect to solvent-solvent interactions, S—S, which are only partially considered. Moreover, this approach considers only one geometrical structure of the cluster (for a given geometry of M), while it is well known that other different structures have an analogous statistical weight. The chosen structure, because of the method employed, corresponds to the most bonding situation available. The consequence is that the role of bonded substructures, for example those involving specific interactions between M and one or more S molecules, in some cases may be overestimated.

This last shortcoming is not present in a second approach which uses computer simulations of liquids to determine statistically averaged descriptions of the system[25]. This method gives a more realistic description of the solvent distribution around the solute, and there are some examples showing how artifacts coming out from the preceding approach may be corrected in this way[26]. The calculations are rather costly, because of the size of the solution sample necessary to get realistic results and of the slow convergence of the mathematical processes (length of the Markov chain in Monte Carlo computations, number of time steps in molecular dynamics). A reasonable simplification is given by the consideration of clusters of smaller size immersed in a medium for which a simplified statistical description is employed: for example a polarizable continuum model of the solvent[27]. An interesting example of the application of this approach (in the MC version) to study a solute conformational change may be found in a recent paper by Jönsson *et al.*[28]. Simulation methods are inherently classical even when the interaction potentials are calculated with quantum mechanical methods. Of consequence at the present state of the art they do not provide detailed information on the solvent effect on the internal characteristics of M, and then an intepretation of the isomerization mechanism. The above quoted paper[28] gives a clear example of this aspect of the question.

We have employed here a simpler approach, which could be considered as a third way to tackle these problems. The solute M is described with quantum-mechanical methods throughout the isomerization process, and the interaction with the solvent is accounted for by an additional term introduced into the hamiltonian, related to the averaged description of the solvent provided by the polarizable continuum model[29–35]. Computational procedures developed in preceding papers (section II) enable us to evaluate solvent effects, in this model of solution, at the desired degree of accuracy. This approach has its specific merits and defects. The microscopic description of the solvent around M, given in different ways by the two preceding approaches, is here missing. The replacement of the full quantum mechanical description of the solute-solvent interaction given by the supermolecule approach with an electrostatic interaction term may be supported however with results of quantum mechanical studies on model systems. According to fairly large empirical evidence, electrostatic terms alone are sufficient to describe the main energetic aspects of the interaction between M and S also when specific interactions are involved (*e. g.* H bonds or non covalent complexes of different kind) and the effect this interaction has on the internal characteristics of M[36,37]. Inclusion of S molecules in the microscopic portion of the solution model is of course necessary when one or more solvent molecules have an »active« role in the process[38]. In any case, the low computational cost of this approach permits one to extend the study to small supermolecule clusters in the continuum medium; this intermediate approach partially eliminates the defects of the global cluster approach, and could be further developed to have a better statistical description of the system (for some suggestions on this subject see Ref. 39).

In the present work we shall use the simplest model, composed of M alone in the continuous dielectric. In this exploratory research attention is devoted to general solvent effects, acting also in solutions in which active participation of the solvent is unlikely, with a view to extending the investigation to solutes bearing bulky substituents. For this last reason we have employed small size basis sets in the calculations, in order to have, in the future, a coherent set of results regarding also compounds of more direct chemical interest.

OUTLINE OF THE COMPUTATIONAL PROCEDURE

The calculation of the wavefunction of M in the solvent, at the geometries of interest, has been performed with the procedure documented in a previous paper[34].

It consists of introducing into the solute hamiltonian $\hat{H}_M^0$ an interaction operator $\hat{V}_\sigma$ related to the potential generated by a surface charge distribution σ spread over the surface of a cavity in the dielectric. This cavity itself is modelled on the given internal geometry of M.

The charge distribution σ is a function, *inter alia*, of the charge distribution of M, ϱ_M, which experiences the polarizing effect of the solvent. For this reason an iterative procedure to determine σ is employed. From an initial definition of σ in terms of the *in vacuo* charge distribution of M:

$$\sigma^0 = \sigma(\varrho_M^0) \tag{1}$$

one obtains a tentative definition of the interaction operator, V_σ^0, and then, by solving the corresponding Schroedinger equation

$$(\hat{H}_M^0 + \hat{V}_\sigma^0)\,\psi' = E'\,\psi' \tag{2}$$

a new charge distribution, ϱ_M', is obtained, which gives in turn a better approximation $\hat{V}_\sigma'$ to the interaction potential. The process converges quickly (2—3 cycles); we shall denote with $\hat{V}_\sigma^f$ the final value.

When $\hat{V}_\sigma^f$ is known it is possible to evaluate several energetic quantities. The principal one has the physical meaning of a free energy:

$$F = \langle \psi^f \,|\, \hat{H}_M^0 + \hat{V}_\sigma^f \,|\, \psi^f \rangle - {}^1\!/_2 \langle \psi^f \,|\, \hat{V}_\sigma^f \,|\, \psi^f \rangle = E_M^f - {}^1\!/_2 \int \varrho_M^f V_\sigma^f \, d\tau \tag{3}$$

This quantity depends on the internal geometry of M, and we may define a F hypersurface, parametrically dependent on the relative nuclear coordinates of M and analogous to the potential energy surface defined for the case of an isolated M molecule[40].

The electrostatic contribution to the solution free energy change ΔF_{sol}, at a given geometry of M, is given by:

$$\Delta F_{el} = F - E_M^0 \tag{4}$$

The derivations of formulas (3)—(4), and their meaning, have been previously discussed[41]. Enthalpy values may be obtained, when required, by performing some additional calculations with the same method, exploiting the Gibbs-Helmholtz equations[42,43].

Expression (3) and (4) consider only a portion of the free energy contributions. A term $P\,\Delta V$ related to the passage of M from the gaseous phase to the solution should be added to Eq. (4). The terms coming out from the nuclear motion partition function of M are here neglected. A qualitative evaluation of their importance *in vacuo* and in solution has been previously reported[39]. More refined studies on isomerization processes should of course take into consideration these terms too, and the present computational scheme should allow their evaluation, at least in principle. Other contributions to F and ΔF_{sol} derive from the work done to build up the cavity in the medium and from the dispersion contributions to the solute-solvent interaction energy. There are several proposals to evaluate ΔF_{cav} terms[44–47], none of which is completely satisfactory. We shall use the formula given by Pierotti[44]. As will be shown in the next section, changes in ΔF_{cav} are modest along the isomerization paths. Available expressions for dispersion contributions in solutions have been calibrated for solutes in equilibrium geometries[48–52], and are not easily adapted to study processes involving the breaking of a bond, as in the present case. On the other hand, in solutions of polar solutes the electrostatic terms are dominant, and therefore we shall neglect the dispersion contributions in the present study.

CALCULATIONS AND RESULTS

One-determinant SCF calculations are not sufficient to describe the energy profile for thermal isomerizations involving the breaking of a double bond. Previous experience[11] has shown that a fairly correct description of such processes is obtained by using a »half-electron« SCF supplemented by a 3×3 CI[53]. We have thus implemented the computational method described in the preceding section in connection with a CI procedure. We report in Table I the partially optimized structures for the stable conformers of N_2H_2 and CH_2NH and for the two transition states corresponding to the rotational and inversional isomerization mechanisms (see also Figure 1). The geometries have been obtained with the Murtagh and Sargent technique[54] with inclusion of the following constraints. Trans diimide: C_{2h} symmetry; cis diimide: C_{2v} sym-

TABLE I

Geometries and Energies of Stable Isomers and TS's of N_2H_2 and CH_2NH[a]

	Geometry		E^0	F_{el}	ΔF_{el}	ΔF_{sol}[b]
N_2H_2						
trans	r (NN) r (NH) $<$ (NNH)	1.321 1.060 104.2°	—108.618463	—108.692909	—6.7	—2.2
cis	r (NN) r (NH) $<$ (NNH)	1.320 1.062 109.7°	—108.606578	—108.624849	—11.5	—6.9
inver. TS	r (NN) r (NH_1) r (NH_2 $<$ (H_1NN)	1.290 1.061 1.006 107.7°	—108.508437	—108.521456	—8.2	—3.6
rot. TS	r (NN) r (NH) $<$ (HNN)	1.530 1.063 96.4°	—108.505032	—108.521038	—10.1	—5.5
CH_2NH						
planar	r (CN) r (CH) r (NH) $<$ (HCN) $<$ (CNH)	1.314 1.090 1.048 107.0° 121.5°	—92.871919	—92.884152	—7.7	—2.9
inver. TS	r (CN) r (NH)	1.260 1.001	—92.801514	—92.807171	—3.5	+1.4
rot. TS	r (CN) r (NH) $<$ (CNH)	1.503 1.060 101.2°	—92.756129	—92.768060	—7.5	—2.7

[a] Distances in Å, angles in degrees, E^0 and F in hartrees, ΔF in kcal/mol.

[b] $\Delta F_{sol} = \Delta F_{el} + \Delta F_{cav} + RT$. ΔF_{cav} refers to acetone as solvent.

metry; diimide invertomeric TS: $< N_1N_2H_2 = 180°$, $r\,(N_1H_1)$ kept fixed at the average of the values found in the trans and cis conformers; diimide rotameric TS: C_2 symmetry and $H_1N_1N_2H_2$ dihedral angle = 90°. Methylenimine: the CH_2 group maintains in all cases a local C_{2v} symmetry, with internal parameters

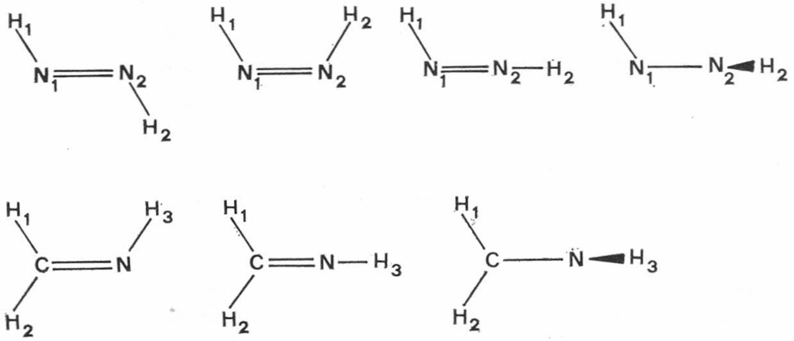

Figure 1. Atom numbering and schematic representation of the geometries of diimide and methylenimine considered in this paper.

taken from microwave measurements[55]; invertomeric TS: C_{2v} symmetry; rotameric TS: C_S symmetry. These constraints have been suggested by previous calculations and by experimental structure determinations. The introduction of symmetry constraints for the transition states allows a distinction between two hypothetical reaction mechanisms, while it is not assured that two kinds of saddle points really coexist in the potential surface of these molecules. The geometries of Table I refer to STO-3G calculations.

Comparison with previous calculations[1–18,56] shows that our geometries give the correct trends for changes occurring along the isomerization paths. The general overestimation of the double bond lengths (experimentally[57], 1.252 Å for trans N_2H_2 and 1.273 for CH_3N) is probably due to the limited CI procedure here adopted, which includes configurations where the π antibonding orbital is occupied. The effect of upgrading the CI level on double bond lengths for equilibrium geometries has been assessed by De Frees *et al.*[57]. No results of comparable accuracy are available for the rotameric forms, which present the maximum elongation of the CN and NN bonds.

Table I gives also the energy *in vacuo* and in solution, the latter calculated according to Eq. (3). Values in solution refer to a solvent with dielectric constant $\varepsilon = 20$. The cavity is defined in terms of four (or five) interlocking spheres, centered on the solute nuclei, each having a radius equal to the pertinent van der Waals value. The values of the radii which yield the best agreement with supermolecule calculations fall in the range 1 to 1.2 times r(van der Waals): the lower limit of the interval is better suited for use in conjuction with minimal basis sets.

Table II gives a prospect of cavitation free energies, calculated with the Pierotti formula, for a set of solvents of interest. The solvent parameters have been taken from the literature[44,47]. The values of the Table refer to $T = 298$ °K.

TABLE II

Cavitation Free Energy for Some Representative Solvents (kcal/mol)[a]

	Cavity for:						
Solvent	N_2H_2 trans	N_2H_2 cis	N_2H_2 inv	N_2H_2 rot	CH_2NH plan	CH_2NH inv	CH_2NH rot
Water	5.42	5.57	5.58	5.62	5.98	6.02	6.02
Methanol	4.08	4.18	4.19	4.22	4.48	4.51	4.51
Acetone	3.88	3.95	3.96	3.98	4.22	4.25	4.25
Cycloesanone	3.60	3.69	3.70	3.31	3.93	3.96	3.96

[a] Cavity apparent diameter from the present calculations, solvent apparent diameter from Pierotti[44] and Abraham and Nasehzadeh[47].

Relative energies and barriers for the isomerization processes are reported in Table III, both *in vacuo* and in solution. The values in solution refer to acetone as solvent (but the choice of a different solvent has no effect on the barrier heights in solution, see Table II).

TABLE III

Energies in Vacuo and in Solution Referred to the Most Stable Conformation (kcal/mol)[a]

	E^0	ΔF	$\Delta F - E^0$		E^0	ΔF	$\Delta F - E^0$
N_2H_2				CH_2NH			
trans	0	0	0	plan	0	0	0
cis	7.3	2.7	—4.8	inv	44.2	48.4	4.1
inv	69.0	67.6	—1.4	rot	72.7	72.9	0.2
rot	71.2	67.8	—3.4				

[a] ΔF includes also cavitation contributions.

Other numerical results will be reported in the following discussion.

DISCUSSION

The present discussion pursues two separate goals: firstly to give a qualitative interpretation of the effect of the solvent on the isomerization barriers, secondly to assess the limits of the present calculations.

Solvent effects, in the absence of covalent solute-solvent interactions, are dominated by electrostatic terms[37]. We recall that H-bonding effects may also be included in an electrostatic picture. In the computational model here employed, solvent effects may be divided into polarization of the solute, accounted for by the iterative calculation of the solute wavefunction, and polarization of the solvent, represented by the surface charge σ. The corresponding energetic contributions are all collected in Eq. (3). Inspection of the partial values provided by the computational program indicates that a qualitative interpretation may neglect the solute polarization.

We shall now discuss the energy contributions coming from solvent polarization and solute-solvent electrostatic interaction, which can be collected in the single term:

$$\tfrac{1}{2} \int_{\mathrm{cav}} \varrho_{\mathrm{M}}{}^{f}\, V_{\sigma}{}^{f}\, \mathrm{d}\tau = \tfrac{1}{2} \int_{\mathrm{surf}} \sigma^{f}\, V_{\varrho}{}^{f}\, \mathrm{d}s \qquad (5)$$

from which it is possible to draw a schematic interpretation of the effects related to changes in the conformation of M. This interpretation is not easily done when ϱ_{M} is given as a one-center expansion. It is convenient to adopt segmental expansions in which groups i related to bonds or lone pairs are separately considered[36,58]:

$$\varrho_{\mathrm{M}} = \sum_{i \in \mathrm{M}} \varrho_i \qquad (6)$$

Each group interacts with the whole σ charge distribution, and as a consequence, the interaction energy (5) combines the characteristics of the groups present in M, with those of V_σ. The spatial relationships between the ϱ_i charge distributions and V_σ therefore take on a great importance. Let us consider diimide firstly. The solute-solvent interaction is mainly due to the dipolar component of the two couples of NH bonds and N lone pairs. In the trans conformation the geometrical arrangement of these groups induces a V_σ potential dominated by a quadrupolar term (see Figure 2b). We remark, in

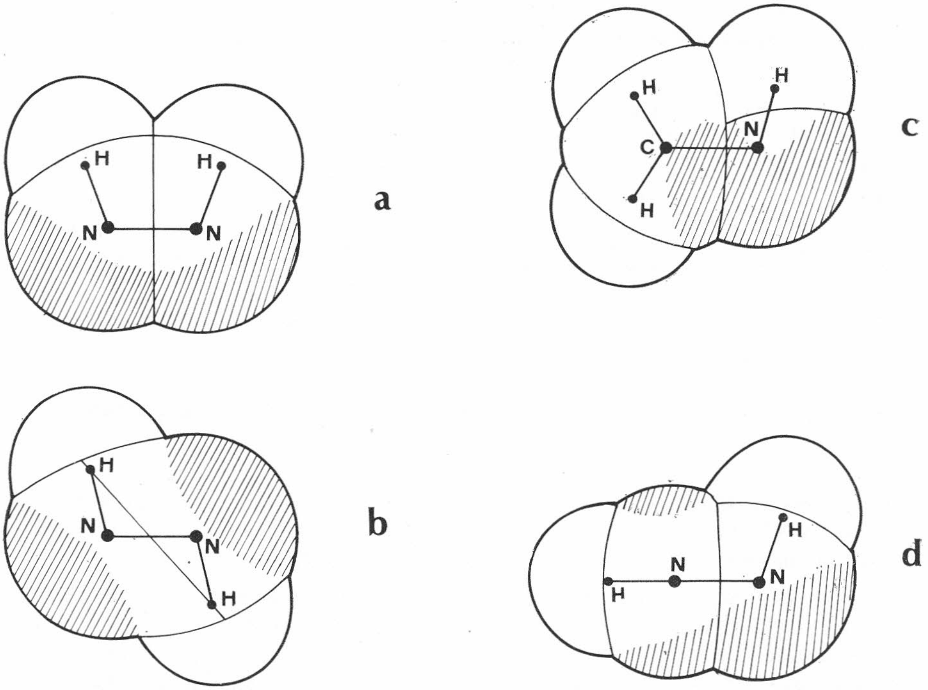

Figure 2. Schematic representation of the cavity surfaces for: a) cis N_2H_2, b) trans N_2H_2, c) planar CH_2NH, d) invertomeric TS for N_2H_2. The shaded areas correspond to positive values of σ.

passing, that the simplest version of the continuum solution model (*i. e.* the Onsager model) would predict a zero interaction energy, while the actual value is close to that of CH_2NH (see Table I) and comparable with that of other small dipolar solutes (unpublished results). The interaction energy is however larger in the cis conformation, because in this case σ is divided into only two portions of opposite sign which favourably interact with lone pairs and NH bonds (see Figure 2a). The rotational TS corresponds to an intermediate situation; the orthogonal arrangement of the two couples of lone pairs and NH bonds induces a polarization of the solvent corresponding to a V_σ dominated by a dipole term, but the interaction is here less favourable because of the relative orientation of the local dipoles of M and the dipolar component of V_σ.

The invertomeric TS presents a noticeable reorganization of the solute electronic distribution. Qualitatively a sp^2 hybridized lone pair on N_2 is replaced by a pure *p* orbital: there is a loss of one polar group and the stabilization energy is lower than in the preceding cases.

In the planar methylenimine V_σ is dominated by a dipolar term: the orientation of the solute polar groups is less favourable than in cis diimide and comparable with that of the invertomeric TS of N_2H_2. V_σ for the rotameric TS of CH_2NH is dominated again by a dipolar term: the relative orientation of groups should lead to the prediction of an interaction energy similar to that of the planar conformer and lower than that of the rotameric TS of N_2H_2 because a CH group is less polar than a N lone pair[37]. The CH_2NH invertomer should present the smallest solute-solvent interaction energy of the whole series, because the change of hybridization of the N-lone pair deprives the molecule of any group of comparable polarity. These qualitative considerations are confirmed by the values of ΔF_{el} reported in Table I. We remark in passing that ΔF_{el} values differ from solute-solvent polarization energy (Eq. 5) only for internal solute polarization and kinetic energy contributions.

A qualitative analysis of solvent effects on the thermal isomerization mechanism of azobenzene and related compounds was performed some years ago by Haberfield *et al.*[59]. The attention of these authors was focussed on the number of *sp* hybridized N-lone pairs present in stable compounds and transition states. Allowance being made for the differences due to the chemical composition of the solutes and to the specific setup of Ref. 59, a general agreement between the results and discussion of that paper and the numerical results and interpretation of the present paper may be put in evidence.

The results of Tables I and III refer to a solvent with $\varepsilon = 20$. An increase of the dielectric constant gives rise to small changes in the relative values of ΔF_{el}. For example analogous calculations performed with $\varepsilon = 40$ give changes in the barrier heights of the order of 0.1—0.2 kcal/mol. Changes of the same order are expected for solvents having $\varepsilon = 80$—100. There are relatively large differences in the absolute value of ΔF_{el}. We report as an example in Figure 5 the values of ΔF_{el} for the planar form of CH_2NH referring to solvents with dielectric constant ranging in the interval 2—100. In the same figure we have plotted the values of ΔF_{el} obtained with the Bell-Onsager model, *i. e.* a point dipole in a spherical cavity. The calculations of Figure 5 refer to a 4-31G basis set which gives a better description of the

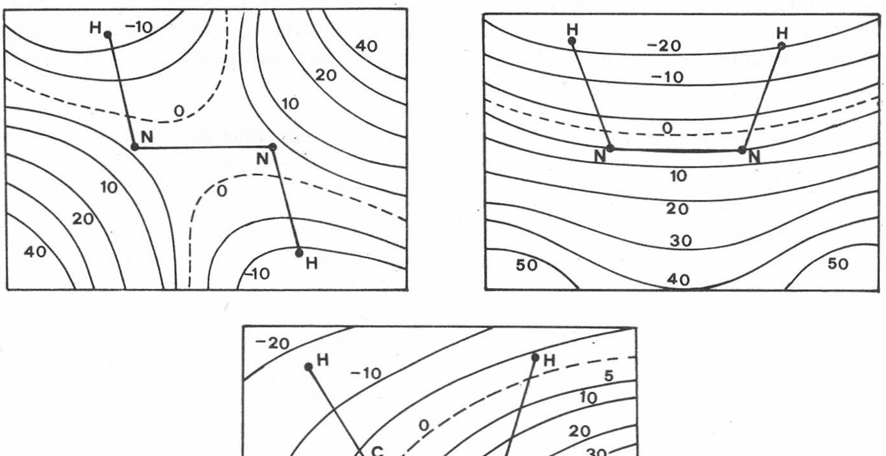

Figure 3. Maps of the electrostatic potential generated by the polarized solvent, V_σ, in a region of the molecular plane inside the cavity. Numerical values are given in kcal/mol and refer to $E = q\,V_\sigma$ (q = proton charge). 4-31G calculations.

solute polarization effects and employ the same number of spheres as above, and radii equal to 1.2 times r (van der Waals). The volume of the Bell-Onsager sphere is the same as that of our cavity. In applying the Bell-Onsager formula we have made use both of a fixed dipole ($\mu = 2.33$ D, from the *in vacuo* 4-31G calculation), and of a variable, reaction field dependent, dipole (from the wavefunctions related to the hamiltonian (2)). The comparison given in the figure is relatively favourable to the Bell-Onsager model, because CH_2NH has a noticeable dipole moment and a compact shape, fitting well a spherical cavity. For other compounds, without such characteristics, larger deviations from the simplified model have been observed (unpublished results).

As shown also by the results of Figure 3, the effect of the polarization of the solute on ΔF_{el} is not negligeable from a quantitative point of view (up to 30% in the STO-3G basis). Moreover, it is presumable that the importance of this contribution should increase for large molecules with more polarizable groups and also for more flexible basis sets.

Changes in the electronic wavefunction produced by an external electrostatic interaction are often brought out by reporting changes in the Mulliken population and in the multipolar expansion terms of the molecular charge distribution (see Table IV). The information gained in this way is however limited because multipole moments reflect the whole charge distribution and the Mulliken populations, though sufficiently detailed, suffer from well known shortcomings. The partition of the molecular charge distribution into fragments related to localized orbitals (see Eq. (6)) has been employed many times in our laboratory to elucidate the effect of external and internal perturbations[60] with good success, and it is reasonable to use it also in the case of solvent effects. The effect of the solvent in the hamiltonian is here represented by V_σ, but when groups are composed of single bonds or lone pairs having in general a noticeable dipole moment (we recall that our groups are electrically

TABLE IV

Dipole Moments (Debye) and Atomic Charges in Vacuo and in Solution. Diimide.

N_2H_2		*In vacuo*	In solution
trans	N_1, N_2	—0.150	—0.173
	H_1, H_2	0.150	0.173
	$\lvert\mu\rvert$	0	0
cis	N_1, N_2	—0.132	—0.174
	H_1, H_2	0.132	0.174
	μ_x[a]	2.815	3.230
inv	N_1	—0.098	—0.159
	N_2	—0.290	—0.291
	H_1	0.123	0.152
	H_2	0.264	0.298
	N_1 (π)	—0.038	—0.051
	N_2 (π)	0.038	0.051
	μ_x[a]	1.357	1.524
	μ_z[a]	1.704	1.958
rot	N_1, N_2	—0.147	—0.181
	H_1, H_2	0.147	0.181
	μ_x, μ_y[a]	1.333	1.542

[a] The z axis coincides with the N_1—N_2 direction; H_1, N_1, N_2 lie in the xz plane.

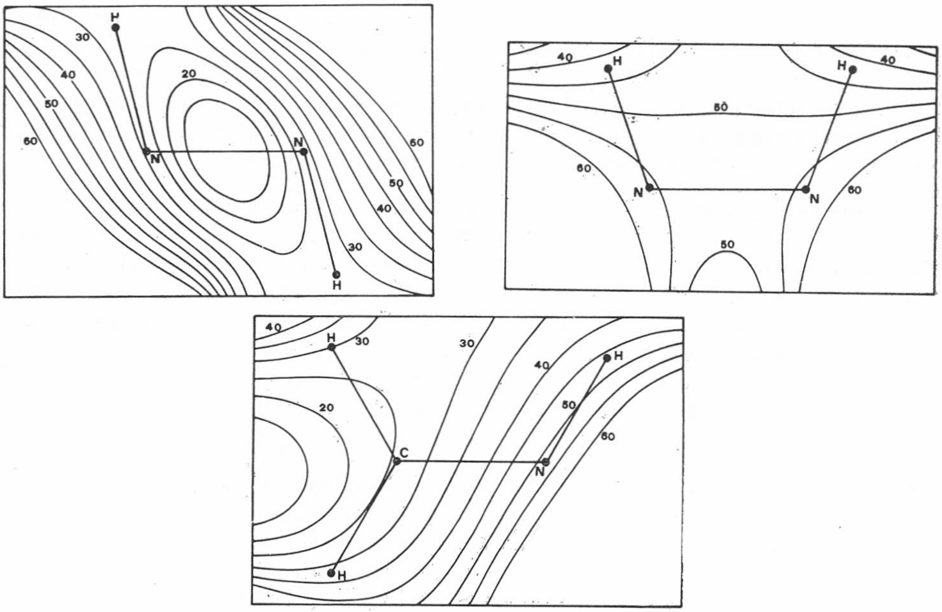

Figure 4. Maps of the absolute value of the electric field generated by the polarized solvent, $|\mathcal{E}_\sigma|$, in a region of the molecular plane inside the cavity. Values are given in arbitrary units (1 a. u. = 27360 esu cm^{-2}); when the fields are given in such units and the dipole moment in debyes, the interaction energy $\vec{\mathcal{E}} \cdot \vec{\mu}$ is directly given in kcal/mol. Numerical values refer to 4-31G calculations.

neutral, because each one contains an adequate amount of nuclear charge) it is convenient to look also at the electrostatic field $\vec{\mathcal{E}}_\sigma$ generated by the surface charge distribution σ.

We give as an example in Figures 4 and 5 the maps of V_σ and $|\mathcal{E}_\sigma|$ for trans diimide and planar methylenimine. It is evident that there is a diffe-

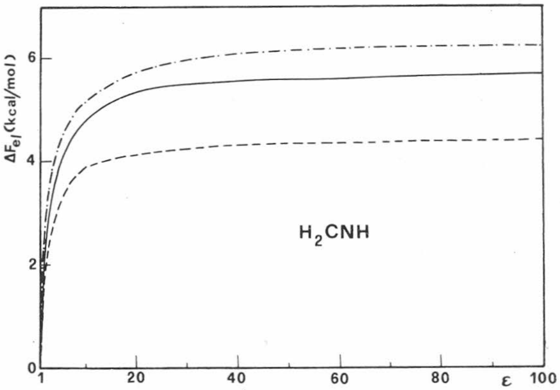

Figure 5. Plot of the values of ΔF_{el} for CH$_2$NH as a function of the dielectric constant. ——— present *ab initio* calculations (4-31G); — — — — — Bell model

rential influence of the solvent on the solute groups. Lone pairs are subject to stronger electric fields than NH and CH bonds. The influence of σ on the central double bond is relatively small, but it is expected to increase in substituted compounds. Analogous maps for cis diimide and for the isomerization TS's present supplementary features, among which we point out the stronger influence of σ on the double bond in the invertomeric TS.

Maps of V_σ and $|\epsilon_\sigma|$ give a detailed but only qualitative description of the origin of the solvent polarizing effect (we remark, in passing, that such picture qualitatively agrees with the description of the effect given by the changes in the Mulliken charges of Table IV). Quantitative, or semi-quantitative, analyses can be performed only when reliable numerical procedures have been defined. A procedure elaborated a few years ago[61] to describe chemical substitution effects and later extended to external perturbers may be tentatively employed in this case too. The value of the field generated by the perturber (in this case σ) at the position of the group charge distribution center is employed as a numerical probe. A further subdivision of $\vec{\epsilon}_{\text{pert}}$ into parallel and perpendicular components, with respect to the main axis of the group distribution, has proved to be useful and sufficient to give evidence of a linear answer of the group to fields of strength comparable to those of solvents, with an apparent group polarizability well transferable from molecule to molecule. This method, applied to CH_2NH in a set of different solvents, gives the results summarized in Figure 6. This limited example sufficies to

TABLE V

Dipole Moments (Debye) and Atomic Charges in Vacuo and in Solution. Methylenimine

CH_2NH		*In vacuo*	In solution
planar	C	—0.004	0.022
	N	—0.259	—0.342
	H_1	0.050	0.072
	H_2	0.068	0.075
	H_3	0.145	0.174
	C (π)	0.020	0.046
	N (π)	—0.020	—0.046
	μ_x[a]	1.357	1.567
	μ_z[a]	—1.162	—1.496
inv	C	0.059	0.061
	N	—0.378	—0.419
	H_1, H_2	0.038	0.048
	H_3	0.242	0.261
	C (π)	0.005	0.016
	N (π)	—0.005	—0.016
	μ_z[a]	0.680	0.574
rot	C	—0.100	—0.092
	N	—0.180	—0.247
	H_1, H_2	0.068	0.085
	H_3	0.143	0.168
	μ_y[a]	1.279	1.478
	μ_z[a]	—0.876	—1.215

[a] The z axis coincides with the C—N direction; H_1, H_2, C, N lie in the xz plane.

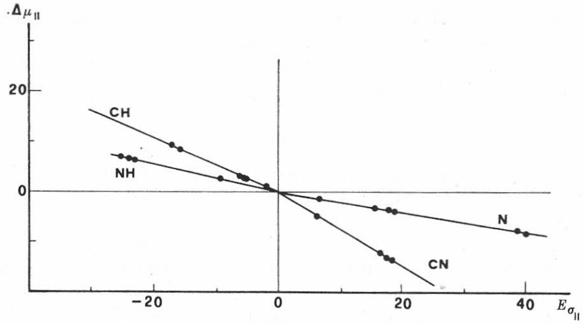

Figure 6. Correlation between the changes in the longitudinal component of the group dipole moment and the $\vec{\epsilon}_\sigma$ component in the same direction. The numerical values of $\vec{\epsilon}_\sigma$ refer to solvents of different dielectric constant and are computed at the position of the relevant group charge center. μ in Debyes, $\vec{\epsilon}_\sigma$ in arb. un. (see Figure 4).

show the higher apparent polarizability of the C=N group (here represented by two banana groups) with respect to the N-lone pair. This trend agrees with information coming from other sources[36,60-61]. Correlation of the changes in the Mulliken population with respect to the same numerical probe are of comparable quality.

Let us return now to the description of the isomerization mechanism provided by our computations. Both *in vacuo* barriers for CH_2NH are probably too high, in comparison with previous calculations[4,6,7,12,18], but all the estimates of the differences between the two barriers, including ours, are in good agreement ($\Delta = 28$—31 kcal/mol). Although the solvent effect reduces this difference by about 4 kcal/mol, it remains too large for a rotational mechanism to be active. Also the barriers for N_2H_2 are probably overestimated even if they fall in the wide range of computed values: rotation 41[11]—84[1,3,5], inversion 45[11]—72[3]. The inversion barrier is probably overestimated by 10 kcal/mol: compare with the accurate value of 58.7 kcal/mol (without zero point corrections) given by Pople *et al.*[18]. There are no results of comparable quality for the rotation mechanism. It is interesting to compare our results with one of the sets of results given by Cimiraglia *et al.*[11]. Both calculations use a 3×3 CI performed over »half-electron« MO's but while the present ones use a STO-3G basis set, the calculations of Ref. 11, which we are considering now, supplement this basis with a set of diffuse *p* orbitals: the barriers are 41.2 (rotation) and 49.2 kcal/mol (inversion). In a relatively flat portion of the energy hypersurface, as could be the case for certain substituted azocompounds, solvent effects may be of some importance in shifting the flow of representative particles, if we adopt a classical dynamics description of the isomerization act, towards paths having a larger rotational character.

The energy difference *in vacuo* between cis and trans diimide (7.3 kcal/mol) compares fairly well with the result of Pople *et al.*[18] (SCF, 7.1 kcal/mol which becomes 5.4 with zero point vibrational energy and electronic correlation corrections). The relatively large solvent stabilization of the cis form indicates the possibility that the cis form is the more stable in solution for some azocompounds

Acknowledgements. — The financial support of the CNR through the Istituto di Chimica Quantistica ed Energetica Molecolare, and of Ministry of Public Education is acknowledged. The authors are indebted to Dr. Bonaccorsi and C. Ghio for their help in performing some calculations.

REFERENCES

1. J. M. Lehn, and B. Munsch, *Theor. Chim. Acta* **12** (1968) 91.
2. B. Cadioli, D. J. David, P. Patella, and U. Pincelli, *Atti Soc. Nat. Mat. Modena C* (1969) 47.
3. L. J. Schaad and H. B. Kinser, *J. Phys. Chem.* **73** (1969) 1901.
4. J. M. Lehn, B. Munsch, and P. Millié, *Theor. Chim. Acta* **16** (1970) 351.
5. N. C. Baird and J. R. Swenson, *Can. J. Chem.* **51** (1973) 3097.
6. R. Macaulay, L. A. Burnelle, and C. Sandorfy, *Theor. Chim. Acta* **22** (1973) 1.
7. G. Merényi, G. Wettermark, and B. Roos, *Chem. Phys.* **1** (1973) 340.
8. N. W. Winter and R. M. Pitzer, *J. Chem. Phys.* **62** (1975) 1265.
9. R. Ahlrichs and V. Staemmler, *Chem. Phys. Lett.* **37** (1976) 77.
10. J. M. Howell and L. J. Kirschenbaum, *J. Amer. Chem. Soc.* **98** (1976) 877.
11. R. Cimiraglia, J. M. Riera, and J. Tomasi, *Theor. Chim. Acta* **46** (1977) 223.
12. P. Russegger, *Chem. Phys.* **34** (1978) 329.
13. E. Flood and P. N. Skancke, *Chem. Phys. Lett.* **54** (1978) 53.
14. D. J. Pasto and D. M. Chipman, *J. Amer. Chem. Soc.* **101** (1979) 2290.
15. C. A. Parsons and C. E. Dykstra, *J. Chem. Phys.* **71** (1979) 3025.
16. C. J. Casewit and W. A. Goddard, *J. Amer. Chem. Soc.* **102** (1980) 4057.
17. V. Bonačić-Koutecký and M. Persico, *J. Amer. Chem. Soc.* **105** (1983) 3388.
18. J. A. Pople, K. Raghavachari, M. J. Frisch, J. S. Binkley, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **105** (1983) 6389.
19. A. S. Zyubin and P. O. Charkin, *Zh. Neorg. Khim.* **27** (1982) 1529.
20. A. Pullman, in: B. Pullman, and R. Parr (Eds.), *The New World of Quantum Chemistry,* Reidel, Dordrecht 1976, p. 149.
21. S. S. Yamabe, S. Kato, H. Fujimoto, and K. Fukui, *Theor. Chim. Acta* **30** (1973) 327.
22. W. Förner, P. Otto, J. Bernhardt, and J. J. Ladik, *Theor. Chim. Acta* **60** (1981) 269.
23. C. D. Richtie, *Pure Appl. Chem.* **51** (1979) 153.
24. J. Bertran, *J. Mol. Struct. Theochem* **93** (1983) 129.
25. E. Clementi, *Lecture Notes in Chemistry,* Vol **19,** Berlin, Springer, 1980.
26. G. Alagona, C. Ghio, and P. A. Kollman, private communication.
27. S. Romano, *Int. J. Quantum Chem.* **20** (1981) 921.
28. B. Jönsson, S. Romano, and G. Karlström, *Int. J. Quantum Chem.,* to be published.
29. M. D. Newton, *J. Chem. Phys.* **58** (1973) 5833.
30. M.-J. Huron and P. Claverie, *J. Phys. Chem.* **78** (1974) 1853.
31. O. Tapia and O. Goscinski, *Mol. Phys.* **29** (1975) 1653.
32. J. L. Rivail and D. Rinaldi, *Chem. Phys.* **18** (1976) 233.
33. J. Hylton-McCreery, R. E. Christoffersen, and G. G. Hall, *J. Amer. Chem. Soc.* **98** (1976) 7191.
34. S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.* **55** (1981) 117.
35. O. Tapia, in: H. Ratajczak and W. J. Orville-Thomas (Eds.), *Intermolecular Interactions,* J. Wiley & S., Chichester 1982, Vol. 3, p. 47.
36. J. Tomasi, in: H. Ratajczak and W. J. Orville-Thomas (Eds.), *Intermolecular Interactions,* J. Wiley & S., Chichester 1982, Vol. 3, p. 119.
37. R. Bonaccorsi, C. Ghio, and J. Tomasi, *Int. J. Quantum Chem.,* to be published.
38. P. Claverie, J. P. Daudey, J. Langlet, B. Pullman, D. Piazzola, and J. M. Huron, *J. Phys. Chem.* **32 (1978) 405.**
39. R. Bonaccorsi, C. Ghio, and J. Tomasi, in: R. Carbò (Ed.), *Current Aspects of Quantum Chemistry 1981,* Elsevier, Amsterdam 1982, p. 407.
40. K. J. Laidler and J. C. Polanyi, in: G. Porter (Ed.), *Progress in Reaction Kinetics,* Pergamon, Oxford 1965, Vol. 3, p. 1.

41. R. Bonaccorsi, R. Cimiraglia, and J. Tomasi, *Chem. Phys. Lett.* **99** (1983) 77.
42. S. Miertuš and J. Tomasi, *Chem. Phys.* **65** (1982) 239.
43. R. Bonaccorsi, P. Palla, and J. Tomasi, *J. Amer. Chem. Soc.*, to be published.
44. R. A. Pierotti, *Chem. Phys.* **76** (1976) 717.
45. T. Halicioglu and O. Sinanoglu, *Ann. N. Y. Acad. Sci.* **198** (1969) 398.
46. J. J. Moura-Ramos, M. Lemmers, R. Ottinger, M. L. Stein, and J. Reisse, *J. Chem. Res.* (S) (1977) 56.
47. M. H. Abraham and A. Nasehzadeh, *J. Chem. Soc. Faraday Trans. 1* **77** (1981) 321.
48. B. Linder, *J. Chem. Phys.* **37** (1962) 963; *Ad. Chem. Phys.* **12** (1967) 225.
49. A. T. Amos and B. L. Burrows, *Theor. Chim. Acta* **29** (1973) 139.
50. M. J. Huron and P. Claverie, *J. Phys. Chem.* **76** (1972) 2123.
51. F. Birnstock, H. J. Hofmann, and H. J. Köhler, *Theor. Chim. Acta* **42** (1976) 311.
52. A. J. Duben and S. Miertuš, *Chem. Phys. Lett.* **88** (1982) 395.
53. L. Salem, *J. Amer. Chem. Soc.* **96** (1974) 3486.
54. B. A. Murtagh and R. W. H. Sargent, *Computer J.* **13** (1970) 185.
55. R. Pearson and F. J. Lovas, *J. Chem. Phys.* **66** (1977) 4149.
56. D. J. DeFrees, K. Raghavachari, M. B. Schlegel, and J. A. Pople, *J. Amer. Chem. Soc.* **104** (1982) 5576.
57. M. D. Harmony, V. W. Laurie, R. L. Kuezkowski, R. M. Schwendemann, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data* **8** (1979) 619.
58. E. Scrocco and J. Tomasi, *Adv. Quantum Chem.* **11** (1978) 115.
59. P. Haberfield, P. M. Block, and M. S. Lux, *J. Amer. Chem. Soc.* **97** (1975) 5804.
60. R. Bonaccorsi, C. Ghio, E. Scrocco, and J. Tomasi, *Isr. J. Chem.* **19** (1980) 109.
61. C. Ghio, E. Scrocco, and J. Tomasi, *Theor. Chim. Acta* **50** (1978) 117; **56** (1980) 61, 75.

SAŽETAK

Procjena utjecaja otapala na mehanizme izomerizacije diimida i metilenimina

Maurizio Persico i Jacopo Tomasi

Inversijski i rotacijski mehanizmi izomerizacije N_2H_2 i CH_2NH razmatrani su primjenom postupka *ab initio*. Pri tome je u hamiltonijan otopljene molekule uključen reakcijski potencijal otapala u obliku dielektričkog kontinuuma. Utjecaj otapala usko je vezan s hibridizacijskim stanjem atoma dušika kao i s relativnom orijentacijom osamljenih parova elektrona. Kod molekule N_2H_2 dolazi do sniženja obiju barijera kao i do stabilizacije cis-oblika s obzirom na trans. U sustavu CH_2NH otapalo povisuje inversijsku barijeru, a snižava barijeru unutrašnje vrtnje.