

TCSCF level, the CSC bending frequency is predicted to be 1179 cm^{-1} for thiirane (C-C stretch coupled to CH_2 wag), 356 cm^{-1} for disrotatory (coupled to CH_2 wag), 479 cm^{-1} for conrotatory (coupled to CH_2 wag), and 355 cm^{-1} for thione methylide. The CH_2 wagging vibrational frequencies also span a large range, from 1186, 1097 cm^{-1} for thiirane, 268, 257 cm^{-1} for disrotatory, 677, 615 cm^{-1} for conrotatory, and 390 cm^{-1} (the other wagging mode is not easily assigned due to heavy coupling between a_2 symmetry CH_2 twisting and wagging motions) for thione methylide at the TZ2P/DZP TCSCF level. The latter values for the disrotatory stationary point are rather low, reflecting the longer C-S bond length and larger CSC bond angle compared with the conrotatory stationary point. Again, the conrotatory and disrotatory stationary points resemble the open structure more than the tightly held ring structure.

The dipole moment predicted for the various structures lies along the C_2 axis or the C_s mirror plane, bisecting the C-C axis. In general, the dipole moment is expected to decrease as the CSC and HCS bond angles are increased, since the projection of the C-S and C-H bond moments onto the axis of the dipole moment is reduced with an increase of the bond angles. The CSC bond angle shows considerably more variation between the different structures than the HCS angle, and thus affects the magnitude of the dipole moment to a greater extent. The dipole moment predicted for the open isomer is significantly smaller in magnitude than that for the ring isomer due to an increased CSC bond angle. The dipole moments for the conrotatory and disrotatory stationary points are intermediate between those of the ring and open forms as a result of intermediate CSC bond angles.

The geometrical structures, physical properties, and relative energies of the four species predicted with the TZ2P/DZP basis set are very similar to those with the TZ2P basis set. The exception is the imaginary frequency for the open structure with the TZ2P/DZP TCSCF method which becomes real at the TZ2P

TCSCF level, although the absolute frequency change is rather small (18i \rightarrow 60 cm^{-1}).

Conclusions

The ring opening of thiirane is predicted to follow a conrotatory mechanism with an activation barrier of $51.3 \pm 4.0 \text{ kcal mol}^{-1}$ with the ZPVE correction, the top of the barrier corresponding to a genuine transition state. The stationary point for disrotatory motion is found to be higher in energy than the conrotatory transition state by $13.2 \pm 4.0 \text{ kcal mol}^{-1}$ with the ZPVE correction and is characterized as a stationary point with Hessian index 2. The most stable structure on the thiirane potential energy surface is the ring isomer which is predicted to lie below the open structure by $34.7 \pm 4.0 \text{ kcal mol}^{-1}$ with the ZPVE correction.

The quantitative predictions for the ring opening mechanisms of thiirane are related to the corresponding results for oxirane. Replacing the second row atom sulfur with oxygen with use of the single-configuration methods (SCF, SCF-CISD) appears to have the effect of stabilizing the ring structure relative to the open isomer and the conrotatory transition state, thus increasing the corresponding energy differences. With the two-configuration methods (TCSCF, TCSCF-CISD), however, the thiirane and oxirane energy differences are very similar.

The ring opening of unsubstituted thiirane, involving the second row atom sulfur, is predicted to follow the W-H rules in agreement with the first row system oxirane. This implies high stereoselectivity for the ring-opening reaction of thiirane. For the case of substituted thiiranes, steric interactions may significantly affect the stereochemistry. The current research, however, provides a detailed picture of the potential energy surface associated with unsubstituted thiirane.

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Solvent Effects. 1. The Mediation of Electrostatic Effects by Solvents

Ming Wah Wong,^{1a} Michael J. Frisch,^{1b} and Kenneth B. Wiberg^{*,1a}

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511, and Lorentzian Incorporated, 127 Washington Avenue, North Haven, Connecticut 06473. Received October 5, 1990

Abstract: Solvent effects on conformational equilibria, rotational barriers, charge distributions, and molecular properties of ionic and neutral dipolar molecules have been investigated by high-level *ab initio* reaction field theory. The calculated solvent effects on the conformational equilibrium of 1,2-dichloroethane and furfural are in good agreement with experiments. The rotational barriers for the interconversion of the *Z* and *E* isomers of (2-nitrovinyl)amine in solution are also reasonably reproduced by reaction field theory. In the presence of a solvent reaction field, the geometry, energy, and charge distribution of methoxide anion are found to alter significantly. For the application of reaction field theory to neutral dipolar species, we have examined the solvent effect of two simple 1,3-dipoles, diazomethane and acetonitrile oxide. Dielectric medium appears to have significant different effects on the calculated electronic structure of these two compounds. In this paper, we also have formulated a correlated version of the Onsager reaction field method for studying solvent effects. In some cases, the use of correlated wave functions is found to produce more reliable results.

Introduction

Electrostatic effects are often important in the gas phase. Conformations with no dipole moment are usually preferred over those leading to dipoles; ions in which the charge is distributed over a large volume element are preferred over those in which the charge is more localized. If these species were placed in a solvent with a high dielectric constant, the electrostatic energies would

be reduced and other factors may become more important.

There are some experimental data supporting such a hypothesis. The *gauche* form of 1,2-dichloroethane has a 1 kcal mol^{-1} higher energy than the *trans* form in the gas phase, but in solvents of high dielectric constant, the energies of the two rotamers become almost equal.² The C=C rotational barriers in "push-pull"

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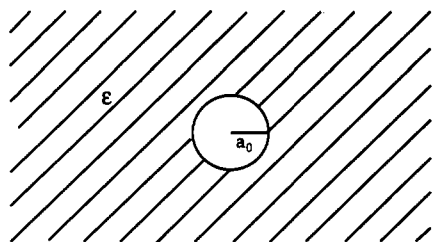


Figure 1. Onsager reaction field model. The solute is placed in a spherical cavity, with radius a_0 , surrounded by a continuous medium of dielectric constant ϵ .

ethylenes are found to be strongly dependent on solvent polarity.³ In some extreme cases, the rotational barriers are estimated to be reduced by 10–15 kcal mol⁻¹ from the gas phase to polar medium.³

The effect of solvents on the energies of organic compounds often is reasonably well related to the dielectric constant of the solvent, so long as specific solvent effects such as hydrogen bonding and donor-acceptor interaction are not present. For example, the difference in energy between the gauche and trans forms for 1,2-dichloroethane is fairly well correlated with the Onsager function,⁴ $(\epsilon - 1)/(\epsilon + 2)$.⁵ This suggests that the Onsager reaction field model⁴ might be appropriate for studying the solvent effect for this equilibrium. The Onsager model has been incorporated in molecular orbital (MO) calculations by Tapia and Goscinski.⁶ Since then, this model has been applied to a number of problems with use of semiempirical MO theory,^{6,7} and some applications using ab initio MO theory have been reported.⁸ However, no detailed examination of the approximations in the theory have been reported. We have now carried out such a study, and it will be the subject of this paper. Note that there are also several other methods that include solvent effects through a self-consistent reaction field (SCRf) technique.⁹ Since many chemical and physical phenomena require the use of correlated wave functions for proper description of the chemical systems involved, a correlated version of Onsager reaction field theory for studying solvent effects is desirable. In this paper, we present an algorithm for implementing this correlated method.

Discussion

Reaction Field Theory. In this model, the solute is placed in a cavity (usually spherical) immersed in a continuous medium with a dielectric constant ϵ (Figure 1).⁴ A dipole in the molecule will induce a dipole in the medium, and the electric field applied to the solute by the solvent (reaction) dipole will in turn interact with the molecular dipole to lead to net stabilization. In MO theory, the electrostatic solvent effect may be taken as an additional term, H_1 , in the Hamiltonian of the isolated molecule, H_0 :

$$H_{rf} = H_0 + H_1 \quad (1)$$

The perturbation term (H_1) describes the coupling between the molecular dipole operator ($\hat{\mu}$) and the reaction field, \bar{R}

$$H_1 = -\hat{\mu} \cdot \bar{R} \quad (2)$$

The reaction (electric) field, \bar{R} , is proportional to the molecular dipole moment, $\bar{\mu}$:

$$\bar{R} = g\bar{\mu} \quad (3)$$

The proportionality constant g , which gives the strength of the reaction field, depends on the dielectric constant of the medium, ϵ ,¹⁰ and on the radius of the spherical cavity, a_0 :⁴

$$g = 2(\epsilon - 1)/(2\epsilon + 1)a_0^3 \quad (4)$$

Note that a general expression of g has been proposed by Tapia and Goscinski to estimate the degree of solute-solvent coupling.⁶ For the case of a self-consistent field wave function, the effects of the reaction field can be incorporated as an additional term in the Fock matrix:

$$F_{\lambda\sigma} = F_{\lambda\sigma}^0 - g\bar{\mu} \langle \phi_\lambda | \hat{\mu} | \phi_\sigma \rangle \quad (5)$$

where ϕ_λ and ϕ_σ are basis functions. When the solvent polarization¹¹ is included, the energy of the system is given by

$$E = \langle \Psi | H_0 | \Psi \rangle - \frac{1}{2} \bar{\mu} \cdot \bar{R} \quad (6)$$

where Ψ is the full wave function of the molecule. Under the assumption of a spherical cavity, the ion-dipole solute-solvent interaction does not contribute to the electronic energy variationally. Thus, for a molecular ion with a total charge Q , a Born charge term¹² can be added to the expression of energy to account for the ion-dipole interaction:

$$E_{(\text{ion})} = E - \frac{1}{2} \left(1 - \frac{1}{\epsilon} \right) Q^2 / a_0 \quad (7)$$

In this case, the dipole moment is not translationally invariant, and in order to be consistent with the spherical cavity model it must be evaluated with the origin at the center of electric charge. If $\bar{\mu}_e$ and $\bar{\mu}_n$ are the electronic and nuclear components of the dipole moment with respect to an arbitrary origin, then the dipole moment with respect to the center of charge is

$$\bar{\mu}' = \bar{\mu}_e(Q + n_e)/n_e + \bar{\mu}_n \quad (8)$$

where n_e is number of electrons in the molecule.

A self-consistent reaction field may be applied to any method of computing electronic energies (i.e., ones that include electron correlation). Given a uniform reaction electric field, \bar{R} , the Hamiltonian is still perturbed by H_1 as given by eqs 2 and 3. However, the electric dipole moment of the solute, $\bar{\mu}$, is not in general given by an expectation value (as is the case for the exact wave function for SCF and other wave functions satisfying a generalization of the Hellman-Feynman theorem);¹³ instead, $\bar{\mu}$ must be computed as the derivative of the solute energy with respect to a uniform electric field.¹⁴ This can be done by using standard derivative techniques for most correlated energies. Our correlated SCRf procedure consists of iteratively solving for a consistent $\bar{\mu}$ and \bar{R} .

1. Choose an electric field, \bar{R} .

2. Compute the SCF and correlation energies and dipole moment in the presence of this field. That is, perform a standard energy and relaxed density calculation, except with H_1 added into the usual one-electron operator.

3. Compute a new reaction field $\bar{R} = g\bar{\mu}$ and return to step 2 if not converged.

Convergence is rapid given the reaction field at the SCF level as an initial guess.

For second-order Møller-Plesset theory (MP2)¹⁵ SCRf calculations, our method differs from the double perturbation method of Tapia et al.¹⁶ in that the effects of the electric field on the energy

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Table I. Calculated Properties of 1,2-Dichloroethane with Different Cavity Radii (a_0)^{a,b}

a_0 (Å)	gauche rotamer				ΔE	
	energy (hartrees)		dipole moment (D)		(gauche-trans)	
	HF	MP2	HF	MP2	HF	MP2
2.50	-997.04230	-997.59662	5.47	5.09	-5.92	-5.20
2.75	-997.03774	-997.59271	4.64	4.29	-3.06	-2.75
3.00	-997.03531	-997.59066	4.20	3.87	-1.54	-1.46
3.25	-997.03384	-997.58948	3.93	3.62	-0.61	-0.72
3.50	-997.03287	-997.58862	3.76	3.46	0.06	0.18
3.75	-997.03221	-997.58784	3.63	3.34	0.41	0.31
4.00	-997.03173	-997.58762	3.55	3.25	0.71	0.44
4.25	-997.03136	-997.58752	3.48	3.21	0.94	0.51
4.50	-997.03109	-997.58725	3.43	3.16	1.11	0.68

^a6-31+G*/HF/6-31G* ($\epsilon = 78.5$) values. ^bThe HF and MP2 total energies of the trans rotamer are -997.03286 and -997.58833 hartrees, respectively.

are accounted for exactly (i.e., summed to all orders in perturbation theory) and there is a self-consistency associated with the exact reaction field. In particular, our method includes the exact effects of the SCRf at the Hartree-Fock level, rather than a second-order approximation to the Hartree-Fock result. Our method is also extremely simple, requiring nothing more than a standard MP2 gradient¹⁷ program for the simplest inclusion of electron correlation, and can be applied to more accurate nonperturbative methods such as quadratic configuration interaction (QCI)¹⁸ and coupled cluster.¹⁹ In this paper, we will report reaction field results at the Hartree-Fock, MP2, and QCISD levels of theory. We have implemented these correlated SCRf methods in the ab initio MO code, GAUSSIAN-91.²⁰

The only adjustable parameter in a solvent effect calculation is the cavity radius, and the question of its choice will be discussed below. As shown in eqs 3 and 4, the calculated reaction field depends on the molecular dipole and polarizability, which are sensitive to the basis set employed in an SCRf calculation. Therefore, the use of an adequate basis set is crucial for the proper description of the solute-solvent interaction. The basis set dependency on the SCRf calculated solvation has been observed in a recent study.²¹ Throughout this paper, we have chosen the 6-31+G* (or 6-31+G**) basis set²² for our highest level SCRf calculations. The dipole moments calculated with use of this basis set have shown to generally provide satisfactory agreement with experimental values.²² The use of diffuse sp functions is important for the proper description of dipolar species and anions that generally bear negative charge on the heavy atoms.

Estimation of Cavity Radius. The choice of cavity radius has been the subject of much discussion.^{9b,d} The simplest approach is to obtain the radius directly from the solute molar volume (V_m):

$$a_0^3 = 3V_m/4\pi N \quad (9)$$

where V_m is given directly by experiment (molecular weight/density)¹⁰ and N is Avogadro's number. The molar volume can also be obtained from its refractivity.²³ Alternatively, one can estimate a_0 from the molecular greatest dimension. In this ap-

Table II. Calculated Geometrical Parameters of Gauche Rotamer of 1,2-Dichloroethane in Different Media^{a,b}

parameter	$\epsilon = 1.0$	$\epsilon = 6.0$	$\epsilon = 35.9$
$r(\text{C}-\text{C})$	1.515	1.514	1.513
$r(\text{C}-\text{Cl})$	1.786	1.790	1.791
$r(\text{C}-\text{Ht})$	1.080	1.080	1.080
$r(\text{C}-\text{Hg})$	1.078	1.078	1.078
$\angle(\text{CCCl})$	112.9	112.8	112.8
$\angle(\text{CCHt})$	109.0	109.1	109.1
$\angle(\text{CCHg})$	111.4	111.5	111.6
$\tau(\text{ClCCHt})$	118.4	118.3	118.2
$\tau(\text{ClCCHg})$	120.9	120.8	120.7
$\tau(\text{ClCCCl})$	70.5	68.9	68.5

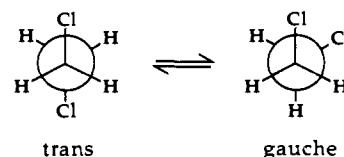
^aHF/6-31G* ($a_0 = 3.65$ Å) values. ^bBond lengths are given in angstroms and bond angles in degrees.

proach, the diameter of the molecule is calculated from the greatest internuclear distance and by adding the van der Waals radii¹⁰ of the two atoms involved.

In order to evaluate which method provides the best estimate of a_0 , we have calculated the gauche/trans energy difference of 1,2-dichloroethane with several values of a_0 and have compared them with the experimental results. The trans rotamer will not be affected by a reaction field since it has no dipole moment. For the gauche form, the greatest dimension is the internuclear distance between the two chlorine atoms (3.7 Å, calculated from the 6-31G*²² gas-phase geometry). Adding the van der Waals radius of these atoms (1.8 Å) leads to an a_0 value of 3.65 Å for the gauche rotamer. For the molar volume approach, a_0 values of 3.15 and 2.25 Å are obtained on the basis of the molecular density and refractivity of 1,2-dichloroethane.

Table I shows the calculated gauche/trans energy difference, by using the 6-31+G* basis set,²² at both the Hartree-Fock and MP2 levels for several values of a_0 . The calculated energy is strongly dependent on the size of the cavity. The energy decreases and the dipole moment increases with decreasing cavity radius. This can be readily understood from the relationship between a_0 and g in eq 4. The experimental data indicate that the energy difference will decrease to near zero in a solvent of high dielectric constant.² Thus, a value of a_0 somewhat smaller than 3.75 Å, for both the Hartree-Fock and MP2 levels of theory, will reproduce the experimental value. This value of cavity radius is close to the a_0 computed from molecular greatest dimension and 0.5 Å larger than the a_0 calculated from the molecular density. However, the a_0 estimated from the molecular refractivity is considerably smaller than the ideal value, and this will lead to overestimation of the solvent effect. Since the molar volume approach provides an experimental unambiguously defined molecular radius, we propose to use eq 9 to determine the a_0 value (with molar volume based on density) and then to add 0.5 Å to the final value. This would be our best estimate of a_0 for relatively compact neutral molecules. The constant term (0.5 Å) is added to account for the van der Waal radii of the surrounding solvent molecules. For ionic species for which molecular density is generally not available, one can use the molecular volume of the corresponding neutral compound or structurally related systems to estimate the cavity radius. A quantum mechanical method of computing molar volume is also being developed.²⁴

Application to Rotational Equilibria. As an initial test of the applicability of reaction field theory to conformational equilibria, we have considered the solvent effects on the equilibrium between the gauche and trans forms of 1,2-dichloroethane. Experimentally, this conformational equilibrium is found to depend strongly on the dielectric property of the medium.²



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Table III. Calculated and Observed Conformer Energy Differences (kcal mol⁻¹) for 1,2-Dichloromethane in Various Solvents

medium	ϵ^a	ΔE (gauche - trans)		
		calculated ^b		observed ^c
		HF	MP2	
vapor	1.0	1.96	1.64	1.20
cyclohexane	2.0	1.32	0.88	0.91
carbon disulfide	2.6	1.13	0.69	0.83
diethyl ether	4.3	0.82	0.54	0.69
ethyl acetate	6.0	0.67	0.41	0.42
pure liquid	10.1	0.49	0.26	0.31
acetone	20.7	0.36	0.14	0.18
acetonitrile	35.9	0.30	0.09	0.15

^a Dielectric constants at room temperature (see ref 10). ^b 6-31+G*/HF/6-31G* ($a_0 = 3.65 \text{ \AA}$) values. ^c See ref 2.

Table IV. Calculated Total and Relative Energies of 1,2-Dichloroethane in Different Media^a

level	$\epsilon = 1.0$			$\epsilon = 35.9^b$	
	trans	gauche	ΔE^c	gauche	ΔE^c
HF	-997.032 86	-997.029 73	1.96	-997.032 38	0.30
MP2	-997.588 33	-997.585 92	1.51	-997.588 19	0.09
MP3 ^d	-997.597 88	-997.595 41	1.55		
MP4 ^d	-997.619 43	-997.617 05	1.49		
QCISD	-997.633 78	-997.636 39	1.64	-997.633 61	0.11

^a Total energies in hartrees and relative energies in kilocalories per mole. ^b The total energy of the trans rotamer is the same as that in vacuo. ^c $E_{\text{gauche}} - E_{\text{trans}}$. ^d Frozen-core approximation.

We shall first consider the effect of a dielectric medium on the structure of 1,2-dichloroethane. As the trans rotamer has no dipole moment, the reaction field has no effect on its structure. For the gauche form, we have optimized the structure with $\epsilon = 1.0$ (corresponding to the gas phase), $\epsilon = 6.0$ (ethyl acetate), and $\epsilon = 35.9$ (acetonitrile). Geometry optimizations were carried out with the 6-31G* basis set, and the optimized parameters are displayed in Table II. The introduction of a dielectric medium seems to have little effect on the calculated geometries. The largest change is found with the C1CC1 torsional angle. This angle decreases by about 2° on going from the gas phase to solution. Note that the optimized geometry with a polar medium ($\epsilon = 35.9$) is essentially the same as that with a nonpolar medium ($\epsilon = 6.0$). Since the calculated geometry of 1,2-dichloroethane is rather insensitive to the dielectric property of the medium, we shall use the gas-phase geometry for SCRF calculations in different media.

Next, we consider the gauche/trans energy difference in solvents of different polarity. The energy calculation is performed with a slightly larger 6-31+G* basis set, and the results are summarized in Table III. The Hartree-Fock calculation gives an energy difference for the gas phase that is somewhat larger than the experimental value. For the "solution" calculations, reaction field theory at the Hartree-Fock level reproduces readily the trend of variation of solvent effects. The average deviation of the theoretical values from the experimental results is 0.23 kcal mol⁻¹. Since electron correction has shown to be important in determining the trans/gauche energy difference of this system,⁵ we also have examined the effect of electron correlation. The results of MP2/6-31+G* calculations are listed in Table III. All the MP2 values are smaller than the corresponding Hartree-Fock values and are in better agreement with the experimental estimates of the gauche/trans energy difference. It is of interest to note that the correlation energy is smaller for a solvent of higher dielectric constant. As seen in Table IV, different correlated methods lead to similar ΔE values in the gas phase. This suggests the MP2 value for "solution" calculations may also provide a good estimate of electron correlation effect. Interestingly, Hirano et al.²⁵ have recently shown that a kinetic energy correlation of -0.30 kcal mol⁻¹ is required for a theoretical estimate of the gauche/trans energy

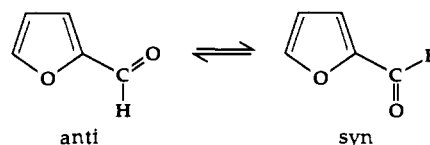
Table V. Calculated and Observed Conformer Energy Differences (kcal mol⁻¹) for Furfural in Various Solvents

medium	ϵ^a	ΔE (syn - anti)	
		calculated ^b	observed ^c
vapor	1.0	0.90	1.0, 1.5, 2.0
carbon tetrachloride	2.2	0.38	0.20
CF ₂ Cl ₂	2.9	0.24	0.34
dimethyl ether	7.9	-0.14	-0.21
dimethyl ether (-120 °C)	12.0	-0.23	-0.58
acetone (-120 °C)	37.4	-0.36	-0.77
dimethyl sulfoxide	45.0	-0.38	-0.84

^a Dielectric constants at room temperature, except where noted (see ref 10). ^b HF/6-31+G*/HF/6-31G* ($a_0 = 3.70 \text{ \AA}$). ^c See ref 2.

difference of 1,2-dichloroethane for proper comparison with the experimental observed value. If one applies this kinetic correction to our correlated ΔE values in the gas phase, the final theoretical estimates will be in very good agreement with experiment.

Furfural provides another case in which a large solvent effect on equilibrium is found. Here, the anti form (with respect to the two oxygens) has a relatively low dipole moment and is favored in the gas phase. However, in polar media, the syn form with a relatively large dipole moment is favored. Extensive experimental studies, including low-temperature NMR, IR, Raman, and microwave spectroscopy, for the conformational equilibrium have been well-documented and reviewed previously.² The relationship between the energy difference and the solvent dielectric constant is shown in Table V. The polarity of the medium is very important in determining the solvent influence on this conformational equilibrium. In particular, the energy difference changes sign with solvent, being approximately zero for a solvent of dielectric constant of about 5 (e.g., chloroform).²



We have performed geometry optimization for both the anti and syn forms in vacuo with the 6-31G* basis set. The calculated dipole moments of the anti and syn forms are 3.50 and 4.35 D, respectively. These values are somewhat higher than the experimental values (3.23 and 3.93 D) but compare reasonably in the relative sizes of the dipoles. SCRF optimizations with $\epsilon = 45.0$ (corresponding to DMSO) show no significant structural change compared to the optimized geometry in vacuo. This again lends us confidence to use the same gas-phase geometry for different "solution" calculations. The cavity radius used for this system is 3.70 Å.

The calculated syn/anti energy differences, at HF/6-31+G* level, in various solvents are collected in Table IV. The solvents stabilize preferentially the conformer with the larger dipole. In condensed dielectric media with $\epsilon > 5$, the SCRF calculations predict that the syn form is favored over the trans form in accordance with the experimental observation. Thus, the dependence of the syn/anti energy difference on solvent polarity is reproduced satisfactorily by the reaction field model. These results again demonstrate the usefulness of reaction field theory in providing qualitative understanding of the solvent effects on conformational equilibria.

Application to Rotational Barrier. Push-pull ethylenes have been the subject of much recent attention.^{3,26} These compounds have a strong electron-donating (e.g., amino) group attached to one end of the double bond and a strong electron-withdrawing (e.g., nitro) group on the other end. They are generally characterized by low rotational barriers, and the magnitudes of these energy barriers are strongly dependent on solvent.³ (2-Nitrovinyl)amine represents the simplest push-pull ethylene, and its

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Table VI. Calculated Geometrical Parameters of (2-Nitrovinyl)amine^{a,b}

parameter	Z isomer ^c			E isomer ^c			rotational TS		
	$\epsilon = 1.0$	$\epsilon = 9.9$	$\epsilon = 36.7$	$\epsilon = 1.0$	$\epsilon = 9.9$	$\epsilon = 36.7$	$\epsilon = 1.0$	$\epsilon = 9.9$	$\epsilon = 36.7$
r(C1-C2)	1.346	1.360	1.363	1.337	1.360	1.361	1.463	1.470	1.472
r(C1-N1)	1.332	1.320	1.317	1.342	1.322	1.318	1.281	1.272	1.271
r(C1-H1)	1.075	1.075	1.075	1.073	1.073	1.073	1.083	1.080	1.080
r(C2-H2)	1.066	1.066	1.066	1.068	1.067	1.067	1.070	1.068	1.068
r(C2-N2)	1.413	1.397	1.394	1.422	1.400	1.396	1.361	1.323	1.319
r(N1-H3)	0.995	0.995	0.995	0.994	0.997	0.998	1.001	1.002	1.002
r(N1-H4)	0.992	0.995	0.996	0.992	0.996	0.997	0.999	1.006	1.007
r(N2-O1)	1.210	1.212	1.212	1.203	1.209	1.211	1.203	1.240	1.246
r(N2-O2)	1.195	1.207	1.210	1.197	1.210	1.212	1.239	1.241	1.242
\angle (N1C1C2)	130.0	130.1	130.1	125.8	125.7	125.7	121.2	123.7	124.1
\angle (H1C1C2)	115.3	115.2	115.2	118.5	118.6	118.6	124.3	121.8	121.2
\angle (H2C2C1)	122.9	122.2	122.0	126.7	125.8	125.5	119.9	119.6	119.0
\angle (N2C2C1)	123.2	123.7	123.8	119.5	120.0	120.0	108.4	118.4	119.9
\angle (H3N1C1)	119.9	120.6	120.7	121.7	122.5	122.6	118.2	120.7	121.1
\angle (H4N1C1)	120.4	120.2	120.3	120.8	121.3	121.3	122.6	122.3	122.2
\angle (O1N2C2)	118.9	119.7	119.9	119.4	120.6	120.1	121.6	120.2	120.1
\angle (O2N2C2)	117.4	117.9	118.0	116.5	117.3	117.4	115.6	119.2	119.8
τ (H1C1C2N1)							182.7	184.6	185.3
τ (H2C1C2N1)							121.1	105.9	104.7
τ (N2C2C1N1)							-101.2	-93.5	-92.1
τ (H3N1C1C2)							4.2	2.2	2.3
τ (H4N1C1C2)							175.9	183.5	184.6
τ (O1N2C2H2)							-28.4	-11.1	-9.0
τ (O1N2C2H2)							152.4	169.1	170.9

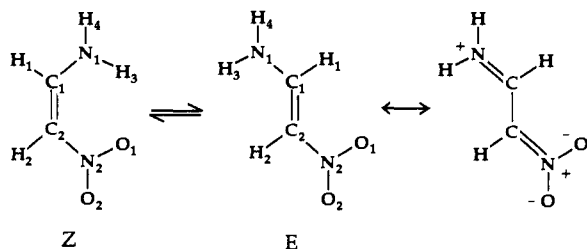
^aHF/6-31G* ($a_0 = 3.50 \text{ \AA}$) values. ^bBond lengths are given in angstroms and bond angles in degrees. ^cPlanar (C_s) structures.

Table VII. Calculated Dipole Moments and Energies of (2-Nitrovinyl)amine^{a,b}

ϵ	level	Z isomer		E isomer		rotational TS		ϵE	
		energy	dipole	energy	dipole	energy	dipole	E - Z	TS - Z
1.0	HF/6-31G*	-336.547 55	6.32	-336.543 19	7.25	-336.473 13	9.59	2.74	46.70
	HF/6-31+G*	-336.560 34	6.48	-336.555 58	7.41	-336.488 54	9.76	2.99	45.06
	MP2/6-31+G*	-337.542 57	5.80	-337.535 62	6.76	-337.469 12	9.52	4.36	46.09
9.9	HF/6-31G*	-336.559 38	8.24	-336.558 01	9.84	-336.503 78	13.83	0.86	34.89
	HF/6-31+G*	-336.573 29	8.65	-336.571 85	10.29	-336.523 25	14.52	0.90	31.40
	MP2/6-31+G*	-337.554 60	8.00	-337.552 79	9.87	-337.503 76	14.65	1.14	31.90
36.7	HF/6-31G*	-336.562 15	8.60	-336.561 35	10.36	-336.509 37	14.52	0.50	33.12
	HF/6-31+G*	-336.576 42	9.06	-336.575 54	10.93	-336.529 86	15.35	0.55	29.22
	MP2/6-31+G*	-337.556 73	8.44	-337.555 62	10.58	-337.509 41	15.52	0.70	29.69

^aTotal energies are given in hartrees, relative energies in kilocalories per mole, and dipole moments in debyes. ^bBased on SCRFF/6-31G* ($a_0 = 3.50 \text{ \AA}$) optimized geometry.

rotational barrier in solution has been studied recently by the AM1 semiempirical method.²⁷ Here, we have reexamined the same problem with ab initio reaction field theory. The important change in (2-nitrovinyl)amine on rotation is that it can incorporate the dipolar resonance structure more readily. Therefore, the charges in the amino and nitro groups become localized in the rotated form, which leads to a larger charge separation. As a result, when it is placed in a medium of high dielectric constant, the rotational barrier should decrease. We wished to see if the effect is reproduced by reaction field theory.



The Z and E isomers and the rotational transition structure around the C=C double bond have been optimized with $\epsilon = 1.0$ (in vacuo), $\epsilon = 9.9$ (o-dichlorobenzene), and $\epsilon = 36.7$ (N,N-dimethylformamide), with the 6-31G* basis set. As evident in Table VI, the solvent reaction field has a strong influence on the mo-

lecular geometry of the transition structure as well as the equilibrium structures. The calculated C=C and C-N bond lengths of the Z and E isomers are found to alter by 0.016–0.026 Å from the gas phase to solution. These changes correspond to the increase in the weight of the more polar resonance form in polar solvents. For the transition structure, the change in geometry is even more pronounced: The N₂-O₁ bond is lengthened by 0.04 Å, which again shows the importance of the dipolar resonance structure, and the ONCH torsional angles increase by almost 20°. Hence, the changes in geometry from the gas phase to solution should be taken into account in higher level energy calculations. Interestingly, the rotational transition structure has a slightly distorted perpendicular orientation ($\tau(\text{NCCN}) = 101.2^\circ$) in the gas phase, whereas it is closer to a 90° form in solution.

Energy calculations with different dielectric media were performed with a larger 6-31+G* basis set at both the Hartree-Fock and MP2 theory levels and are summarized in Table VII. In agreement with experiment, the Z configuration is favored in both the gas phase and in solution.²⁸ Our best estimate of the E/Z energy difference in the gas phase is 4.4 kcal mol⁻¹. This energy difference decreases with increasing solvent polarity. This is consistent with the experimental observation that a larger ratio of the E isomer was observed in polar solvents.²⁸ As shown in Table VII, the calculated dipole moment of the rotational transitional structure is considerably larger (by 2–3 D) than the Z and E isomers. Consequently, the 90° rotated form is more

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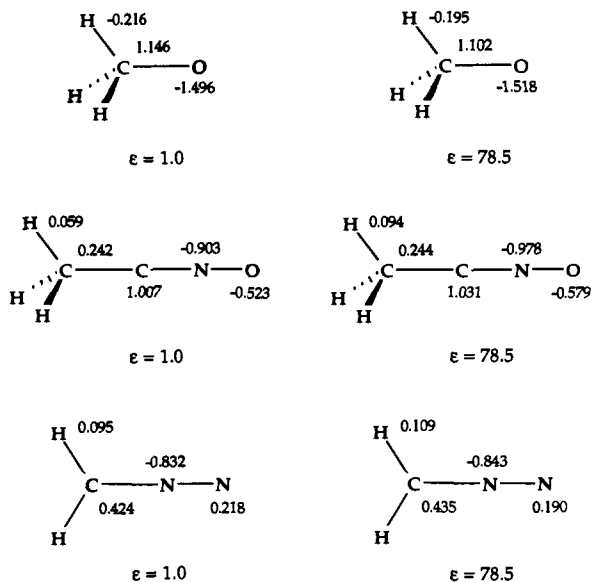


Figure 2. Changes in electron population on going from the gas phase ($\epsilon = 1.0$) to a polar medium ($\epsilon = 78.5$).

stabilized than the equilibrium structures in polar media. The calculated rotational barrier in the gas phase is 46.1 kcal mol⁻¹, substantially smaller than "normal" alkenes (e.g., 65 kcal mol⁻¹ for ethylene).²⁹ The corresponding AM1 value is 37.2 kcal mol⁻¹.²⁷ This energy barrier is found to decrease considerably in polar media, by 13–15 kcal mol⁻¹. Note that the inclusion of diffuse functions (6-31G* \rightarrow 6-31+G*) leads to a significant decrease in the barrier height, by 3–4 kcal mol⁻¹ (Table VII). On the other hand, inclusion of electron correlation (HF \rightarrow MP2) has little effect on the calculated barriers. Our best calculated rotational barriers with $\epsilon = 9.9$ and 36.7 are 31.9 and 29.7 kcal mol⁻¹, respectively, somewhat higher than the earlier AM1 results (23.0 and 21.4 kcal mol⁻¹)²⁷ and the experimental estimates (21.1 and 19.2 kcal mol⁻¹).³⁰ However, the change in rotational barrier from $\epsilon = 9.9$ to 36.7 is readily reproduced by ab initio reaction field theory.

Application to Charge Distribution in Ions. We have examined the structures of alkoxide ions calculated for the gas phase.³¹ With methoxide ion, we found a large degree of charge transfer from carbon to hydrogen, which serves to increase the volume over which the charge is distributed, resulting in a lower electrostatic energy. A remarkably short C–O bond length is one consequence of this charge distribution. When the ion is transferred to a solvent of high dielectric constant, we would expect the electrostatic stabilization to become less important. The charge on the hydrogens should decrease, and the C–O bond length should increase. The results of present calculations in the gas phase ($\epsilon = 1.0$) and in a polar medium ($\epsilon = 78.5$) are shown in Table VIII and Figure 2. The a_0 value, 2.80 Å, for this system was estimated from the molar volume of methanol, which is a conservative estimate because the ion is missing the hydroxyl hydrogen and has a shorter C–O bond length. The electron populations were derived by numerical integration of the charge densities, by using the boundary conditions derived by Bader's theory of atoms in molecules.³² The inclusion of reaction field, indeed, results in a lengthening of the C–O bond length (by 0.011 Å) and shortening of the C–H lengths (0.006 Å). Accordingly, there is a significant transfer of negative charge from the hydrogens to the oxygen atom. This anion is calculated to have a large stabilization energy of 3.0 kcal mol⁻¹ in aqueous solution. For comparison, the stabilization energy of methanol under the same environment is 1.5 kcal mol⁻¹. When the Born charge term (see eq 7) is included,

Table VIII. Structures,^{a,b} Dipole Moments (μ), and Energies of Methoxide Anion, Diazomethane, and Acetonitrile Oxide in Different Media^{c,d}

compound	parameter	$\epsilon = 1.0$	$\epsilon = 78.5$
CH_3O^- (C_{3v})	$r(\text{C}-\text{O})$	1.311	1.322
	$r(\text{C}-\text{H})$	1.133	1.127
	$\angle(\text{HCO})$	116.5	116.1
	μ^e	2.61	3.35
	energy ^f	-114.77621	-114.78104 ^f
CH_2N_2 (C_{2v})	$r(\text{N}-\text{N})$	1.116	1.120
	$r(\text{C}-\text{N})$	1.280	1.276
	$r(\text{C}-\text{H})$	1.068	1.069
	$\angle(\text{HCN})$	117.9	118.0
	μ^g	1.48	2.07
	energy ^h	-148.31723	-148.31881
	energy ⁱ	-148.31723	-148.31881
CH_3CNO (C_{3v})	$r(\text{C}-\text{C})$	1.471	1.476
	$r(\text{C}-\text{N})$	1.130	1.129
	$r(\text{N}-\text{O})$	1.214	1.230
	$r(\text{C}-\text{H})$	1.082	1.082
	$\angle(\text{HCC})$	109.9	109.8
	μ^j	4.60	5.97
	energy ^k	-207.31415	-207.32151

^a Bond lengths are given in angstroms and bond angles in degrees. ^b HF/6-31G* values. ^c Total energies in hartrees and dipole moments in debyes. ^d a_0 values for methoxide anion, methyl azide, and acetonitrile oxide are 2.80, 3.50, and 3.00 Å, respectively. ^e MP2/6-31+G**//HF/6-31G* values. ^f The total energy including the Born charge term is -114.87423 hartrees. ^g MP2/6-31+G**//HF/6-31G* values.

the net solvation energy of methoxide ion is 61.6 kcal mol⁻¹. In summary, polarizable media have strong influence on the structure, energy, and charge distribution of methoxide anion.

Application to Dipolar Structures in Neutral Molecules. 1,3-Dipolar addition is an important process in synthetic organic chemistry. There has been considerable controversy over whether the addition reactions to alkenes should be considered as an ionic process or as a free radical process.³³ Experimental studies to date favor the free radical mechanism of 1,3-dipolar addition.³³ In this connection, it seemed of interest to examine some typical reagents and to determine their charge distributions in both the gas phase and in solution. Since diazoalkanes and nitrile oxides are among the most common 1,3-dipoles used in 1,3-dipolar cycloaddition,³⁴ we have chosen the simple diazomethane and acetonitrile oxide to study the influence of reaction field on the electronic nature of these species. We have examined their structures, energies, and charge distributions in vacuo ($\epsilon = 1.0$) and in a polar medium ($\epsilon = 78.5$). The calculated results are given in Table VIII and Figure 2. Diazomethane is found to be only slightly influenced by a dielectric medium. The calculated geometrical parameters are virtually the same in the two media. The change of electron population on going from the gas phase to aqueous solution is very small (Figure 2). The calculated solvation energy is only 1.0 kcal mol⁻¹. In contrast to diazomethane, the solvent reaction field has a strong influence on the electronic structure of acetonitrile oxide. The most significant structural change is the lengthening of the N–O bond length, by 0.016 Å, in a medium of high dielectric constant. With the inclusion of solvent polarization effect, acetonitrile oxide develops greater local charge (i.e., increased charge separation). On going from the gas phase to a polar medium, there is a shift of charge density from the methyl group to the NO moiety. This dipolar molecule is calculated to have a larger solvation energy of 4.6 kcal mol⁻¹. The difference in reaction field effect for these two compounds can be attributed to the large difference in their dipole moments. The calculated dipole moment for acetonitrile oxide (4.60 D) is considerably larger than that for diazomethane (1.48 D). Contrary to common expectation, both diazomethane and acetonitrile oxide resemble a 1,2-dipole rather than a 1,3-dipole in the gas phase

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as well as in solution. Despite the large difference in solvent effect, both the diazoalkane and nitrile oxide are effective reagents for 1,3-dipolar addition.³⁴ Hence, it would be reasonable to conclude that the charge effect of these species is not important in 1,3-dipolar cycloaddition.

Conclusions

In this paper, we have reported a correlated version of Onsager's formalism of a reaction field method for studying solvent effects. We have applied this model to study solvent effects on conformational equilibria, rotational barriers, and charge distributions and molecular properties of ionic and neutral dipolar species. This method is able to provide reasonable estimates of the solvent effects in conformational equilibria and rotational barriers. Furthermore, it provides a good qualitative understanding of the effect of electrostatic interaction of the ionic or neutral dipolar species with its surrounding medium. Thus, Onsager's reaction field theory

appears to be a promising approach to examine the nonspecific electrostatic solvent-solute interaction. We are currently applying this model to study solvent effects on reaction rates and excited states.²⁴ The use of more realistic cavity shapes also is being studied.

Calculations

The calculations were carried out with the GAUSSIAN-91 system of programs²⁰ and were run on a Multiflow Trace 14/200 computer. Standard basis sets were used.²² The analysis of the wave functions was carried out with the PROAIM programs²⁵ running on a DEC-3100 workstation.

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Assignment of the \tilde{A} State in Bicyclobutane. The Multiphoton Ionization Spectrum and Calculations of Transition Energies

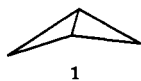
Valerie A. Walters,^{†,‡} Christopher M. Hadad,[‡] Yvonne Thiel,[‡] Steven D. Colson,[‡] Kenneth B. Wiberg,^{*,‡} Philip M. Johnson,[§] and James B. Foresman[‡]

Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut 06511, State University of New York, Stony Brook, New York 11794, and Carnegie Mellon University, Pittsburgh, Pennsylvania 15213. Received October 29, 1990

Abstract: The two-photon spectrum of bicyclo[1.1.0]butane has been obtained via resonance enhanced multiphoton ionization. A comparison with the one-photon spectrum shows that the first band at 44000–48000 cm^{-1} is an allowed A_1 transition corresponding to an s Rydberg state. Vibrational cooling in a jet expansion causes some of the lower energy components of the spectrum to disappear, indicating that they are hot bands. The 0–0 band origin of the transition was found to be 45 944 cm^{-1} . The vibrational components for the parent and for the 1,3- d_2 and 2,2,4,4- d_4 isotopomers have been assigned. The transition energies have been calculated at the CIS/6-311(2+)G* level of theory, and an A_1 state is predicted to have the lower energy. The structure of the excited state was calculated and found to be essentially the same as that of the bicyclobutane radical cation. The vibrational frequencies also were calculated and agreed well with the observed frequencies. The nature of the lower energy transitions is discussed with the aid of charge density difference maps for going from the ground state to each of the first 20 excited states. All of these may be regarded as Rydberg states.

Introduction

Bicyclobutane (1) is an ideal model system for the study of the electronic structure of saturated small-ring molecules because it is of a size that is both experimentally interesting and theoretically tractable. This strained hydrocarbon consists of two cyclopropane rings joined by a common C–C bond. The microwave spectrum¹ showed the molecule to have C_{2v} symmetry in the ground electronic state with an angle between the two rings of 122.7°. Further information on the ground state was obtained from a recent reassignment of the ground-state vibrations coupled with a normal coordinate analysis.²



Information on the structure of bicyclobutane in excited electronic states was provided by the ultraviolet absorption spectrum that was obtained and analyzed in one of our laboratories.^{3,4} The UV spectra of bicyclobutane- d_0 , - d_2 , and - d_4 are

reproduced in Figures 1–3. The spectrum for each molecule exhibits three regions of well-resolved vibrational structure, two of which exhibit almost identical vibrational features and appear to be related in some way. The region of most pronounced structure for each molecule is found in the lowest energy band (\tilde{A}) which is observed between 44000 and 48000 cm^{-1} and shown in expanded form at the top of each figure. A second structured region, which exhibits similar vibrational spacing to the first region, appears between 58000 and 62000 cm^{-1} . For both of these regions, the vibrational spacing shows the expected variation with deuteration. An additional region of structure appears between 48000 and 51000 cm^{-1} . In bicyclobutane, the vibrational spacing in this third region is approximately twice that in the other two regions.

Bicyclobutane has C_{2v} symmetry, and therefore a one-photon transition to an A_1 , B_1 , or B_2 electronic state is electric dipole allowed, whereas a transition to an A_2 state is forbidden. On the

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[†] Present address: Lafayette College, Easton, PA 18042.

[‡] Yale University.

[§] State University of New York.

[‡] Carnegie Mellon University.