

Solvent Interaction within the Hartree-Fock SCF Molecular Orbital Formalism

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A theoretical model is presented by which the effects of a solvent on a molecular system are incorporated into the Hartree-Fock SCF molecular orbital formalism prior to the solution of the quantum mechanical problem. The proposed model assumes that the polar nature of the solvent can be characterized by a single parameter. The effects of aprotic solvents on certain molecular parameters of N,N-dimethylformamide and N-nitrosodimethylamine have been studied, using a semi-empirical Mulliken type MO method incorporating the proposed solvent interaction model. These molecular parameters include the hindered rotation barrier, net charges at the atomic center, and the initial $n \rightarrow \pi^*$ transition.

Key words: Solvent-effect – N,N-dimethylformamide – N-nitrosodimethylamine

1. Introduction

Hartree-Fock SCF molecular orbital calculations [1], *ab initio* and/or semi-empirical, are rapidly becoming a common adjunct to the study of molecular properties. As a rule, these theoretical studies view the molecule as it probably exists in the gas phase. With small molecules, this is of little concern since many molecular properties are experimentally determined in the gas phase and the analogy with the theoretical picture is quite good. However, as theoretical methods and computer technology advance, theoretical studies will involve larger molecules, the experimental studies of which are more likely to have been done in solution.

Klopman [2] has suggested an interesting physical model for incorporating solvent effects in theoretical studies. His solvaton theory was used to calculate correction terms to the molecular energy, using MO coefficients which had been determined by a conventional semi-empirical MO method. Although MO's are used to determine solvent effects, the MO solutions do not reflect the presence of the solvent.

It would seem that the more realistic way to account for solvent effects is to incorporate these interactions into the molecular system prior to solving the quantum mechanical problem. The Hamiltonian of the system then contains the solvent interaction terms and this modified Hamiltonian can be used in the Hartree-Fock SCF MO method to determine a wave function which reflects the solute-solvent interaction. In principle, this has been done by others. For example,

Clementi [3] used a series of fixed magnitude point charges to model a solvent in studying perturbations of calculated polymer energy bands.

The actual theoretical model suggested in this work is primitive and may ultimately be limited to few real situations, but it does illustrate this approach to the solute-solvent interaction problem. A very probable limitation may be an inability to account for the unusual effects of hydrogen bonding solvents, a problem which has been under consideration since Wyman's [4] and Onsager's [5] early work. To demonstrate what this approach may yield, and perhaps point the direction to further development, spectral shifts, rotation barriers and other molecular properties for N, N-dimethylformamide (DMF) and N-nitrosodimethylamine (NDA) have been calculated, using the proposed theoretical model.

2. Theoretical Model for Solute-Solvent Interaction

Upon addition of a solute at infinite dilution to an aprotic solvent of dielectric constant, ϵ , it is assumed that a number of charges (solvatons) are induced in the solvent. One solvaton is associated with each atomic center of the solute molecule. Further, the strength of the interaction between the solute molecule and the solvatons depends on the polar nature of the solvent. This dependence is assumed to be a function of a single parameter, the dielectric constant, of the solvent. The Hamiltonian, \bar{H} , of the molecular system with M electrons and N nuclei in the solvent is then taken as (in atomic units):

$$\begin{aligned} \bar{H} = & \sum_{i=1}^M \left[\left(-\frac{1}{2} \nabla^2 - \sum_{n=1}^N \frac{Z_n}{r_n} \right) + \frac{1}{2} \sum_{j=1}^M \frac{1}{r_{ij}} + \frac{(\epsilon-1)}{2\epsilon} \sum_{s=1}^N \frac{Q_s}{r_{si}} \right] \\ & + \frac{1}{2} \sum_{i=1}^N \sum_{n=1}^N \frac{Z_i Z_n}{r_{in}} - \frac{(\epsilon-1)}{2\epsilon} \sum_{s=1}^N \sum_{n=1}^N \frac{Q_s Z_n}{r_{sn}} \end{aligned} \quad (1)$$

where Q_s is the induced solvent (solvaton) charge, r_{si} is the electron-solvaton distance, r_{sn} is the nucleus-solvaton distance, and $(\epsilon-1)/2\epsilon$ is the function of the solvent dielectric constant which determines the degree of solvent-solute interaction. The term

$$\frac{(\epsilon-1)}{2\epsilon} \sum_{i=1}^M \sum_{s=1}^N \frac{Q_s}{r_{si}} \quad (2)$$

is the interaction energy of the electrons and the induced solvent charges while

$$- \frac{(\epsilon-1)}{2\epsilon} \sum_{s=1}^N \sum_{n=1}^N \frac{Q_s Z_n}{r_{sn}} \quad (3)$$

represents the interaction energy between the induced solvent charges and the nuclear core charges. The other terms of Eq. (1) constitute the normal molecular Hamiltonian.

The assumed solute-solvent interaction term is simply the Born equation [6] and its use has been suggested by others such as Klopman [2]. Although arguments may be given for its use, its application to this situation is without rigorous justification. Empirically, the expression $(\epsilon - 1)/2\epsilon$ has the correct behavior for the present situation, that is, it approaches 0 as $\epsilon \rightarrow 1.0$ and approaches a finite limit (0.5) as $\epsilon \rightarrow \infty$. The Born equation is an energy term as it should be for inclusion in the Hamiltonian operator.

The ground state of the closed shell molecular system is assumed to be adequately described by an asymmetrical product of molecular orbitals which are expanded as linear combinations of atomic orbitals (LCAO). The molecular orbital solutions are obtained by the Hartree-Fock variational method described by Roothaan [1] using the Hamiltonian given in Eq. (1).

In order to evaluate the elements, $D_{\mu\nu}$, of the new solvent interaction matrix, additional assumptions must be made regarding solvation charge, Q_s , and electron-solvation distance, r_{si} . First, Q_s is assumed to be equal to the negative of the Mulliken [7] "gross charge", or net charge, for the atomic center with which solvation s is associated. Second, the electron-solvation distance r_{si} is evaluated in two ways. For AO's associated with the same atomic center as solvation s , r_{si} is the Van der Waal's radius of the particular atom type. If the AO's and solvation are associated with different atomic centers, the solvation is assumed to be centered on the atomic center associated with s and r_{si} is evaluated accordingly.

The above physical model of solute-solvent interaction is essentially that suggested by Klopman [2]. In this case, however, it has been incorporated into the Hamiltonian of the Hartree-Fock SCF method. Now, in addition to the electron interaction part G of the Fock operator matrix, F , there is a second part, D , which must be evaluated using previously obtained solutions for the MO's. Consequently, D is treated in a manner analogous to G and the quantum mechanical problem solved by iteration as usual. In this respect, the present solvent interaction matrix is handled differently from that of the fixed magnitude point charge solvent model used by Clementi [3].

In the proposed solvent interaction model, the solvation charge is assumed to be proportional, but opposite in sign, to the net charge of the corresponding atomic center. Consequently, in the vicinity of an atomic center with a net positive charge, the molecular electrons would be subject to a repulsive force due to the presence of the negative solvation, thus causing a further reduction in the electronic charge at that center. Conversely, at a negative atomic center there will be a further increase in the electronic charge at that center due to the presence of the positive solvation. This concentration of negative charge at the negative centers will tend to increase the molecular energy by virtue of the electron-electron repulsion terms of the usual molecular Hamiltonian. Consequently, the signs of the new solvent-interaction terms of the Hamiltonian Eq. (1) have been chosen so that the molecular energy tends to be lowered by the solvent-induced separation of molecular charge. In the case of the specific molecules studied in this work, the balancing of energy raising and energy lowering terms results in a net lowering of the molecular energy, or increased stabilization of the molecular system, in the presence of increasing solvent interaction.

3. Method of Calculation

Theoretical calculations incorporating the proposed solvent-solute interaction model were done, using a semi-empirical, valence electrons only, Mulliken Type SCF MO method with exact kinetic energy described previously [8, 9]. Values of the orbital and atom dependent empirical calibration parameters of this method, $\alpha(\psi)_A$, have been given before for carbon and hydrogen [8]. For nitrogen and oxygen, values of +0.41233, -0.57786, +0.48378, and -0.64340 were used for $\alpha(2s)_N$, $\alpha(2p)_N$, $\alpha(2s)_O$, and $\alpha(2p)_O$, respectively.

Elements of the solvent interaction matrix, $D_{\mu\nu}$, were approximated in a manner consistent with the approximations of this method. That is, the integrals

$$D_{ss} \equiv D_A \quad (4)$$

are calculated for each atomic center A , using the valence S orbitals of that atom. Then $D_{\mu\nu}$ is approximated as

$$D_{\mu\nu} = (1/2) S_{\mu\nu}(D_A + D_B). \quad (5)$$

Elements of the combined one-electron Hamiltonian and solvent interaction matrices are thus given by

$$\begin{aligned} H_{\mu\nu} + D_{\mu\nu} &= T_{\mu\nu} + V_A + D_A + \alpha(\psi)_A \\ H_{\mu\nu} + D_{\mu\nu} &= T_{\mu\nu} + (1/2) S_{\mu\nu}[(V_A + V_B) + (D_A + D_B)] \end{aligned} \quad (6)$$

where $T_{\mu\nu}$ is the kinetic energy integral and V_A is the nuclear attraction integral, μ and ν being valence orbitals on atoms A and B , respectively. No convergence difficulties were experienced; however, the program does contain the correction extrapolation process described by Nesbet [10]. Electronic transitions were calculated using a limited configuration interaction procedure consisting of all singly excited configurations from the three highest filled MO's to the three lowest virtual orbitals. The CI matrix elements were evaluated by means of the formula given by Pople [11], using the Mulliken integral approximations [9] consistent with the basic method [8].

Values used for the effective Van der Waal's radii were 2.268, 3.006, 2.836, and 2.647 a.u. for hydrogen, carbon, nitrogen and oxygen, respectively [12]. The value for carbon was estimated from a consideration of carbon bond lengths and the progression of radii values for oxygen and nitrogen.

4. Results and Discussion

Table 1 presents the coordinates for the planar geometries of N,N-dimethylformamide (DMF) and N-nitrosodimethylamine (NDA) used in this study. Non-planar geometries consist of 90° rotations about the C₁-N and N₁-N₂ bonds of DMF and NDA, respectively. Geometries were estimated from experimental geometries of molecules such as formamide [13] and bond lengths and angles in similar molecular environments [14]. Geometries were not optimized with the semi-empirical MO method used.

Table 1. Molecular geometries and the net charges on atoms as a function of solvent interaction coefficient

| Atom | Geometry (planar) ^a | | | Charges ^b as function of solvent interaction coefficient ^c | | | | |
|------------------------|--------------------------------|---------|---------|--|--------|--------|--------|--------|
| | X | Y | Z | 0.00 | 0.10 | 0.25 | 0.40 | 0.4875 |
| N,N-Dimethylformamide | | | | | | | | |
| H ₁ | 2.0070 | 0.0 | 3.0340 | +0.069 | +0.052 | +0.022 | -0.008 | -0.009 |
| H ₂ | 2.0214 | 0.0 | -3.3372 | +0.149 | +0.166 | +0.210 | +0.315 | +0.472 |
| H ₃ | 3.1478 | 1.6988 | -0.7809 | +0.158 | +0.176 | +0.221 | +0.328 | +0.485 |
| H ₄ | 3.1478 | -1.6988 | -0.7809 | +0.158 | +0.176 | +0.221 | +0.328 | +0.485 |
| H ₅ | -2.0214 | 0.0 | -3.3372 | +0.139 | +0.155 | +0.199 | +0.304 | +0.460 |
| H ₆ | -3.1478 | 1.6988 | -0.7809 | +0.170 | +0.188 | +0.234 | +0.341 | +0.497 |
| H ₇ | -3.1478 | -1.6988 | -0.7809 | +0.170 | +0.188 | +0.234 | +0.341 | +0.497 |
| C ₁ | 0.0 | 0.0 | 2.538 | +0.231 | +0.258 | +0.297 | +0.306 | +0.224 |
| C ₂ | 2.3968 | 0.0 | -1.4118 | -0.323 | -0.382 | -0.531 | -0.894 | -1.443 |
| C ₃ | -2.3968 | 0.0 | -1.4118 | -0.317 | -0.375 | -0.525 | -0.887 | -1.429 |
| N | 0.0 | 0.0 | 0.0 | -0.323 | -0.308 | -0.264 | -0.129 | +0.114 |
| O | -1.9560 | 0.0 | 3.8380 | -0.282 | -0.293 | -0.316 | -0.344 | -0.355 |
| N-Nitrosodimethylamine | | | | | | | | |
| H ₁ | 2.0214 | 0.0 | -3.3372 | +0.159 | +0.180 | +0.235 | +0.368 | +0.545 |
| H ₂ | 3.1478 | 1.6988 | -0.7809 | +0.179 | +0.201 | +0.257 | +0.391 | +0.566 |
| H ₃ | 3.1478 | -1.6988 | -0.7809 | +0.179 | +0.201 | +0.257 | +0.391 | +0.566 |
| H ₄ | -2.0214 | 0.0 | -3.3372 | +0.152 | +0.172 | +0.228 | +0.361 | +0.536 |
| H ₅ | -3.1478 | 1.6988 | -0.7809 | +0.182 | +0.204 | +0.261 | +0.396 | +0.569 |
| H ₆ | -3.1478 | -1.6988 | -0.7809 | +0.182 | +0.204 | +0.261 | +0.396 | +0.569 |
| C ₁ | 2.3968 | 0.0 | -1.4118 | -0.360 | -0.438 | -0.638 | -1.110 | -1.731 |
| C ₂ | -2.3968 | 0.0 | -1.4118 | -0.369 | -0.447 | -0.646 | -1.115 | -1.728 |
| N ₁ | 0.0 | 0.0 | 2.4600 | -0.026 | -0.026 | -0.039 | -0.095 | -0.190 |
| N ₂ | 0.0 | 0.0 | 0.0 | -0.139 | -0.108 | -0.026 | +0.178 | +0.465 |
| O | -1.9312 | 0.0 | 3.5750 | -0.139 | -0.143 | -0.150 | -0.161 | -0.169 |

^a Coordinates in atomic units.

^b Calculated from Mulliken population analysis. Ref. [7].

^c Coefficient is value of the term $(\epsilon - 1)/2\epsilon$ in Eq. (1).

The Mulliken defined [7] gross atomic charges as a function of solvent interaction are also presented in Table 1. In general, the magnitudes of the changes observed at the various atomic centers appear comparable when viewed as a per cent change of the initial (0.0 interaction) net charge and seem to agree with what might be expected in a reaction-field type of solvent interaction model. That is, as solvent polarity and solvent interaction increase, there is an increasing separation of charge, or polarization, in the solute molecules.

As might be predicted, the changes noted in the charge distributions of both molecules are basically similar. In the methyl groups of both DMF and NDA, increased solvent interaction leads to an increased shift of electrons from the initially (0.0 interaction) electron-deficient hydrogens to the initially negative carbon center, thus causing a considerable negative charge to form on the methyl carbons. In both molecules, the initially negative amine nitrogen loses electronic charge with increasing solvent interaction until it is electron-deficient and has a net positive charge. This negative charge is apparently shifted into the

Table 2. Molecular properties as a function of solvent interaction

| Molecular properties | Solvent interaction coefficient ^a | | | | |
|--|--|-----------|-----------|-----------|-----------|
| | 0.00 | 0.10 | 0.25 | 0.40 | 0.4875 |
| N,N-Dimethylformamide | | | | | |
| Total energy ^b (planar) ^c | -53.22161 | -53.25419 | -53.30961 | -53.40143 | -53.52888 |
| C ₁ -N bond rotation barrier ^d | 0.01256 | 0.01160 | 0.01255 | 0.02113 | 0.03596 |
| Energies of upper orbitals (planar) | | | | | |
| π^* | + 0.17443 | + 0.17935 | + 0.18954 | + 0.21029 | + 0.23927 |
| π | - 0.42572 | - 0.42036 | - 0.40765 | - 0.37803 | - 0.33536 |
| n | - 0.42900 | - 0.42453 | - 0.41401 | - 0.38866 | - 0.35040 |
| σ | - 0.47182 | - 0.46753 | - 0.45780 | - 0.43622 | - 0.40693 |
| Energies of upper orbitals (nonplanar) | | | | | |
| π^* | + 0.14017 | + 0.14402 | + 0.15167 | + 0.16663 | + 0.18751 |
| n | - 0.40209 | - 0.39756 | - 0.38697 | - 0.36190 | - 0.32337 |
| σ | - 0.42749 | - 0.42226 | - 0.41050 | - 0.38454 | - 0.34711 |
| π | - 0.47490 | - 0.47068 | - 0.46116 | - 0.44018 | - 0.41095 |
| Singlet transition energies (eV) | | | | | |
| $n \rightarrow \pi^*$ (planar) | 5.892 | 5.932 | 5.981 | 5.916 | 5.604 |
| $n \rightarrow \pi^*$ (nonplanar) | 5.472 | 5.490 | 5.492 | 5.355 | 4.979 |
| $\pi \rightarrow \pi^*$ (planar) | 10.616 | 10.592 | 10.505 | 10.260 | 9.906 |
| $\pi \rightarrow \pi^*$ (nonplanar) | 10.744 | 10.755 | 10.961 | 10.525 | 10.331 |
| Bond populations (planar) ^e | | | | | |
| O-C ₁ | 1.197 | 1.197 | 1.197 | 1.193 | 1.185 |
| C ₁ -H ₁ | 0.670 | 0.668 | 0.664 | 0.655 | 0.648 |
| C ₁ -N | 0.900 | 0.903 | 0.914 | 0.940 | 0.976 |
| N-C ₂ | 0.745 | 0.744 | 0.742 | 0.736 | 0.724 |
| N-C ₃ | 0.745 | 0.745 | 0.743 | 0.739 | 0.732 |
| N-Nitrosodimethylamine | | | | | |
| Total energy ^b (planar) ^c | -57.78535 | -57.83092 | -57.91461 | -58.05480 | -58.21800 |
| N ₁ -N ₂ bond rotation energy ^d | 0.02881 | 0.02649 | 0.02524 | 0.03092 | 0.04033 |
| Energies of upper orbitals (planar) | | | | | |
| π^* | + 0.16131 | + 0.16876 | + 0.18388 | + 0.21227 | + 0.24477 |
| n | - 0.43819 | - 0.43112 | - 0.41591 | - 0.38596 | - 0.35184 |
| π | - 0.43946 | - 0.43183 | - 0.41333 | - 0.37277 | - 0.32459 |
| σ | - 0.48533 | - 0.47853 | - 0.46291 | - 0.43108 | - 0.39731 |
| Energies of upper orbitals (nonplanar) | | | | | |
| π^* | + 0.12381 | + 0.13004 | + 0.14217 | + 0.16368 | + 0.18740 |
| σ | - 0.40035 | - 0.39272 | - 0.37537 | - 0.33853 | - 0.29229 |
| n | - 0.45459 | - 0.44730 | - 0.43143 | - 0.40012 | - 0.36473 |
| π | - 0.48536 | - 0.47945 | - 0.46548 | - 0.43586 | - 0.40161 |
| Singlet transition energies (eV) | | | | | |
| $n \rightarrow \pi^*$ (planar) | 3.535 | 3.527 | 3.522 | 3.507 | 3.413 |
| $n \rightarrow \pi^*$ (nonplanar) | 3.212 | 3.191 | 3.164 | 3.129 | 3.042 |
| $\pi \rightarrow \pi^*$ (planar) | 10.714 | 10.709 | 10.635 | 10.397 | 10.139 |
| $\pi \rightarrow \pi^*$ (nonplanar) | 10.659 | 10.667 | 10.625 | 10.444 | 10.225 |
| Bond populations (planar) ^e | | | | | |
| O-N ₁ | 1.016 | 1.015 | 1.013 | 1.005 | 0.992 |
| N ₁ -N ₂ | 0.860 | 0.863 | 0.871 | 0.889 | 0.908 |
| N ₂ -C ₁ | 0.735 | 0.736 | 0.735 | 0.727 | 0.711 |
| N ₂ -C ₂ | 0.751 | 0.751 | 0.750 | 0.744 | 0.730 |

^a Coefficient is value of the term $(\epsilon - 1)/2\epsilon$ in Eq. (1).

^b All energies in atomic units (a.u.) except transition energies which are in electron volts (eV).

^c Planar refers to molecular conformations given in Table 2. Nonplanar refers to molecular conformation with 90° rotation about C₁-N bond in DMF and N₁-N₂ bond in NDA.

^d Planar conformation is lowest energy for positive values of rotation barrier.

^e From Mulliken definitions, Ref. [7].

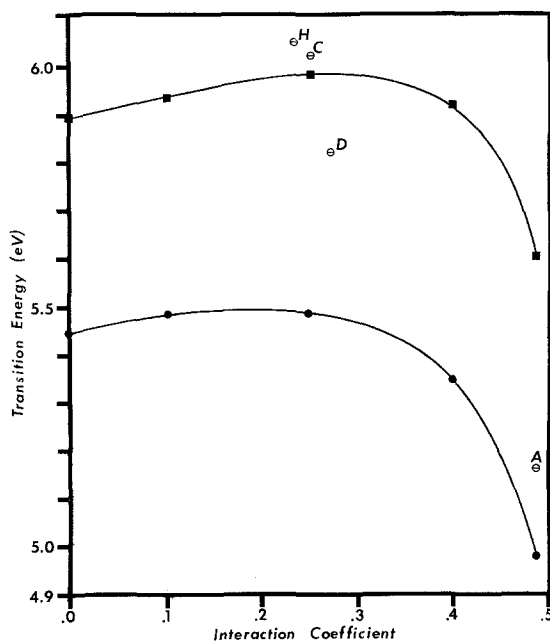


Fig. 1. Calculated $n \rightarrow \pi^*$ transition of planar (■) and nonplanar (●) N-N-dimethylformamide as a function of solvent interaction. Experimental values (⊖) for this transition in *n*-hexane (H), cyclo-hexane (C), dioxane (D), and acetonitrile (A) taken from Ref. [20]. The interaction coefficient is the value of $(\epsilon - 1)/2\epsilon$ in Eq. (1)

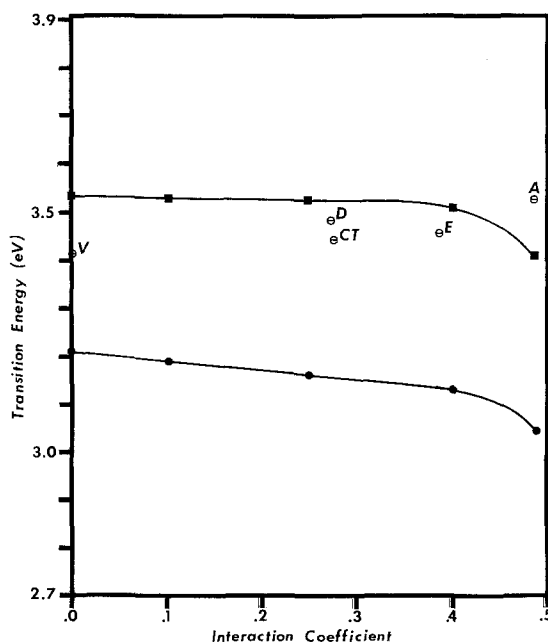


Fig. 2. Calculated $n \rightarrow \pi^*$ transition of planar (■) and nonplanar (●) N-nitrosodimethylamine as a function of solvent interaction. Experimental values (⊖) for this transition in dioxane (D), carbon tetrachloride (CT), diethylether (E), and acetonitrile (A) taken from Ref. [21]. Transition in vapor state (V) also shown. The interaction coefficient is the value of $(\epsilon - 1)/2\epsilon$ in Eq. (1)

CHO group of DMF and NO group of NDA. In NDA, both the nitrogen and oxygen of the NO group gain negative charge with increasing solvent interaction. In DMF, the aldehyde proton changes from an initially positive net charge to slightly negative with increasing solvent interaction; the oxygen also gains negative charge, while the aldehyde carbon initially loses negative charge and then regains it at the higher levels of solvent interaction. Thus, it appears as if the aldehyde proton initially absorbs negative charge with increasing solvent interaction, then "saturates", causing the shifting electronic charge to begin building up on the aldehyde carbon.

Table 2 presents a number of calculated molecular parameters of DMF and NDA as a function of the interaction coefficient. Of these parameters, probably the bond rotation barriers and spectral shifts are most interesting because of possible comparisons with experimental data.

The predicted solvent effects on the rotational barriers of DMF and NDA appear quite similar. Both molecules show a minimum barrier in the region of small solvent interaction, 0.10–0.25 interaction coefficient, which increases monotonically with increasing solvent interaction. Consequently, it would appear that in highly polar solvents, the barrier is greatest and rotation out of the planar configuration is diminished. This will be discussed more later.

Recent experimental studies indicate a small but significant solvent effect on the activation energy, E_a , of bond rotation at low concentrations of DMF in aprotic solvents [15]. However, due to the apparently small effect, the investigators concluded that further studies at higher dilutions were required to properly define the solvent effect. Typical values obtained for the DMF rotation barrier were in the range of 20–25 kcal/mole, while the calculated value varies from 7.88–22.57 kcal/mole. Other studies of the solvent effect on the rotation barrier of DMF are available, but the results are reported in terms of the free energy of activation, ΔF^* [16] or NMR spectral shifts [17].

Study of the rotation barrier of NDA is less extensive than that of DMF. A rotational barrier of 23 kcal/mole has been reported [18], while the calculated barrier varies from 18.08–25.31 kcal/mole. Solvent effects on the NDA barrier have been studied [19], but the results are reported as chemical shifts only.

The large discrepancy between experimental and calculated values is probably due to the MO method used [8]. The absolute calculated values probably have limited significance; however, as is usually the case, the semi-empirical calculations are relied on to give an indication of important trends by means of internally consistent relative values.

Of the calculated electronic transitions given in Table 2, special emphasis is placed on the behavior of the lowest $n \rightarrow \pi^*$ transition for two reasons. First, the transition can readily be studied experimentally, especially in NDA. Second, the limited CI procedure used in this study has probably yielded fair accuracy for this transition, while on the other hand, the lowest $\pi \rightarrow \pi^*$ transition underwent little adjustment in the CI procedure and consists primarily of the single $\pi \rightarrow \pi^*$ configuration included in the CI calculation. The $n \rightarrow \pi^*$ transitions of DMF and NDA as functions of the interaction coefficient are shown in Figs. 1 and 2, respectively. The transitions have been determined for both the planar and nonplanar molecular configurations.

The $n \rightarrow \pi^*$ transition of DMF increases slightly in energy (blue shift) to a maximum near the interaction value corresponding to an ϵ value of about 3.0 and then drops (red shifts) as the interaction increases. This seems to correlate well with an experimental study by Mayahi *et al.* [20]. This study is ideal for comparison with the predictions of the theoretical model in that the study included a number of aprotic solvents and an attempt was made to extrapolate the solvent induced spectral shifts to infinite dilution. The appropriate interaction coefficients for the experimental points in Fig. 1 were calculated from $(\epsilon - 1)/2\epsilon$ using the dielectric constants of the solvents.

The $n \rightarrow \pi^*$ transition of NDA gradually decreases in energy (red shift) initially and finally more rapidly in the range of strong interaction. The experimental points have been extracted from a study by Haszeldine and Mattinson [21]. The appropriate interaction coefficients have been determined as described for DMF. Superficially, the experimental points do not appear to correlate well with the theoretical predictions, particularly for strong interactions.

The experimental spectral changes induced by various solvents can, however, be rationalized with the theoretical predictions for both DMF and NDA by considering the effects of solvent interaction on the bond rotation barriers (Table 1). If the observed transition may be considered to be an average of transitions occurring in molecules in various conformations between planar and nonplanar, then this observed average would be shifted (blue) toward the transition of the planar form as the rotation barrier increased, causing the population to be shifted in favor of the planar form. If the rotation barrier decreased, thus favoring free rotation, the observed transition would be red-shifted away from the planar form transition. Consequently, in spite of the predicted red shift in the transition of NDA for strong solvent interaction, the increased rotation barrier could shift the population in favor of the planar form with its higher energy transition. This idea is not new, having been considered by Haszeldine and Mattinson [21] but doubted because they felt the spectral differences between the planar and nonplanar forms would not be great. However, this is apparently not true and with certain limitations, such as noncomplexing solvents, may be a

Table 3. Dipole moments^a of planar and nonplanar configurations as functions of solvent interaction

| Interaction coefficient ^b | 0.00 | 0.10 | 0.25 | 0.40 | 0.4875 |
|--------------------------------------|-------|-------|-------|-------|--------|
| N,N-Dimethylformamide | | | | | |
| Planar form | 2.694 | 2.735 | 2.886 | 3.299 | 3.893 |
| Nonplanar form | 2.186 | 2.224 | 2.354 | 2.678 | 3.114 |
| $\Delta\mu^c$ | 0.508 | 0.511 | 0.532 | 0.621 | 0.779 |
| N-Nitrosodimethylamine | | | | | |
| Planar form | 2.969 | 2.972 | 3.076 | 3.476 | 4.060 |
| Nonplanar form | 2.516 | 2.507 | 2.565 | 2.821 | 3.185 |
| $\Delta\mu^c$ | 0.453 | 0.465 | 0.511 | 0.655 | 0.875 |

^a Debye units.

^b Coefficient is value of the term $(\epsilon - 1)/2\epsilon$ in Eq. (1).

^c $\Delta\mu = \mu(\text{planar form}) - \mu(\text{nonplanar form})$.

quite reasonable mechanism. This mechanism could be readily explored experimentally by temperature dependency studies. Other arguments [22] against mechanisms of this general type seem to neglect the possible differences between hydrogen bonding and other solvents. The $\pi \rightarrow \pi^*$ transitions for the planar and nonplanar molecular forms of DMF and NDA are sufficiently close and the trend toward lower transition energies with increased solvent interaction is rapid enough so that the bond rotation barrier effects considered should not mask the general red shift of this transition with increasing solvent interaction.

Mulliken bond populations [7] for certain bonds are also given in Table 2. These bond populations appear quite stable over the complete range of model solvent interaction. The greatest changes appear in the C_1-N bond of DMF and N_1-N_2 bond of NDA, which gain electrons with increasing interaction. Consequently, there is what might be termed an increase in the double bond character of the bonds about which the hindered rotation of these molecules occurs.

In Table 3, the calculated dipole moments of both the planar and nonplanar configurations of DMF and NDA are presented as a function of solvent interaction. Also given are the differences, or $\Delta\mu$, between the dipole moments of the planar and nonplanar conformations for each value of solvent interaction. The planar conformation dipole moment is the greater in all cases.

Two observations may be made concerning the effect of solvent interaction on the dipole moments. First, the dipole moment of both DMF and NDA increases as the interaction coefficient increases, which is in agreement with the elementary electrostatic concept of an induced reaction field in a polarizable dielectric. Second, for both DMF and NDA, $\Delta\mu$, which is the dipole moment of the planar form relative to the nonplanar form, increases with increasing solvent interaction. This parallels the increase in the rotational barrier with increasing solvent interaction discussed above. This correlation of solvent-induced changes in the calculated rotational barriers and calculated dipole moments apparently agrees with a widely used general rule that conformations or configurations which possess higher dipole moments are more stabilized by solvents of high dielectric constant. This, of course, does not imply that the quantum mechanical treatment of the present work gives a superior or inferior description of rotational barriers than one based on dipole moments, but rather shows that the present treatment leads to the same conclusions as an earlier generalization based on experience.

A final comment should be made concerning the use of a solvent interaction coefficient whose maximum value is 0.5. First, this limit is implicit in the assumptions of the proposed theoretical model. However, this limit, or something close to it, seems to be dictated empirically also. Trial calculations made with larger interaction coefficients produced results which no longer resembled a perturbation of the original molecular system, but rather a fundamentally different system.

5. Conclusion

In conclusion, the solvent effects on some molecular properties of N,N-dimethylformamide (DMF) and N-nitrosodimethylamine (NDA) predicted by the proposed theoretical model appear quite reasonable. In the limited instances

where correlatable experimental evidence is available, agreement with the theoretical trends can be established. Obviously, more detailed experimental studies of solvent effects are required in order to fully develop the proposed model. Some limitation may also be placed on the present results by use of a semi-empirical MO method, although the method used is of the full overlap Mulliken type. At present, the problems of hydrogen bonding solvents, protonation, and their relationship to the theoretical solvent model suggested in this study are being explored.

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