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MC/MO Study of the Electronic Structure and Hyperfine Coupling Constant of the Nitrogen of the $(CH_3)_2NO$ Radical in Hydrogen-Bonding and Non-Hydrogen-Bonding Solvents

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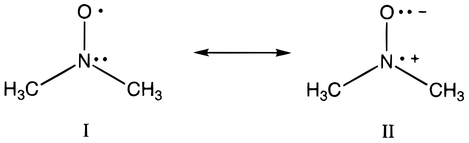
A combination of Monte Carlo (MC) simulation and ab initio molecular orbital (MO) calculation was applied to dimethyl nitroxide (DMNO) in H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions, and the solvent effect on the electronic structure and hyperfine coupling constant (hfcc) of nitrogen in DMNO was analyzed. The solution structures were picked up from the MC simulations, and a ROHF-SCI calculation with the MIDI-4 basis set was carried out for a supermolecule including one DMNO and a few solvent molecules surrounded by other solvent molecules approximated by point charges. The calculated hfcc of the N atom in DMNO in these solvents reflects the dielectric constant and the hydrogen-bonding ability of solvent and agrees with the experimental trend observed for di-*tert*-butyl nitroxide in solutions. In the H_2O and CH_3OH solutions, there are solvent molecules that are hydrogen-bonding and have a strong interaction with DMNO. For this interaction, the hfcc is larger in the CH_3OH solution than in the CH_3CN solution, although the dielectric constant of CH_3CN is larger than that of CH_3OH. Electron transfer between DMNO and the solvent molecules was acting in two directions: one from DMNO to solvent molecules around the N−O group and the other from solvent molecules to DMNO around the methyl groups. These electron transfers polarize the π-electron system of DMNO in the same direction as the electrostatic interaction does and increase the hfcc of the N atom.

I. Introduction

Nitroxide radicals are very popular radicals in various research areas.[1−14] ESR spectra of dimethyl nitroxide (DMNO), $(CH_3)_2NO$, have been observed in H_2O and $CHCl_3$;[1] the hyperfine coupling constant (hfcc) of the N atom (a_N) is larger in H_2O than in $CHCl_3$. Di-*tert*-butyl nitroxide (DTBN), $((CH_3)_3C)_2NO$, is a stable radical, and its a_N value has been determined in various solvents.[2−12] The a_N value of DTBN is larger in polar solvents. This solvent effect has been understood as a perturbation of the resonance of the π-electron system of the N−O group (Scheme 1).[15] In a polar solvent, the ionic structure II is favored, the spin density on the nitrogen atom increases, and the a_N value increases. However, the experiment also shows that the situation is not so simple. The hfcc is larger in a hydrogen-bonding solvent than in a polar non-hydrogen-bonding solvent, and there are in fact two distinct contributions to the solvent effect: the macroscopic electrostatic contribution and the hydrogen-bonding ability of the solvent. It is necessary to include both interactions to examine the solvent effect on the nitroxide radicals theoretically.

The Monte Carlo/molecular orbital (MC/MO) combined method should be appropriate to elucidate the solvent effect on DMNO. In this method, an MC simulation is carried out to generate the configurations of the solvent molecules in a solution, and the electronic structure of DMNO is evaluated by averaging the results of ab initio MO calculations for the solution structures. In our previous papers,[13,14] the solvent effect on the electronic structure of DMNO in the H_2O and $CHCl_3$ solutions was analyzed by using the MC/MO combined method. The electronic structure of DMNO in hydrogen-bonding solutions was well understood, and the solvent effect on the hfcc of DMNO calculated by an unrestricted Hartree−Fock (UHF) method agreed qualitatively with the experiment.[14] However, this a_N value was highly overestimated.

SCHEME 1



In the present study we extend our previous study to non-hydrogen-bonding polar solvents and clarify the difference between hydrogen-bonding and non-hydrogen-bonding solvents. The spin densities were calculated by a restricted open-shell Hartree−Fock (ROHF) calculation followed by singly excited configuration interaction (SCI) calculation, which is accepted to be more reliable than the UHF method.[16] The hfcc of nitrogen in DMNO was calculated in four solvents, H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$, by the MC/MO combined method using the ROHF-SCI/MIDI-4 method, and the electronic structure of DMNO in these solutions was analyzed.

II. Methods of Calculation

MC Simulation. The molecular structure of DMNO was optimized by the ROHF/MIDI-4d calculation in vacuo, while experimental geometries[17] were adopted for H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$. The TIP3P parameters proposed by Jorgensen et al.[18] were used for H_2O, and the OPLS parameters[19,20] were used for CH_3OH, CH_3CN, and $(CH_3)_2CO$. The parameters for DMNO that are suitable for the TIP3P parameters were determined by ROHF/MIDI-4d calculations in this work. The intermolecular interaction energy between *i* and *j* molecules was calculated by a potential function constructed by the

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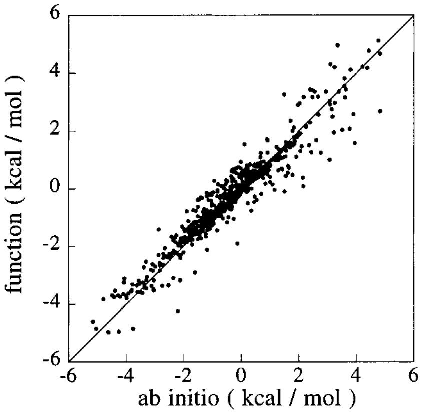

Figure 1. Comparison of the interaction energies calculated by the ROHF/MIDI-4d method and those calculated by the potential function for the DMNO−H_2O dimer.

TABLE 1: Determined Potential Function Parameters for DMNO

site	A (kcal Å^{12}/mol)$^{1/2}$	C (kcal Å^{6}/mol)$^{1/2}$	q (electrons)
N	1040.88	27.08	0.102
O	600.21	24.77	−0.348
CH_3	2858.58[a]	47.82[a]	0.123

[a] Reference 20.

Lennard-Jones (LJ) (12-6) terms and the Coulomb term,

$$E_{ij} = \sum_{r\in i}\sum_{s\in j}\left(\frac{A_rA_s}{R_{rs}^{12}} - \frac{C_rC_s}{R_{rs}^{6}} + \frac{q_rq_se^2}{R_{rs}}\right)$$

where r and s are interaction sites in molecules i and j, respectively. R_{rs} is the distance between sites r and s, A and C are the LJ parameters, and q is a charge. The ROHF/MIDI-4d calculations were carried out for 1389 configurations of DMNO−H_2O dimers, which were selected in the vicinity of energy minima or selected randomly. Interaction sites were located on each atom of DMNO except the methyl group, which was treated as a united atom whose interaction site was located on the carbon atom. For the methyl groups, the LJ parameters determined by Jorgensen et al.[20] were used. Parameter fitting was carried out by the Fletcher−Powell nonlinear least-squares method.[21] The determined parameters are listed in Table 1. Figure 1 shows the comparison of the interaction energies obtained by ROHF/MIDI-4d calculations and those obtained by the potential function for the 1389 DMNO−H_2O dimer configurations. A reasonable agreement is observed.

MC simulations for the H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions were carried out for the NPT ensembles according to the standard Metropolis method.[22] Each solution included one DMNO molecule and 215 solvent molecules in a cubic cell, and the periodic boundary condition was employed. The pressure of the system was set at 1 atm, and the temperature, at 298 K. The Owicki−Scheraga−Jorgensen preferential sampling technique[23] was employed. Each simulation covered at least 2000k steps for equilibration, followed by additional 3000k steps for averaging. MC simulations were carried out using our SIMPLS program.

MO Calculation. After establishing equilibrium for the solution structure in the MC simulation, the solution structures were picked up at every 10k steps for the H_2O solution or at every 30k steps for the CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions, and the ab initio SCI-ROHF/MIDI-4 calculation was applied to the solution successively. Solvent molecules located inside the cutoff length from the solute molecule were represented by point charges; magnitudes of the point charges were the same as those used in the potential functions. Some of the solvent molecules that were close to the solute molecule were selected and treated explicitly as a supermolecule together with the solute molecule. Thus, the ab initio SCI calculation was carried out for the supermolecule including one DMNO and the selected solvent molecules surrounded by other solvent molecules approximated by point charges.

Solvent molecules taken in the supermolecule were selected according to the distance parameter, defined between the sites of the solute and solvent molecules,[14]

$$\tilde{R}_{rs} = \frac{R_{rs}}{r_r + r_s}$$

where r_r and r_s are van der Waals radii of sites r and s, respectively, and R_{rs} is the distance between these sites. Solvent molecules were selected in the order of $\tilde{R}_{rs}$. The number of solvent molecules included in the supermolecule was varied from 0 to 5 in the H_2O solution and from 0 to 2 in the CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions.

The ROHF wave function of a doublet state mixes with only one of the singly excited configuration functions, and it is accepted that the SCI wave function including this type of excited configuration functions reproduces well the experimental hfcc of π-radicals.[16] In the present study, this type of SCI calculation was carried out, and the configuration functions included in the CI calculation were selected on the basis of the magnitude of the interaction energy between the ground configuration and the excited one. The second-order contribution (ΔE_s) to energy is represented by[24]

$$\Delta E_s = \frac{|\langle\Psi_s|H|\Psi_0\rangle|^2}{\langle\Psi_0|H|\Psi_0\rangle - \langle\Psi_s|H|\Psi_s\rangle}$$

where Ψ_0 and Ψ_s are the wave functions of the grand configuration and the singly excited configuration, respectively. The Ψ_s functions whose ΔE_s are larger than 5.0×10^{-7} hartree were included in the CI calculation.

The hfcc was obtained by averaging the a_N values of 300 or 100 solution configurations, which were calculated by the following equation[25]

$$a_N = \frac{8\pi}{3} g_e \beta_e \hbar \gamma_N \rho(r_N)$$

where g_e and β_e are the g factor and Bohr magneton of a free electron, respectively, γ_N is the gyromagnetic ratio of nitrogen, and $\rho(r_N)$ is the spin density at the nitrogen nucleus, which is calculated from the CI wave function.

MO calculations were carried out using our ABINIT program on the GAIA300 personal supercomputers.

III. Results and Discussion

A. MC Simulation. The radial distribution functions (rdf) between the O atom in DMNO and each site in the solvent molecule are shown in Figures 2−5. Figures 2 and 3 show that hydrogen-bonding interactions exist in H_2O and CH_3OH solutions. The first peaks of O−O and O−H rdfs in these solutions are very sharp and the O−H peak is inside the O−O peak, reflecting a hydrogen-bonding between the O atom of DMNO and H_2O or CH_3OH. In the CH_3CN and $(CH_3)_2CO$ solutions (Figures 4 and 5), a hydrogen-bonding interaction is not

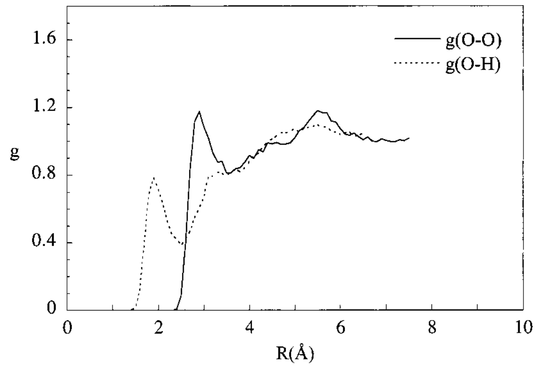

Figure 2. Radial distribution functions between the O atom in DMNO and the O and H atoms in H_2O.

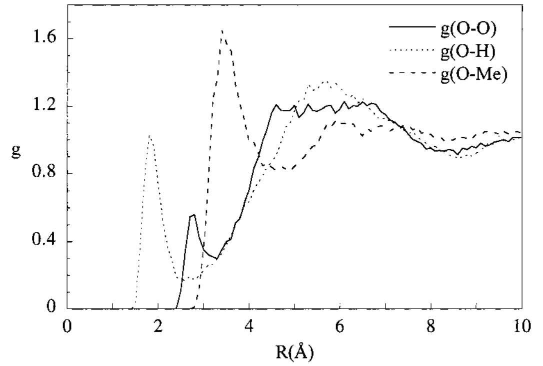

Figure 3. Radial distribution functions between the O atom in DMNO and the O and H atoms and the methyl group in CH_3OH.

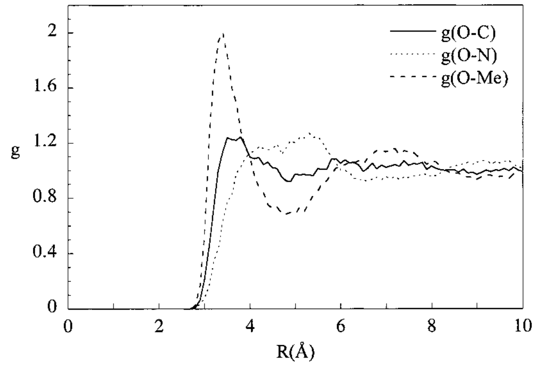

Figure 4. Radial distribution functions between the O atom in DMNO and the C and N atoms and the methyl group in CH_3CN.

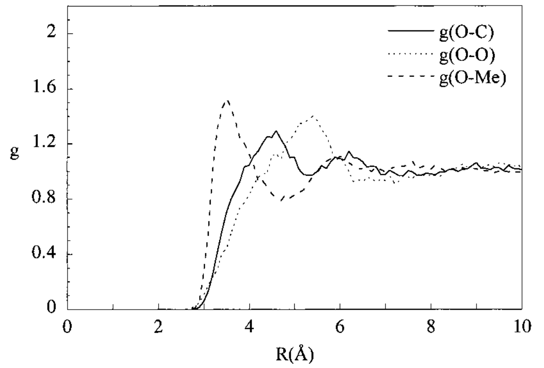

Figure 5. Radial distribution functions between the O atom in DMNO and the C and O atoms and the methyl groups in $(CH_3)_2CO$.

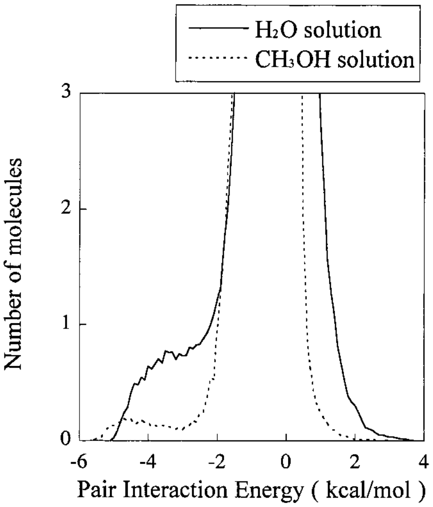

Figure 6. Solute−solvent energy pair distributions in hydrogen-bonding solvents.

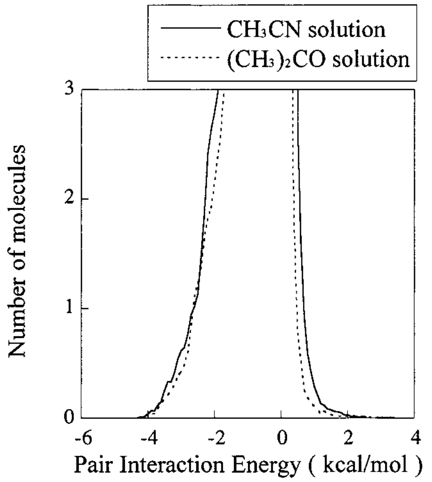

Figure 7. Solute−solvent energy pair distributions in non-hydrogen-bonding solvents.

recognized. The methyl group sites have the first peak at 3.4 and 3.5 Å in the CH_3CN and $(CH_3)_2CO$ solutions, respectively. No specific interactions are recognized between the solute and solvent molecules in the CH_3CN and $(CH_3)_2CO$ solutions.

Figures 6 and 7 show the energy pair distribution (epd), epd(x), which is the averaged number of solvent molecules having the solute−solvent pair interaction energy of x kcal/mol. The low band in the CH_3OH solution and the shoulder band in the H_2O solution appearing in the lower energy region represent the solvent molecules that are hydrogen-bonding with DMNO. Assuming that the region where epd is lower than −2.7 kcal/mol in H_2O and −3.0 kcal/mol in CH_3OH can be assigned as a hydrogen-bonding region, the averaged number of solvent molecules that are hydrogen-bonding with DMNO is 1.33 and 0.33 for the H_2O and CH_3OH solutions, respectively. Averaged hydrogen-bonding energy is −4.77 kcal/mol in the H_2O solution and −1.38 kcal/mol in the CH_3OH solution.

In the CH_3CN and $(CH_3)_2CO$ solutions, no hydrogen-bonding regions exist in the epd. Calculated interaction energies of the DMNO solutions are listed in Table 2. The solute−solvent interaction energy (E_{sx}) is the largest in the H_2O solution. DMNO is stabilized most in H_2O. The E_{sx} value is larger in the CH_3CN solution than in the CH_3OH solution. Although a hydrogen-bonding interaction exists between DMNO and CH_3OH in the CH_3OH solution, DMNO is stabilized in CH_3CN more than in CH_3OH. As may be seen from Figures 6 and 7, the number of solute−solvent pairs that have a stabilization energy larger than −2 kcal/mol is larger in the CH_3CN solution than in the CH_3OH solution. Because of these solute−solvent

TABLE 2: Averaged Total (E_{Tot}) and Solute−Solvent (E_{sx}) Interaction Energies (in kcal/mol) Obtained by MC Simulation, and Measured Solvent Dielectric Constants and Electric Dipole Moments

solvent	E_{tot} (kcal/mol)	E_{sx} (kcal/mol)	ϵ^a	μ^a (Debye)
H_2O	−9.78	−15.84	78.30	1.8
CH_3OH	−8.44	−13.12	32.66	1.7
CH_3CN	−6.98	−14.78	35.94	3.5
$(CH_3)_2CO$	−6.53	−13.07	20.56	2.7

[a] Reference 15.

TABLE 3: ROHF-SCI/MIDI-4 hfcc of N in DMNO (in Gauss)[a,b]

	no. of solvent molecules taken in the supermolecule[c]					
solvent	0	1	2	3	4	5
H_2O[d]	14.34	15.05	15.37	15.56	15.68	15.75
CH_3OH[e]	12.61	13.04	13.22			
CH_3CN[e]	12.32	12.60	12.77			
$(CH_3)_2CO$[e]	12.11	12.45	12.65			

[a] Calculated hfcc in the gas phase is 10.97 G. [b] Experimental values are 17.1 G for DMNO in H_2O from ref 1 and 17.12, 16.16, 15.65, and 15.48 for DTBN in H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$, respectively, from ref 10. [c] The other solvent molecules were approximated by point charges. [d] These results were averaged over 300 configurations of the solution. [e] These results were averaged over 100 configurations of the solution.

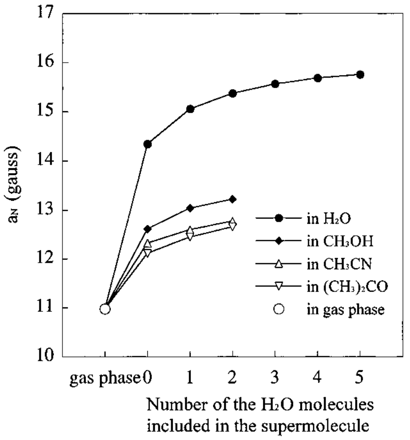

Figure 8. ROHF-SCI/MIDI-4 hfcc of the N atom in DMNO.

interactions, the averaged solute−solvent interaction energy E_{sx} is larger in CH_3CN. The dielectric constant and dipole moment of CH_3CN are larger than those of CH_3OH, and CH_3CN is more polar than CH_3OH. It is thus interesting to understand why a_N is larger in the less polar CH_3OH solution than in the more polar CH_3CN solution.

B. MO Calculation. *1. Point Charge Model.* The calculated a_N values of DMNO are listed in Table 3 and plotted in Figure 8 against the number of solvent molecules included in the supermolecule. When all solvent molecules were represented by point charges, the a_N value was increased by 3.37, 1.64, 1.35, and 1.14 G in the H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions, respectively, as compared with that in the gas phase. The a_N value is the largest in the H_2O solution and is the smallest in the $(CH_3)_2CO$ solution. The a_N value of DTBN has been observed in various solvents; it increases with increasing solvent dielectric constant, and it is larger in a hydrogen-bonding solvent than in a non-hydrogen-bonding solvent when two solvents have the same magnitude of dielectric constant.[6,7,9,10,11] The calculated hfcc in the four solutions agrees with these experimental facts for DTBN. The present calculation has shown that the solvent effect on a_N is caused primarily by the electrostatic interaction between DMNO and the solvent, and the a_N value is larger in the hydrogen-bonding solvents. Since the hydrogen-bonding solvent molecule has a specific orientation to the solute molecule, the resulting large electrostatic interaction polarizes the π N−O bond and increases the spin density on the N atom. This is the reason that the a_N value in the CH_3OH solution is larger than that in the more polar CH_3CN solution even in the point charge model calculations.

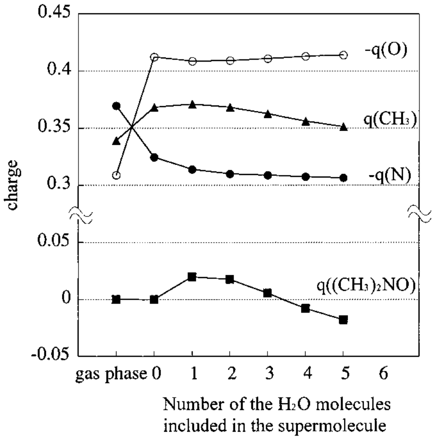

Figure 9. Mulliken charges at the O and N atoms and the methyl groups and the charge of DMNO. The O and N atomic charges are multiplied by −1, and $q(CH_3)$ values are the averaged charges of two methyl groups.

2. Supermolecule Model in Aqueous Solution. Distribution of selected H_2O molecules is similar to that which we reported previously.[14] Most H_2O molecules selected first are located near the O atom in DMNO. When the selection comes later, distribution of H_2O becomes uniform around DMNO.

When one H_2O molecule was taken into account explicitly and an ab initio SCI calculation was applied to the DMNO−H_2O supermolecule surrounded by point charges of other H_2O molecules, appreciable electron transfer was recognized between DMNO and the H_2O molecule. The charge of DMNO is +0.0198; electron transfer occurs from DMNO to the H_2O molecule. When the number of H_2O molecules that are included in the supermolecule increased, the a_N value increased; the a_N value seems to converge. This tendency is the same as that of our previous result.[14] In our previous UHF calculations,[14] the a_N value was considerably larger than the experimental value. A remarkable improvement was observed in the present SCI calculation of hfcc.

Mulliken atomic charges are widely used for the analysis of the electronic structure of an interacting molecular system. Although the use of Mulliken charge has little relevance for highly polar systems,[26] it is useful for a qualitative understanding of the electronic structure of DMNO in solution.

Figure 9 shows the Mulliken atomic charges at the O and N atoms and the CH_3 groups in DMNO and the charge of DMNO as a function of the number of water molecules included in the supermolecule. The trends observed in the charge distribution and the total charge of DMNO are similar to our previous UHF calculation.[14] In an isolated DMNO, the N and O atoms have negative charges, while the CH_3 groups have positive ones. When all solvent molecules were approximated by point charges, the negative charges of the O atom increased while that of the N atom decreased. This can be understood by the π-electron reorganization in aqueous solution (Scheme 1). The contribution of the resonance structure II becomes more important. This polarization of the N−O group II withdraws electrons from the CH_3 groups and the CH_3 groups become more positive. When one water molecule was taken into account explicitly in the supermolecule, the negative charge of N decreased. However, the negative charge of O did not increase but slightly decreased. This comes from the fact that the σ lone pair electrons at the O atom transfer from DMNO to the water molecule. In this sense, the O atom became more positive. However, this σ-electron transfer was compensated by the π-electron reorganization; the π-electron density of the O atom increased, and the contribution of the resonance from II increased. As a result, the Mulliken charge of the O atom in DMNO was almost unchanged. It may be said that the transfer of the σ lone pair electrons to the H_2O molecule polarizes the π-electron system of the N−O group in the direction which, is the same as that caused by the electrostatic interaction and increases the N spin density.

When the second and third H_2O molecules were included explicitly in the supermolecule, the positive charges of the CH_3 groups decreased. This is due to the reverse electron transfer from H_2O to DMNO through the CH_3 groups. The variation in the charge of DMNO also supports the electron-transfer mechanism in aqueous solution; electron transfer occurs in two directions, from DMNO to H_2O through the O atom and from H_2O to DMNO through the CH_3 groups.

Spin delocalization was also recognized between the solute and solvent molecules. An excess of β-spin electron transfers from DMNO to the H_2O molecule and the spin density (α-spin density) of DMNO becomes lager than 1.000. However, its amount was less than 0.001.

3. Supermolecule Models in the CH_3OH, CH_3CN, and $(CH_3)_2CO$ Solutions. Distribution of selected solvent molecules in the CH_3OH solution is similar to that in the H_2O solution; the solvent molecule near the N−O group was first selected in the supermolecule calculation. On the other hand, in the CH_3CN and $(CH_3)_2CO$ solutions, the solvent molecules selected in the supermolecule calculation were distributed uniformly around DMNO at each selection.

When CH_3OH molecules were taken into account explicitly in the CH_3OH solution, a trend observed in the calculated a_N values was similar to that in the H_2O solution. However, the magnitude of the solvent effect was smaller than that of the H_2O solution. In the supermolecule calculation in the CH_3CN or $(CH_3)_2CO$ solution, the increase in hfcc was less than that in the CH_3OH or H_2O solution. Although the experimental trend for the hfcc shift is reproduced well by the point charge approximation, the supermolecule calculation increases the hfcc shift in the CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions. This suggests that the relaxation of the electronic structure of DMNO caused by the electron transfer between DMNO and solvent molecules affects the hfcc shift to some extent.

A large a_N value in the less polar CH_3OH solution than the more polar CH_3CN solution is understood by analyzing the calculated hfcc for each solution structure. Figure 10 shows the distributions of the calculated hfcc for 100 samples in the CH_3OH and CH_3CN solutions. In the CH_3OH solution, there are solution structures that exhibit very large hfcc. The hydrogen-bonding solvent molecules have a specific orientation to the N−O group and its electrostatic interaction contributes to the larger hfcc in CH_3OH.

4. Mulliken Charges of Solvent Molecules around DMNO. To examine the difference in the electronic structure of DMNO between a hydrogen-bonding solvent and a non-hydrogen-bonding polar solvent, the solvent molecules in a supermolecule were classified into two groups, the O and Me side groups, and their Mulliken charges were compared. The N atom of DMNO was selected as the origin of the Cartesian coordinates, and the N−O bond axis was defined as the z axis; the z coordinate of the O atom of DMNO was 1.253 Å and that of the C atom in CH_3 of DMNO was −0.716 Å. When the z coordinate of a reference atom in a solvent molecule was larger than 1.25 Å, the solvent molecule was grouped into the O side group, while the solvent molecule whose z coordinate was less than −0.50 Å was grouped into the Me side group. The reference atom was O in H_2O and CH_3OH, C of CN in CH_3CN, and C of CO in $(CH_3)_2CO$. The averaged Mulliken charges of the solvent molecules in the O and Me side groups were calculated for the solution structures in which two solvent molecules were included in the supermolecule and are shown in Table 4.

Solvent molecules in the O side region have negative charges, while the solvent molecules in the Me side region have positive charges. These show that electron transfer occurs from the O atom of DMNO to the solvent molecule and from the solvent molecule to the methyl groups of DMNO, as was pointed out above. The magnitude of electron transfer is the largest in the H_2O solution in both the O and Me side regions. Table 4 also

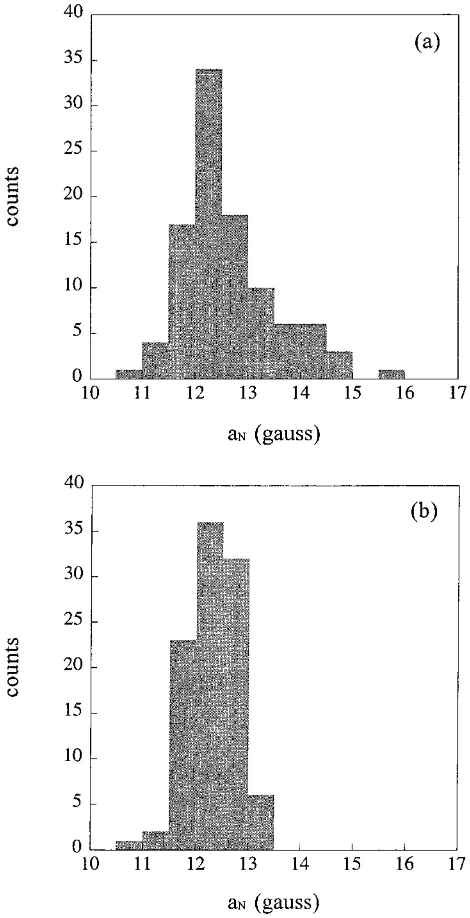

Figure 10. Distributions of calculated hfcc of the N atom of DMNO (a) in the CH_3OH solution and (b) in the CH_3CN solution.

TABLE 4: Averaged Charge of the Solvent Molecule in the O Side and Me Side Groups[a]

	solvent			
	H_2O[b]	CH_3OH[c]	CH_3CN[c]	$(CH_3)_2CO$[c]
O side	−0.0198	−0.0175	−0.0121	−0.0112
Me side	0.0197	0.0051	0.0037	0.0025

[a] Calculated from a model in which two solvent molecules are included in the supermolecule surrounded by other solvent molecules as point charges. [b] These results were averaged over 300 configurations of the solution. [c] These results were averaged over 100 configurations of the solution.

shows that the electron transfer from the O atom of DMNO to solvent molecules occurs efficiently in the hydrogen-bonding solvents, and this may be attributed to the oriented configuration of the solvent molecule in the hydrogen-bonding solvents.

IV. Conclusion

An MC/MO combined method with ROHF SCI/MIDI-4 calculation was applied to DMNO in H_2O, CH_3OH, CH_3CN, and $(CH_3)_2CO$ solutions. In the present MC/MO method, solvent configurations were generated by MC simulation and some of the solvent molecules were explicitly taken into account in ab initio SCI calculations of hfcc. The electron delocalization between solute and solvent molecules was included. This is not taken into consideration in the continuum model of the solvent effect and existing QM/MM hybrid methods. In aqueous solution, electron transfer occurs between DMNO and solvent molecules in two directions: from DMNO to H_2O through the O atom in the N−O group and from H_2O to DMNO through the methyl groups. About 25% of the solvent effect on the hfcc of nitrogen in DMNO was caused by this electron delocalization. The hfcc of the N atom, a_N, was improved remarkably by the present SCI calculations from our previous UHF calculations, and the experimentally observed solvent effect on the a_N value was well reproduced. The calculated a_N value was larger in the hydrogen-bonding solvent, CH_3OH, than in the non-hydrogen-bonding solvent, CH_3CN. In a hydrogen-bonding solvent, a specific orientation of a solvent molecule produces large electrostatic interaction with DMNO and polarizes the π-electron system of the N−O group. The electron transfer and the electrostatic interaction both make the N−O bond polarize in the same direction and increases the hfcc of the N atom. The present study rationalized the theoretical result that only electrostatic consideration predicts correctly the increase of the hfcc of nitrogen in DMNO in polar solvents and the experimental fact that the hfcc of nitrogen in DMNO is larger in hydrogen-bonding solvents.

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