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INDO-SCPT Calculations of the Solvent Dependence of Some Carbon-Proton Spin-Spin Coupling Constants

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Summary. A theoretical study of the effects of non-specific solute-solvent interactions on the directly bonded carbon-proton couplings $^1J(\mathrm{C—H})$, in acetaldehyde, acetone and acrylonitrile is presented. The solvent induced changes in these couplings calculated by an INDO-SCPT procedure incorporating a modified solvaton model are in satisfactory agreement with experiment and show significant improvement over the INDO-FPT calculations using the Klopman-Germer solvaton model.

Keywords. Solvent effects; NMR spin-spin couplings; INDO-SCPT calculations.

INDO-SCPT-Rechnungen der Lösungsmittelabhängigkeit einiger C—H-Kopplungskonstanten

Zusammenfassung. Es wird eine theoretische Studie zu den nichtspezifischen Lösungsmittelwechselwirkungen auf die Spin-Spin-Kopplungen direkt aneinander gebundener C- und H-Atome von Acetaldehyd, Aceton und Acrylnitril vorgestellt. Die vom Solvens induzierten Änderungen der Kopplungskonstanten werden von der INDO-SCPT-Methode unter Verwendung eines modifizierten Solvationsmodells zufriedenstellend wiedergegeben. Die Übereinstimmung mit den experimentellen Daten ist besser als INDO-FPT-Rechnungen mit dem Klopmann-Germer-Solvaton-Modell.

Introduction

The influence of solvents on the electronic structure of molecules has long been known, but the incorporation of solvation effects in quantum chemical calculations has only recently [1–3] received sufficient attention.

In general, solvation effects are determined by specific or short-range solute-solvent interactions (such as hydrogen bonding, complex formation, etc.) and by non-specific or long-range solute-solvent interactions which depend on the dielectric properties of the solvent.

Theoretical representation of the non-specific interactions has been almost exclusively based on the dielectric continuum models where the solute molecule is immersed in a continuously polarizable dielectric medium. At present, several approaches [2–10] are available for the incorporation of non-specific solvation effects within the SCF-LCAO-MO framework.

Methods based on the self-consistent reaction field (SCRF) [4–6] and effective charge [7–11] representations of the dielectric continuum are the most widely used in the literature.

Calculations based on these methods have been reported in such diverse fields as enthalpies of solvation [12], protein core effects [2–3], electronic absorption and emission spectroscopy [13–16] and NMR chemical shifts and spin-spin coupling constants [17–25].

The solvent dependencies of NMR parameters provide a convenient test for the effectiveness and validity of various solvation models. In recent years, extensive calculations of the solvent dependencies of NMR parameters have been reported by Ando and Webb and coworkers [17–25] using the Klopman-Germer solvaton model [7–8] with varying degree of success. These calculations, while successful in providing a satisfactory description of the solvent effects on nitrogen shieldings [22], were unable to provide a reasonable account of the solvent dependence of spin-spin couplings involving protons [17, 19, 20]. The solvent induced changes in these couplings are over-estimated seriously by these calculations which employ the Klopman-Germer solvation model in conjunction with the INDO-FPT method.

The present study was undertaken with a view to account for some of the reported over-estimations of solvent effects on carbon-proton couplings. We have employed a modified version of the solvaton model in conjunction with the INDO-SCPT method for the calculation of spin-spin couplings. Presently, we report the results of INDO-SCPT calculations of the solvent dependencies of directly bonded carbon-proton couplings in acetaldehyde, acetone and acrylonitrile.

Theoretical Methods

In the effective charge models of the continuum [2, 3, 7–11], the solute molecule is presented as an assembly of partial charges Q_B, centred at the nuclei (B) interacting with the solvent molecules which are represented by a set of effective or "virtual" charges Q_B^S, called "solvatons" given by

$$Q_B^S = -\mathrm{f}(\varepsilon)\, Q_B, \tag{1}$$

where Q_B is the net charge associated with the atomic centre B, and $\mathrm{f}(\varepsilon)$, which is a function of the dielectric constant ε of the solvent, has been expressed differently by various authors [8–10]. In the Klopman-Germer solvaton model [7–9], $\mathrm{f}(\varepsilon)$ is given by

$$\mathrm{f}(\varepsilon) = \frac{1}{2}(1 - \varepsilon^{-1}), \tag{2}$$

whereas, in the virtual charge model of Constanciel and Tapia [10], $\mathrm{f}(\varepsilon)$ is given by

$$\mathrm{f}(\varepsilon) = 1 - \varepsilon^{-1/2}. \tag{3}$$

However, in view of the crudeness of the electrostatic model employed in these theories the $\mathrm{f}(\varepsilon)$ should be understood as an empirical calibrating factor [9, 13]. Thus, Eq. (2) is employed in the present work to facilitate numerical comparison with previous calculations [17].

The effective electronic Hamiltonian of a solute molecule with M electrons and N nuclei embedded in a dielectric continuum of the solvent (S) is given by [10],

$$H_{\mathrm{eff}}(\mathrm{S}) = H^{\circ}_{\mathrm{eff}} - \sum_{i}^{M}\sum_{\mathrm{B}}^{N} Q^{\mathrm{S}}_{\mathrm{B}}/r_{\mathrm{B}i}, \tag{4}$$

where H°_{eff} is the effective electronic Hamiltonian of an isolated solute molecule in the gas phase. $Q^{\mathrm{S}}_{\mathrm{B}}$ is the solvaton charge associated with the atomic centre B [Eq. (1)] and $r_{\mathrm{B}i}$ is the electron-solvaton (B) distance. Eq. (4) resembles that employed by Germer [5] except for the electron-solvaton interaction term which has been erroneously given a positive contribution, as pointed out by Tapia [2, 3, 10].

Using the variational method [2, 10] within the ZDO approximation of SCF-LCAO-MO formalism, the matrix elements of the Fock operator in presence of the solvent (S) are given by

$$F^{\mathrm{S}}_{\mu\mu} = F^{\circ}_{\mu\mu} - \sum_{\mathrm{B}}^{\mathrm{N}} Q^{\mathrm{S}}_{\mathrm{B}}\Gamma^{\mathrm{S}}_{\mathrm{AB}} = F^{\circ}_{\mu\mu} + \mathrm{f}(\varepsilon)\sum_{\mathrm{B}}^{\mathrm{N}} Q_{\mathrm{B}}\Gamma^{\mathrm{S}}_{\mathrm{AB}} \qquad (\mu\in\mathrm{A})$$

and

$$F^{\mathrm{S}}_{\mu\nu} = F^{\circ}_{\mu\nu}, \qquad (\mu \neq \nu) \tag{5}$$

where $F^{\circ}_{\mu\nu}$ are elements of the Fock matrix in absence of the solvent and $\Gamma^{\mathrm{S}}_{\mathrm{AB}}$ is the electron-solvaton interaction integral defined as

$$\Gamma^{\mathrm{S}}_{\mathrm{AB}} = \left\langle \Phi_{\mu} \left| \frac{1}{r_{\mathrm{B}i}} \right| \Phi_{\mu} \right\rangle \qquad (\mu\in\mathrm{A}). \tag{6}$$

The $\Gamma^{\mathrm{S}}_{\mathrm{AB}}$ integrals are evaluated as follows. If the atomic orbital Φ_{μ} and the solvaton charge $Q^{\mathrm{S}}_{\mathrm{B}}$ are associated with the same centre then $\Gamma^{\mathrm{S}}_{\mathrm{AB}} = 1/r_{\mathrm{A}}$, where r_{A} represents the Paulings van der Waals radius of the particular atom [26], but when they are associated with different atomic centres, then $\Gamma^{\mathrm{S}}_{\mathrm{AB}} = 1/R_{\mathrm{AB}}$, where R_{AB} is the interatomic distance. Eq. (5) was employed in an SCF procedure, where allowance is made for the variation of the solvaton charges.

The nuclear spin-spin coupling constants have been calculated using the formulation given by Blizzard and Santry [27] of the self-consistent perturbation theory (SCPT) with the necessary modifications [28, 29] in the framework of the INDO approximation. The calculations were performed on the NEC ACOS-6 computer system of the University of Basrah.

Experimental molecular geometries were used for acetaldehyde [30], acetone [31] and acrylonitrile [32].

Results and Discussion

In the INDO approximation, the calculated C—H couplings depend upon the product $S_{\mathrm{C}}(0)\cdot S_{\mathrm{H}}(0)$, where $S_{X}(0)$ refers to the s-electron density at nucleus X. The present theoretical results are reported by using values of 0.3724 and 4.0318 au^{-3} for $S_{\mathrm{H}}(0)$ and $S_{\mathrm{C}}(0)$, respectively, taken from Pople et al. [33]. The corresponding values of Blizzard and Santry [27] are 0.318 and 2.767 au^{-3}.

The results presented in Table 1 for the solvent dependencies of ${}^{1}J(\mathrm{C—H})$ in acrylonitrile, acetaldehyde and acetone show that the INDO-SCPT calculations using a modified solvaton model are generally in satisfactory agreement with

Table 1. Comparisons of calculated and observed solvent dependences of $^1J(\mathrm{C—H})$ couplings (in Hz) in acrylonitrile, acetaldehyde and acetone

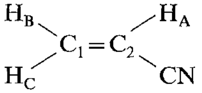
Solvent/Dielectric constant ε			Molecule/Couplings (Hz)						
			Acrylonitrile						
			$^1J(C_1H_8)$	$^1J(C_1H_C)$	$[^1J(C_1H_B) + {}^1J(C_1H_C)]^c$		$^1J(C_2H_A)$		
	ε		SCPT^a	SCPT^a	SCPT^a	FPT^b	SCPT^a	FPT^b	Obs.^{b}
CCl_4	2.238	J	160.91	160.49	321.4	347.9	135.72	221.6	178.3
		ΔJ	0.00	0.00	0.0	0.0	0.00	0.0	0.0
$CHCl_3$	4.806	J	161.88	161.27	323.15	376.3	136.63	238.8	179.0
		ΔJ	0.97	0.78	1.75	28.6	0.91	17.2	0.7
THF	7.58	J	162.21	161.53	323.74	387.3	136.93	244.9	179.7
		ΔJ	1.30	1.04	2.34	39.4	1.21	23.3	1.4
3-Pentanone	17.00	J	162.53	161.78	324.31	403.3	137.24	251.8	179.2
		ΔJ	1.62	1.29	2.91	55.4	1.52	30.2	0.9
Acrylonitrile	33.00	J	162.66	161.88	324.54	403.7	137.36	252.1	179.9
		ΔJ	1.75	1.39	3.14	55.8	1.64	30.5	1.6
DMSO	46.68	J	162.70	161.92	324.62	406.0	137.39	252.3	180.9
		ΔJ	1.79	1.43	3.22	58.1	1.67	30.7	2.6

Table 1 (continued)

			Acetaldehyde						Acetone[e]
			^1J(C—H) in CHO			J(C—H) in CH_3			^1J(C—H)
	ε		SCPT[a]	FPT[d]	Obs.[d]	SCPT[a]	FPT[d]	Obs.[d]	SCPT[a]
Gaseous state	1.00	J	161.71	163.44	169.68	115.38	117.09	126.22	118.30
		ΔJ	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_6H_{12}	2.02	J	162.86	164.91	170.98	116.76	119.77	126.88	119.50
		ΔJ	1.15	1.47	1.30	1.38	2.68	0.66	1.20
$CHCl_3$	4.806	J	162.89	164.98	172.12	116.95	120.67	127.26	119.75
		ΔJ	1.18	1.54	2.44	1.57	3.58	1.04	1.45
Acetone	20.00	J	162.98	165.04	172.58	118.20	121.43	127.10	120.74
		ΔJ	1.27	1.60	2.90	2.82	4.34	0.88	2.44
DMSO	46.68	J	162.98	165.04	173.43	118.30	121.56	127.11	120.83
		ΔJ	1.27	1.60	3.75	2.92	4.47	0.89	2.53

[a] This work

[b] Taken from Ref. [19]

[c] Experimental data are subject to large uncertainties (see Ref. [19] for details)

[d] Taken from Ref. [21]

[e] Although no accurate experimental data are available for acetone, early measurements (Ref. [36]) show an increase in ^1J(C—H) upon increasing ε

experiment and are significantly better than those obtained by the FPT-solvaton method.

In all cases, the observed tendency [17, 19, 21] of the directly bonded carbon-proton couplings, ${}^1J$(C—H) to increase with increasing dielectric constant is reproduced by the INDO-SCPT calculations. However, it should be stressed here that, while the calculated solvent dependencies are confined to non-specific interactions, the experimental data [34, 35] may contain additional contributions from specific solute-solvent interactions which may augment or oppose the non-specific effects. It is of interest to note that early investigators [36] have tentatively attributed the observed increase in ${}^1J$(C—H) in acetone in polar solvents to hydrogen bonding between the carbonyl group and the solvent.

In acetaldehyde, although the observed increase in ${}^1J$(C—H) in polar solvents is reproduced by FPT and SCPT calculations, both methods predict ${}^1J$(C—H) in CH_3 to be more sensitive to solvent dielectric effects than ${}^1J$(C—H) in CHO in disagreement with observation [21]. Therefore, it would be instructive to analyze the influence of polar media on the charge distribution in acetaldehyde. Examination of the results presented in Table 2 reveal a transfer of charge density out of the C—H bonding regions to the oxygen leading to an increase in the dipole moment of the molecule with increasing dielectric constant. Since the calculated ${}^1J$(C—H) couplings depend only upon the contact interaction [37], the increase in the calculated ${}^1J$(C—H) couplings imply [17] a greater s-electron density at the coupled nuclei in polar media.

The change in s-electron density due to a polar solvent is greatest in the aldehydic hydrogen showing a significant increase, but opposed by a decrease in the s-electron density of the carbonyl carbon. On the other hand, the s-electron density of C in CH_3 increases, while that of the methyl hydrogens remain unchanged with increasing dielectric constant. Thus, it seems reasonable to suggest that the low sensitivity of the calculated ${}^1J$(C—H) in CHO stems from opposing changes in the s-electron densities at the coupled nuclei.

Table 2. INDO-solvaton results for the dependence of charge distribution in acetaldehyde upon dielectric constant

		$\varepsilon = 1.0$	$\varepsilon = 2.02$	$\varepsilon = 20.0$	$\varepsilon = 46.68$
Charge densities					
C in CHO	total	3.6646	3.6482	3.6324	3.6313
	s-density	1.0484	1.0472	1.0460	1.0460
C in CH_3	total	4.0169	4.0150	4.0129	4.0128
	s-density	1.0625	1.0639	1.0653	1.0654
O	total	6.2718	6.2868	6.3015	6.3025
	s-density	1.7682	1.7677	1.7672	1.7672
H in CHO		1.0674	1.0707	1.0739	1.0741
H in CH_3 (average)		0.9931	0.9931	0.9931	0.9931
Dipole moment					
μ in Debye		2.5440	2.6270	2.7090	2.7150

In acrylonitrile, the present INDO-SCPT calculations show that upon a change of solvent from CCl_4 ($\varepsilon = 2.238$) to *DMSO* ($\varepsilon = 46.68$) the ${}^1J(C_2—H_A)$ coupling constant is increased by 1.67 Hz in satisfactory agreement with observation. Similar changes are predicted for ${}^1J(C_1H_B)$ and ${}^1J(C_1H_C)$, but no accurate experimental data are available for comparison. The sum of couplings $[{}^1J(C_1H_B) + {}^1J(C_1H_C)]$ estimated [19] by the analysis of the ABX system (X is C_1) show large uncertainties which led Konda et al. [19] to suggest that $[{}^1J(C_1H_B) + {}^1J(C_1H_C)]$ is independent of the solvent. Evidently, further experimental investigations are required. By judicious choice of solvents, the effects of specific solute-solvent interactions (such as hydrogen-bonding and complex-formation) may be eliminated.

The results of Table 1 evidently show that the FPT-solvaton calculations, although able to reproduce qualitatively the tendency of ${}^1J(C—H)$ couplings to increase with increasing dielectric constant, greatly over-estimate the solvent induced changes as a consequence of the well-documented [37–39] convergence problems sometimes encountered in the FPT calculations of the Fermi contact term of the spin-spin coupling constants.

In the FPT method, the coupled Hartree-Fock (CHF) equations are solved iteratively in presence of a finite spin-dependent perturbation which removes the spin closed-shell symmetry. The iterative process may converge with no change in molecular energy but in cases of non-convergent calculations successive iterations may lead [39] to a decrease in molecular energy accompanied by a growth of α spins in one MO and of β spin in another one resulting in calculated spin-spin coupling constants which are greatly over-estimated.

In the FPT-solvaton method, the electron-solvaton interaction terms are added to the Fock matrix elements for both spin and electrons (see Eqs. (4) and (5) of Ref. [19]) which may lead to additional convergence problems of which the case of acrylonitrile is a typical example.

Alternatively, the present INDO-SCPT-solvaton calculations are carried out by performing normal INDO-solvaton calculations in absence of magnetic interactions and the resulting MOs and orbital energies are then used in SCPT calculations of the spin-spin coupling constants.

In conclusion, the present INDO-SCPT calculations using a modified solvaton model provide a satisfactory account of the effects of non-specific solute-solvent interactions on the spin-spin coupling constants.

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