Spectroscopy with the polarizable solvent diiodomethane

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The polarizable solvent CH_2I_2 causes ^1H NMR upfield chemical shifts of 1.5 ppm as well as bathochromic shifts of a dye greater than those caused by polar solvents such as methanol.

Diiodomethane has a density of 3.3, a boiling point of 180 °C and a relative permittivity of 5.3. Its outstanding physical property is, however, a refractive index of 1.748. This compares with 1.333 for water and 1.560 for bromobenzene. Even carbon disulfide (with the highest refractive index among the common solvents) has a value of only 1.628. Refractive indices arise from a light wave's oscillating electric field being countered by a corresponding oscillating field from a molecule's electrons. The velocity of the propagating wave is thereby reduced. Thus, the refractive index of 1.748 for diiodomethane reflects a particularly high electron mobility around the two iodine atoms. More specifically, the longitudinal polarizability for C–I bonds is as much as 9 times greater than for the C–C bond.[1]

Compared to hydrogen-bonding, ion-pairing, charge-transfer and π-stacking, intermolecular polarizability effects on organic compounds are rather poorly understood. The question here, therefore, is how systems are perturbed when embedded in a sea of polarizable electrons as provided by diiodomethane. Judging from its relative permittivity of 5.3, the solvent appears to be apolar in nature. This may be misleading because the dielectric constant, derived from a 'bulk' measurement, fails to depict specific interactions occurring at the molecular level.

One indication that diiodomethane does in fact influence spectral properties comes from an NMR study of ^{129}Xe in 46 solvents.[2] Among these solvents, diiodomethane induces by far the largest chemical shift of δ 335. This may be compared to δ 225 for carbon disulfide, δ 248 for iodomethane and δ 196 for water. It was also shown that proton gas-to-liquid NMR shifts for CH_4, being a complex function of the refractive indices, is greatest for diiodomethane among several poly-brominated and chlorinated solvents.[3] Diiodomethane has also been used as one of 37 solvents for a study of the visible molecular absorption spectrum of cyanine dyes.[4] A modest red shift of *ca.* 25 nm was observed in switching from methanol to diiodomethane. Molecular absorption bands correlate with $(n^2 - 1)/(2n^2 + 1)$ where n is the refractive index of the solvent.

Before carrying out any spectroscopy, we felt it desirable to obtain a sense of the solubilizing power of diiodomethane. The following compounds are miscible with diiodomethane: acetonitrile, benzene, chloroform, cyclohexene, dioxane, ethanol, ethyl acetate, ethyl ether and tetrahydrofuran. The following are immiscible: bromine, hexane, hexan-1-ol, ethyl vinyl ether and water. Acrylic acid and cyclohexane show modest solubility. In general, aromatic groups seem to help solubilize compounds in diiodomethane.

NMR spectra were obtained with a 500 MHz spectrometer on samples in 5 mm tubes containing 0.14 m solute in CD_2I_2. $SiMe_4$ in $CDC1_3$ was used as an external reference. Since no differences were observed between CD_2I_2 (Aldrich), (stabilized with copper) and CD_2I_2 purified by vacuum distillation, all experiments used the former.

A total of 17 diverse solutes in CD_2I_2 were examined by ^1H NMR. The vast majority of signals shifted upfield relative to those in $CDC1_3$, by 1.5 ± 0.1 ppm. For example, uncorrected[5] cyclohexene signals shifted from δ 5.58, 1.90 and 1.52 in $CDC1_3$ to δ 4.09, 0.43 and 0.03, respectively, in CD_2I_2. Other representative examples from the group of 17 (including an alkene, carboxylic acid, nitrile, ketone *etc.*) are given in Table 1. Since the shifts were more or less uniform regardless of the proton type, there was little simplification of the spectra except in four cases (anisole, phenetole, butyl phenyl ether and thioanisole). These simplifications arose from one proton of a multi-proton multiplet fortuitously shifting slightly differently (*ca.* 0.1 ppm) than the other components. Fig. 1 shows the improved peak resolution of the thioanisole spectrum in CD_2I_2 relative to $CDCl_3$. Note that since spectra in $CDCl_3$ and CCl_4 are very similar, the observed differences between CD_2I_2 and $CDCl_3$ cannot be ascribed to hydrogen-bonding to the latter solvent. A change from $CDCl_3$ to CD_2I_2 caused upfield shifts in the ^{13}C NMR spectra of less than 1 ppm.

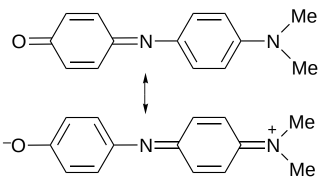
No variation in chemical shift was observed with thioanisole in diiodomethane as the temperature was varied from 10 to 30 °C (6 °C being the freezing point of the solvent). The chemical shifts of the toluene signals in various mixtures of CD_2I_2 and $CDC1_3$ were found to be linearly related to the percentage of CD_2I_2 in the solvent. All these results point to a nonspecific solvent effect arising from solvent in the aggregate as opposed to definable molecular complexes. Accordingly, it appears that solutes are immersed in a continuum where their spontaneous electric moments create a reaction field in the solvent which, in turn, affects the magnetic shielding at the solute nuclei. Diiodomethane with its high refractive index would be expected to excel in this regard.[6]

Visible spectrophotometry gave more detailed information on the solvation properties of diiodomethane at the molecular level. The experiments used *N*,*N*-dimethindoaniline (phenol blue) dissolved at a concentration of 2×10^{-5} m in several solvents including diiodomethane. Phenol blue has a solvent-

Table 1 ^1H NMR chemical shifts in $CDCl_3$ and CD_2I_2

Solute	δ ($CDCl_3$)	δ (CD_2I_2)	Δδ/ppm
Naphthalene	7.789	6.309	1.480
	7.422	5.957	1.465
o-Phenetidine	6.675	5.125	1.550
	6.617	5.060	1.557
	3.953	2.471	1.482
	3.690	2.054	1.636
	1.327	−0.124	1.451
Acetophenone	7.866	6.344	1.522
	7.475	6.071	1.404
	7.374	5.958	1.416
	2.519	1.088	1.431
Ethyl benzoate	7.947	6.369	1.578
	7.447	6.038	1.409
	7.333	5.910	1.423
	4.279	2.763	1.516
	1.294	−0.153	1.457
Toluene	7.167	5.764	1.390
	7.055	5.674	1.402
	2.277	0.911	1.366
Iodobenzene	7.650	6.105	1.454
	7.277	5.811	1.466
	7.053	5.599	1.545

sensitive λ_{max}, and for this reason it has been widely exploited as a polarity probe.[7] Table 2 lists the absorbance maxima in select solvents ranging in polarity from hexane to water. It is seen that there is a red shift as the solvent becomes more polar. For example, λ_{max} shifts from 545 nm in hexane to 654 nm in water. This is traditionally explained by the polar solvents stabilizing the transition dipole which resembles, as a crude model, the dipolar resonance contributor of the dye. The resulting spectral shift, of the dipole-induced dipole type, depends upon both the change in dipole moment of the solute and the refractive index of the solvent. A dispersive interaction is also possible in which a rapidly fluctuating transition moment creates an induced dipole in solvent molecules; this effect likewise depends upon the solvent polarizability and, hence, the refractive index.



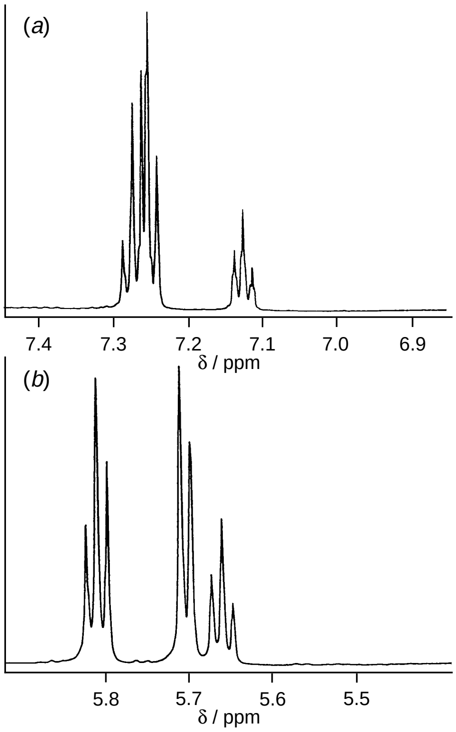


Fig. 1 ^{1}H NMR spectra of the aromatic portion of thioanisole in (*a*) $CDCl_2$ and (*b*) CD_2I_2. The simplification in CD_2I_2 results from the *ortho*-protons being shifted upfield 0.1 ppm more than the *meta*- and *para*-protons.

Table 2 Absorbance maxima for phenol blue in several solvents

Solvent	λ_{max}/nm
Hexane	545
Benzene	573
Dimethylformamide	593.5
Chloroform	595
Propan-2-ol	603
Ethanol	605
Methanol	607.5
Diiodomethane	617
Water	654

Diiodomethane adopts a remarkable position in the list of solvents in Table 2. According to our particular reporter dye, only water exceeds diiodomethane in apparent ‘polarity’. Even methanol is not quite as polar as diiodomethane. We know of no similar case in which there is such a large disparity between a ‘bulk’ polarity (as manifested by a relative permittivity of 5.3) and the corresponding ‘spectrophotometrically-based’ polarity (as manifested by the λ_{max} of phenol blue). The shifts with phenol blue are, we presume, so much greater than with cyanine dyes because phenol blue extensively charge-separates in the excited state whereas cyanine dyes merely distribute a cationic charge. Diiodomethane clearly stabilizes transient ionic charge far beyond what is normally expected from an aprotic, and seemingly apolar, solvent.

Diiodomethane would be an interesting solvent with which to carry out kinetic studies, but experimental difficulties have thus far prevented us from doing so. Three problems were encountered: (*a*) insolubility of either the reactant or product in the solvent; (*b*) strong absorbance of the solvent below 400 nm; and (*c*) reactivity of the solvent under the reaction conditions. Information on the ability of polarizable systems to stabilize polar transition states would be particularly useful to those involved in enzyme mechanisms. Methionine, with its polarizable sulfur, frequently resides near active sites with no apparent function.

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