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Solvent Effects on the Five Shielding Constants in Tetramethylsilane and Cyclohexane[1a]

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Abstract: Intrinsic solvent shifts of the four ^{1}H and ^{13}C resonances of tetramethylsilane (TMS) and cyclohexane have been determined in 38 aromatic and nonaromatic solvents, and compared with ^{29}Si shifts for 15 of these solvents. Apparent ^{13}C and hydrogen solvent shifts in 54 additional solvents have been measured. The maximum ranges of intrinsic solvent shifts are 0.6, 4.0, and 0.7 ppm for ^{1}H, ^{13}C, and ^{29}Si, respectively, of TMS; and 0.6 and 1.5 ppm for ^{1}H and ^{13}C, respectively, of cyclohexane. Trends in the observed TMS and cyclohexane solvent effects are compared and contrasted. The intrinsic solvent shifts have been subjected to factor analysis calculations. The results indicate that for most of the solvents in which intrinsic shifts were determined, these shifts are described by just two statistically significant solvent influences. Attempts to identify these influences with particular "physically significant" solute–solvent interactions are described.

The classic paper by Buckingham, Schaefer, and Schneider[2] (referred to hereafter as BSS) delineated a set of postulated contributions to the resonance shift imparted by a solvent on a solute ("solvent shift"). Since then, much effort has been expended toward gaining further insight into the various postulated contributions.[2–4] The BSS approach is summarized in eq 1,

$$\Delta\sigma = \sigma_b + \sigma_a + \sigma_w + \sigma_E \quad (1)$$

where $\Delta\sigma$ is the observed solvent shift, σ_b is the overall bulk susceptibility effect, σ_a arises from anisotropy in the magnetic susceptibility of the solvent molecules, σ_w reflects van der Waals interactions between solute and solvent molecules, and σ_E stems from permanent or induced "reaction field" dipoles in neighboring solvent molecules which polarize the solute and hence alter its electronic environment. Concurrently, Schaefer and Schneider[5] focussed on an additional effect, the *specific* association property which arises from the formation of weak complexes between a solvent and solute. Hydrogen bonding is an example. The "polar effect," a relatively small contribution for nonpolar solutes, arising from dipole-induced dipole interactions between a polar solvent and the solute, was included in σ_E by BSS, although other workers[6,7] have chosen to consider this contribution to be part of the van der Waals effect σ_w, which, in the BSS view, primarily encompasses the generally stronger dispersion interaction between solute and solvent. We shall consider σ_w to represent only dispersion interactions, and σ_E to embrace only polar effects, including those attributed to the reaction field.

In spite of the attention given to the last three terms of eq 1, both through empirical correlations and postulated models, the detailed nature of these interactions remains obscure and shrouded in substantial controversy.[3,4,8,9] Nevertheless, recent experimental work[2,3,8–17] has clearly demonstrated that the hydro-

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[2] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[3] P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967).

[4] J. Ronayne and D. H. Williams, *Ann. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, 2, 83 (1969).

[5] T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218, 1224 (1960).

[6] B. Linder, *ibid.*, **33**, 668 (1960).

[7] B. B. Howard, B. Linder, and M. T. Emerson, *ibid.*, **36**, 485 (1962).

[8] M. A. Raza and W. T. Raynes, *Mol. Phys.*, **19**, 199 (1970).

[9] P. H. Weiner, E. R. Malinowski, and A. R. Levinstone, *J. Phys. Chem.*, 74, 4537 (1970).

[10] P. Laszlo, A. Speert, R. Ottinger, and J. Reisse, *J. Chem. Phys.*, **48**, 1732 (1968).

[11] J. Homer, *Tetrahedron*, **23**, 4065 (1967).

[12] W. T. Raynes and M. A. Raza, *Mol. Phys.*, **17**, 157 (1969).

[13] J. Homer, E. J. Hartland, and C. J. Jackson, *J. Chem. Soc. A*, 931 (1970).

[14] E. R. Malinowski and P. H. Weiner, *J. Amer. Chem. Soc.*, **92**, 4193 (1970).

[15] P. H. Weiner and E. R. Malinowski, *J. Phys. Chem.*, **75**, 1207, 3160, 2971 (1971).

[16] J. K. Becconsall, G. D. Daves, Jr., and W. R. Anderson, Jr., *J. Amer. Chem. Soc.*, **92**, 430 (1970); J. Homer and P. M. Whitney, *J. Chem. Soc., Chem. Commun.*, 153 (1972).

[17] M. Bacon, G. E. Maciel, W. K. Musker, and R. Scholl, *ibid.*, **93**, 2537 (1971).

gens of nonpolar solutes, for which the reaction field effect is usually considered negligible,[2] are subject to solvent shifts of several tenths of a part per million. Most of this work has focussed on the ubiquitous hydrogen internal reference, tetramethylsilane (TMS).[18] Some of the results have been interpreted as evidence[10,13] that TMS forms weak complexes with aromatic solvents, while ostensibly less polarizable nonpolar hydrocarbons, such as neopentane and cyclohexane, do not. This interpretation is based on the finding that TMS experiences a decreased shielding, relative to hydrocarbon solutes, in ternary solutions in aromatic solvents,[10] compared to solutions in nonaromatic solvents. Other findings were rationalized in terms of "solute exposure" to the surrounding solvent molecules.[8,12] For example, the observation of large solvent shifts experienced by the peripheral methyl hydrogens of tetraethylsilane, relative to the inner methylene hydrogens, supports the idea of closer contact with the solvent of the methyl hydrogens. This is one of the few pieces of direct experimental evidence that different regions of a solute molecule experience different degrees of interaction with the solvent. Other evidence is offered in conjunction with the present results (*vide infra*).

Solvent effects investigations in nonaqueous media of nuclides other than hydrogen have been rather sparse. Most of what has been done centers on the resonances of ^{13}C and ^{19}F.[3] Spiesecke and Schneider[19] and Becconsall and Hampson[20] disclosed large (several parts per million) solvent effects on the ^{13}C resonances of methyl iodide.[19,20] Maciel and coworkers[21,22] uncovered similarly large ^{13}C solvent effects on polar carbonyl groups, and more recently a paper has appeared that demonstrates solvent shifts of several ppm for the ^{13}C resonance of chloroform.[23]

In a preliminary report of the present work, it was pointed out that the ^{13}C of TMS exhibits a range of solvent shifts about three times that of the hydrogen resonance.[17] The silicon resonance of TMS is influenced by solvent to about the same degree as is the hydrogen. This preliminary study is the only one thus far reported on ^{13}C solvent effects on a nonpolar solute and demonstrates that such solutes are also subject to ^{13}C solvent shifts of >1 ppm.

This study centers on the tetrahedral TMS and on the more oblate cyclohexane as solutes. The primary aspect of this investigation is a study of "intrinsic" (*i.e.*, *not* susceptibility effect) solvent shifts[17] on the ^1H and ^{13}C signals of these solutes, dissolved in a series of monohalocyclohexanes, in a series of mono- and polyhalo- and methylbenzenes, and in some noncyclic, organic solvents. In addition, we consider here corresponding data on the ^{29}Si resonance of TMS in 15 of these solvents.[24] These "intrinsic" shifts hinge on hydrogen shifts obtained on these solutes by a previously described method[16,17] (see the Experimental Section) which allows an external reference to be employed with bulk susceptibility effects effectively eliminated. This procedure has provided a set of multinuclide data that are unique among available data for attempting to separate and *isolate* the several contributions to the observed solvent effect. Since we have intrinsic solvent shifts of the five nuclei of TMS and cyclohexane, we anticipate mapping the sensitivities of various regions of the solute molecule to the most important solvent shift contributions.

The second aspect of the present investigation is the measurement of ^{13}C solvent shifts of TMS and cyclohexane in over 50 additional solvents, using an internal referencing technique rather than the *intrinsic* shift approach. The overall goal of this research is essentially twofold: (a) to characterize the potential utility of TMS and cyclohexane as ^{13}C internal references (also, ^{29}Si internal reference in the case of TMS) from the point of view of the sensitivity of their resonances to solute–solvent interactions; and (b) to investigate the nature and origins of the solvent shifts which operate in these systems. The tool chosen for analyzing the data of this investigation is the factor analysis technique recently applied to studies of hydrogen solvent effects.[9,14] This body of data reported here seems ideally suited to the application of the factor analysis method.

Experimental Section

(1) **Materials.** The solvents employed in this solvent effect study constitute two groups: (a) halogenated or methylated benzenes and cyclohexanes, and (b) all others, encompassing both aromatic and nonaromatic solvents. Group a[25] was nearly all Eastman White Label or Aldrich chemicals. Vpc checks on these solvents indicated they were of at least 99% purity. Most of the iodine-containing reagents were slightly colored by free iodine; these were washed with aqueous $Na_2S_2O_3$ until they were colorless, then dried over anhydrous $CaCl_2$. The iodocyclohexane, a K and K product, was initially strongly colored by iodine; the $Na_2S_2O_3$ treatment rendered it nearly colorless. All of the other halogenated or methylated benzenes were Eastman White Label samples, with the following exceptions: 1,2,3-trimethylbenzene, Aldrich Purissimum grade; *p*-chloroiodobenzene and *o*-chlorobromobenzene, Aldrich; and *p*-fluorobromobenzene, Penisular Chem Research Co.

Of group b the following solvents (see Table I of Discussion) were Matheson Coleman and Bell (MCB) spectrograde quality: methanol, nitromethane, nitroethane, ethyl acetate, acetonitrile, *n*-hexane, tetrahydrofuran, acetone, propionitrile, 1,4-dioxane, dimethylformamide, methylene chloride, chloroform, carbon tetrachloride, pyridine, and carbon disulfide. The following of this group were supplied by Aldrich: *n*-propylamine, cyclohexene, 2,2-dimethylallene, triethylamine, 2-chloropropane, cyclohexanone, ethylbenzene, cumene, *sec*-butylbenzene, *tert*-butylbenzene, 1,4-diisopropylbenzene, cyclopropylbenzene, 2-bromopropane, ethyl isothiocyanate, *N*,*N*-dimethylaniline, aniline, and $C_6H_5C(CH_3)_2OH$. Nitrobenzene, anisole, benzonitrile, and benzaldehyde were Eastman White Label products. The 2-butyne came from Peninsular Chem Research. The methyl and ethyl iodide were K and K materials, vpc pure. The norbornadiene, which had been distilled before use, was supplied by Mr. Harry Dorn. Vpc checks on the materials of this group also indicated purity of at least 99%. A solvent purity of 99% was deemed adequate for this study; therefore, the solvents were used as received, except as noted above. The solutes of this study, TMS and cyclohexane, were Aldrich nmr grade and MCB spectrograde, respectively.

(2) **Nmr Measurements.** The ^{13}C solvent shifts of TMS and cyclohexane were obtained in natural abundance on 20 vol % solutions of these solutes. Solutions of this concentration were necessary in order to obtain adequate ^{13}C sensitivity in the experiments to be described.

The carbon experiments were performed on a modified Varian

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(18) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(19) H. Spiesecke and W. G. Scheider, *J. Chem. Phys.*, **35**, 722 (1961).

(20) J. K. Becconsall and P. Hampson, *Mol. Phys.*, 10, 21 (1965).

(21) G. E. Maciel and G. C. Ruben, *J. Amer. Chem. Soc.*, **85**, 3903 (1963).

(22) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2752 (1965).

(23) R. L. Lichter and J. D. Roberts, *J. Phys. Chem.*, **74**, 912 (1970).

(24) R. Scholl, Ph.D. Thesis, University of California, Davis, Calif., 1972.

(25) Mark R. Bacon, Ph.D. Thesis, University of California, Davis, Calif., 1972.

Associates HA-100 spectrometer; the modifications have been described elsewhere.[26] The field-frequency stabilization was accomplished by locking on the ^{19}F resonance of a capillary of trifluoroacetic acid positioned inside the 8-mm (o.d.) nmr tube by means of Teflon spacers. The ^{13}C resonances were measured while minimum-power, coherent proton decoupling was maintained at a predetermined, fixed frequency that was the same in all experiments. This frequency was stabilized to ±0.1 Hz by phase locking it to a Hewlett-Packard 5100 synthesizer. The ^{13}C resonance of TMS was therefore *internally* referenced to the proton resonances of TMS; likewise the ^{13}C signal of cyclohexane was referenced to that solute's proton resonances. A constant, coherent decoupling frequency implies a constant *effective* magnetic field at the protons, although, of course, the *applied* magnetic field had to be changed from sample to sample in order to maintain the proton resonance condition, *i.e.*, to spin-decouple completely the hydrogens from carbon. The technique was sufficiently selective that a change of decoupling frequency of 1 Hz on either side of optimum produced noticeable deterioration of decoupling. The result is that the directly observed ^{13}C shifts reflect solvent effects on *both* the carbon *and* the protons of TMS or cyclohexane. These shifts are referred to as "apparent" solvent shifts, $\Delta\sigma^{\mathrm{a}}{}_{\mathrm{C(TMS)}}$, and $\Delta\sigma^{\mathrm{a}}{}_{\mathrm{C(CHX)}}$ for the ^{13}C shifts of TMS and cyclohexane, respectively. They are referenced to the apparent ^{13}C shielding of pure TMS and "apparent" ^{13}C shift of pure cyclohexane (taken as 0 ppm), observed under identical conditions. The carbon signals typically had a signal-to-noise ratio of 10 to 1 in a single scan. The experimental uncertainties in the carbon shifts determined by the above procedure are less than ±0.02 ppm.

Apparent ^{29}Si solvent shifts of TMS were obtained in the same manner on the same spectrometer and are reported elsewhere, along with some of the details of the experimental techniques and modifications of the equipment.[27]

The "apparent" solvent shifts, $\Delta\sigma^{\mathrm{a}}{}_{\mathrm{C(TMS)}}$ and $\Delta\sigma^{\mathrm{a}}{}_{\mathrm{C(CHX)}}$, are of limited fundamental value because they reflect hydrogen solvent effects in TMS or cyclohexane as well as solvent effects on ^{13}C. An independent, reliable route to the "intrinsic" or "local" (free of bulk susceptibility effects) shifts of the protons is highly desirable for at least two reasons: (a) the proton solvent shifts of TMS and cyclohexane are of interest in themselves; and (b) independent determination of these shifts allows proton solvent effects to be subtracted from the apparent ^{13}C shifts, leaving intrinsic carbon shifts that reflect solvent effects on only the ^{13}C.

For obtaining hydrogen shifts free of extraneous influences (*i.e.*, solvent effects on a reference, and those effects due to bulk susceptibility differences), we employed the method of Becconsall, Daves, and Anderson.[16] This approach, called the "reference independent" technique by its developers,[16,28] makes use of the difference in sample-to-field geometry between a conventional nmr electromagnet and a superconducting solenoid. In the former arrangement the main magnetic field is applied perpendicular to the cylindrical sample axis (in the customary laboratory frame of reference the field is considered to be along the z axis and the axis of the sample coincident with the y axis). For this geometry, the bulk susceptibility contribution, $\sigma^{\perp}{}_{\mathrm{b}}$, is given by the well-known formula[29]

$$\sigma^{\perp}{}_{\mathrm{b}} = (2/3)\pi\chi_{\mathrm{V}} \tag{2}$$

where χ_{V} is the bulk susceptibility of the medium. However, for the parallel orientation (solenoid field and sample axis both along the z axis) the contribution is[16]

$$\sigma^{||}{}_{\mathrm{b}} = -(4/3)\pi\chi_{\mathrm{V}} \tag{3}$$

These two independent relations form the basis for eliminating σ_{b} from the observed chemical shifts. The *observed* shift of solute i in solvent α is

$$\sigma^{\alpha}{}_{\mathrm{i}} = \sigma_{\mathrm{b}} + \sigma^{\alpha}{}_{\mathrm{in(i)}} \tag{4}$$

where $\sigma_{\mathrm{in(i)}}$ is the desired "intrinsic" shift independent of bulk susceptibility. For the perpendicular (electromagnet) field orientation, $\sigma^{\alpha\perp}{}_{\mathrm{i}} = \sigma^{\perp}{}_{\mathrm{b}} + \sigma^{\alpha}{}_{\mathrm{in(i)}}$, and for the parallel (solenoid) orientation, $\sigma^{\alpha||}{}_{\mathrm{i}} = \sigma^{||}{}_{\mathrm{b}} + \sigma^{\alpha}{}_{\mathrm{in(i)}}$. Entirely analogous expressions apply for solute i in solvent β. Combining these expressions leads to *observed* shift differences for the solute in the two solvents.

$$\sigma^{\beta\perp}{}_{\mathrm{i}} - \sigma^{\alpha\perp}{}_{\mathrm{i}} = (2/3)\pi(\chi^{\beta}{}_{\mathrm{V}} - \chi^{\alpha}{}_{\mathrm{V}}) + \sigma^{\beta}{}_{\mathrm{in(i)}} - \sigma^{\alpha}{}_{\mathrm{in(i)}} \tag{5a}$$

$$\sigma^{\beta||}{}_{\mathrm{i}} - \sigma^{\alpha||}{}_{\mathrm{i}} = -(4/3)\pi(\chi^{\beta}{}_{\mathrm{V}} - \chi^{\alpha}{}_{\mathrm{V}}) + \sigma^{\beta}{}_{\mathrm{in(i)}} - \sigma^{\alpha}{}_{\mathrm{in(i)}} \tag{5b}$$

From (5a) and (5b) it is apparent that

$$\sigma^{\beta}{}_{\mathrm{in(i)}} - \sigma^{\alpha}{}_{\mathrm{in(i)}} = (1/3)[\sigma^{\beta||}{}_{\mathrm{i}} - \sigma^{\alpha||}{}_{\mathrm{i}} + 2(\sigma^{\beta\perp}{}_{\mathrm{i}} - \sigma^{\alpha\perp}{}_{\mathrm{i}})] \tag{6}$$

solely in terms of the observed shift differences for the two geometries with the volume susceptibility term eliminated.

The experimental procedure was simply to place in the nmr tube a capillary containing a solution of solute i in solvent α (or pure solute, if that is the desired reference) and to fill the tube with a solution of the same solute in solvent β. The chemical shift difference between the resonances of the desired nucleus (the technique has so far been applied directly only to hydrogen) of the solute in the two solutions was measured on a standard electromagnet system and on a superconducting solenoid system.

Hydrogen shifts with the applied magnetic field parallel to the sample axis were obtained relative to a capillary of pure TMS at 220 MHz on a Varian Associates HR 220 spectrometer. The field-perpendicular shifts were measured on a Varian A60-A operating at 60 MHz. Through eq 6, these pairs of hydrogen resonance positions of TMS for each solvent can be combined to yield "intrinsic" hydrogen solvent shifts, $\Delta\sigma_{\mathrm{H(TMS)}}$, relative to pure TMS, free of bulk susceptibility influences and precise to ±0.02 ppm or better; they represent the shifts which would be obtained if "perfect" susceptibility corrections could be applied to externally referenced chemical shifts. This procedure was applied to 20 vol % TMS solutions in a systematic series of over 30 halogenated benzenes and cyclohexanes as solvents; also employed as solvents were a few methylbenzenes and several additional liquids. For these experiments precision 5-mm (o.d.) nmr tubes (Wilmad "Royal Imperial" grade) were used. In them were positioned precision 1.2-mm (o.d.) capillaries filled with pure TMS reference. These capillaries were held in place, accurately concentric with the nmr tube, by carefully cut Teflon spacers. The assemblies were checked for imperfections by holding them up to a light source and observing them while they were rotated. Further evidence of the quality of these homemade coaxial cells was manifested by the rather low intensity of spinning side bands observed on either spectrometer (Varian HR 220 or A60-A). Spinning side bands are inevitable for concentric cylinder sample cells, as demonstrated, *e.g.*, by Malinowski and coworkers.[30,31] A particular sample was run in the same cell assembly on both spectrometers, undisturbed between experiments, to further assure accurate results.

A few checks were made on the reliability of this method of circumventing the bulk susceptibility problem. If the method is accurate, the same results should be obtained whether the solution is in the main tube and the pure solute (as reference) in the capillary (as the samples were normally run) or *vice versa*. In the somewhat extreme cases of benzene solvent and iodocyclohexane solvent, we sealed the 20% TMS solutions in the capillary and placed the pure TMS in the annular region. Measurements of TMS resonance positions in these samples gave the same results within experimental error (less than ±0.02 ppm) as did shift measurements on the normal samples.

An additional check was performed. Pure TMS in both the main tube and capillary should give a net (intrinsic) shift of 0 ppm if the method of Becconsall, Daves, and Anderson[16] is successful in removing bulk susceptibility effects. An actual check, under conditions of optimum spectrometer resolution, on a pure TMS sample gave a hydrogen shift of 0.00 ± 0.01 ppm.

Probe temperatures of all three spectrometers used in these experiments were within 2 of 40°. The slight individual temperature

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(26) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1970).

(27) R. Scholl, G. E. Maciel, and W. K. Musker, *J. Amer. Chem. Soc.*, **94**, 6376 (1972).

(28) The term "reference independent" is not strictly appropriate to our method of obtaining these shifts since the ^{1}H shifts of TMS reported herein were obtained relative to a capillary of pure TMS. We prefer the term "intrinsic" to "reference independent" as applied to solvent shifts.

(29) W. C. Dickinson, *Phys. Rev.*, **81**, 717 (1951).

(30) R. F. Spanier, T. Vladimiroff, and E. R. Malinowski, *J. Chem. Phys.*, **45**, 4355 (1966).

(31) E. R. Malinowski and A. R. Pierpaoli, *J. Magn. Resonance*, **1**, 509 (1969).

Table I. Apparent and Intrinsic Solvent Shifts of ^{1}H, ^{13}C, and ^{29}Si Resonances of TMS and ^{1}H and ^{13}C Resonances of Cyclohexane[a]

Solvent	$\Delta\sigma^a{}_{C(TMS)}$ [b]	$\Delta\sigma_{H(TMS)}$ [c]	$\Delta\sigma_{C(TMS)}$ [d]	$\Delta\sigma_{Si(TMS)}$ [e]	$\Delta\sigma^a{}_{C(CHX)}$ [f]	$\Delta\sigma_{H(CHX)}$ [g]	$\Delta\text{-}\delta_{C(TMS-CHX)}$ [h]	$[\Delta\text{-}\sigma^a{}_{C(TMS)} - \Delta\sigma^a{}_{C(CHX)}$ [i]$]$	$\Delta\text{-}\sigma_{C(CHX)}$ [j]	$\Delta\text{-}\sigma'_{C(CHX)}$ [k]
Hexafluorobenzene	1.75	0.33	2.08	0.38	0.27	0.37	28.97	28.97	0.52	0.64
2-Butyne	0.63	−0.10	0.53		−0.072	−0.04	28.06	28.19	−0.02	−0.11
Fluorobenzene	0.036	0.27	0.31	0.32	0.048	0.34	27.49	27.50	0.23	0.39
Cyclohexane	0.16	−0.036	0.12	−0.05		0	27.55	27.65	−0.02	
Acetone	0.088	0.03	0.12			0.08	27.54		−0.01	
p-Fluorotoluene	0.056	0.224	0.28		0.036	0.20	27.47	27.51	0.22	0.24
TMS		0.00	0.00				27.41			
o-Fluorochlorobenzene	−0.105	0.21	0.11		−0.036	0.30	27.39	27.42	0.13	0.26
p-Xylene	−0.13	0.24	0.11		−0.048	0.30	27.37	27.41	0.15	0.25
Toluene	−0.14	0.26	0.12		−0.057	0.32	27.39	27.41	0.14	0.26
1,2,4-Trimethylbenzene	−0.16	0.22	0.062	0.28	−0.060	0.20	27.39	27.39	0.08	0.14
Methylene chloride	−0.175	−0.08	−0.26		0.008	−0.03	27.40	27.30	−0.25	−0.02
Benzene	−0.26	0.30	0.04	0.49	−0.060	0.37	27.28	27.29	0.17	0.31
Chlorocyclohexane	−0.26	−0.085	−0.35	−0.10	−0.072	−0.05	27.29	27.30	−0.23	−0.12
m-Chlorotoluene	−0.33	0.17	−0.16		−0.088	0.26	27.22	27.25	0.03	0.17
o-Chlorotoluene	−0.34	0.20	−0.13		−0.11	0.30	27.27	27.26	0.01	0.19
p-Chlorotoluene	−0.37	0.17	−0.20		−0.088	0.26	27.23	27.21	−0.02	0.17
Pyridine	−0.34	0.34	0.00	0.48	−0.056	0.44	27.12	27.21	0.38	0.38
m-Fluorobromobenzene	−0.36	0.14	−0.22		−0.10	0.23	27.20	27.23	−0.01	0.13
Chlorobenzene	−0.42	0.20	−0.22	0.33	−0.11	0.29	27.16	27.18	0.03	0.18
3,4-Dichlorotoluene	−0.46	0.11	−0.35		−0.15	0.20	27.21	27.18	−0.15	0.05
o-Dichlorobenzene	−0.50	0.15	−0.35	0.30	−0.16	0.25	27.13	27.15	−0.07	0.09
Bromocyclohexane	−0.51	−0.11	−0.62	−0.11	−0.16	−0.07	27.16	27.14	−0.37	−0.23
Chloroform	−0.53	−0.14	−0.67		0.016	−0.09	27.07	26.94	−0.33	−0.07
1,2,4-Trichlorobenzene	−0.59	0.068	−0.52	0.18	−0.19	0.15	27.06	27.09	−0.17	−0.04
o-Bromotoluene	−0.62	0.17	−0.45		−0.20	0.26	27.04	27.07	−0.08	0.06
Bromobenzene	−0.68	0.17	−0.51	0.33	−0.22	0.26	26.99	27.03	−0.09	0.04
Carbon disulfide	−0.77	−0.23	−1.00		−0.63	−0.15	27.33	27.35	−1.02	−0.78
m-Chlorobromobenzene	−0.75	0.077	−0.67		−0.25	0.18	26.95	26.99	−0.21	−0.07
Carbon tetrachloride	−0.82	−0.16	−0.98		−0.036	−0.14	26.88	26.71	−0.45	−0.18
m-Fluoroiodobenzene	−0.90	0.13	−0.77		−0.30	0.23	26.85	26.89	−0.22	−0.07
Iodocyclohexane	−0.97	−0.15	−1.12	−0.15	−0.26	−0.10	26.82	26.78	−0.53	−0.36
m-Dibromobenzene	−1.00	0.039	−0.96		−0.33	0.14	26.78	26.82	−0.33	−0.19
m-Iodotoluene	−1.05	0.090	−0.96		−0.33	0.18	26.75	26.77	−0.30	−0.15
Iodobenzene	−1.24	0.11	−1.13	0.27	−0.39	0.20	26.60	26.64	−0.32	−0.19
o-Chloroiodobenzene	−1.27	0.80	−1.19		−0.43	0.18	26.63	26.65	−0.41	−0.25
1,2,4-Tribromobenzene	−1.28	0.035	−1.14		−0.44	0.14	26.59	26.65	−0.32	−0.30
m-Bromoiodobenzene	−1.48	0.014	−1.49	0.11	−0.50	0.09	26.45	26.51	−0.53	−0.41
m-Diiodobenzene	−1.90	−0.002	−1.90		−0.62	0.06	26.24	26.21	−0.73	−0.56

[a] Shifts in ppm with respect to the resonance of the appropriate nuclide in the pure liquid (TMS or cyclohexane). [b] Apparent ^{13}C shift of TMS (20 vol %) obtained as described in the Experimental Section. [c] Intrinsic ^{1}H shift of TMS (20 vol %) obtained as described in the Experimental Section. [d] Intrinsic ^{13}C shift of TMS, $\Delta\sigma_{C(TMS)} = \Delta\sigma^a{}_{C(TMS)} + \Delta\sigma_{H(TMS)}$. [e] Intrinsic ^{29}Si shift of TMS (20 vol %), $\Delta\sigma_{Si(TMS)} = \Delta\sigma^a{}_{Si(TMS)} + \Delta\sigma_{H(TMS)}$. [f] Apparent ^{13}C shift of cyclohexane (20 vol %) obtained as described in the Experimental Section. [g] Intrinsic ^{1}H shift of cyclohexane (2 vol %) in a ternary mixture with 20 vol % TMS and 80 vol % solvent; obtained from $\sigma_{H(TMS)}$, as described in the text. [h] Directly observed ^{13}C shift difference between TMS and cyclohexane in a ternary solution that contains 20 vol % TMS and 2 vol % cyclohexane in a solvent. [i] Difference between apparent ^{13}C shifts of a solution that contains 20 vol % TMS in a solvent and another solution that contains 20 vol % cyclohexane in the same solvent. These shift differences have all been altered by 27.49 ppm so that the value for hexafluorobenzene solvent equals 28.97 ppm, the observed value of $\Delta\delta_{C(TMS)-CHX}$. [j] Intrinsic ^{13}C shift of cyclohexane in a ternary solution that contains 2 vol % cyclohexane and 20 vol % TMS in a solvent; obtained from $\Delta\delta_{C(TMS)}$ and $\Delta\delta_{C(TMS-CHX)}$ as described in the text. [k] Intrinsic ^{13}C shift of cyclohexane, based upon $\Delta\sigma^a{}_{C(CHX)}$ obtained on binary solutions of 20 vol % cyclohexane in each solvent, and upon $\Delta\sigma_{H(CHX)}$ values.

differences are considered to contribute negligible error to the measurements.

The samples were not vacuum degassed. A few were purged with dry nitrogen gas; they gave the same ^{1}H and ^{13}C resonance positions within experimental error as did similar unpurged samples.

Results and Discussion

(1) Intrinsic Shifts. The intrinsic carbon shifts of TMS, depending only on solvent effects of that nucleus, are derived simply by adding the intrinsic hydrogen solvent shifts, $\Delta\sigma_{H(TMS)}$, to the apparent carbon shifts, $\Delta\sigma^a{}_{C(TMS)}$, determined as described above. The intrinsic ^{1}H and ^{13}C solvent shifts of cyclohexane were derived from hydrogen and carbon chemical shift differences between solutions containing 20 vol % TMS and 2 vol % cyclohexane in each solvent. (It was determined that the addition of 2% cyclohexane did not affect the TMS resonance positions by rerunning several TMS carbon spectra after addition of cyclohexane and noting the TMS ^{13}C shifts were the same as before.) The intrinsic hydrogen shifts of cyclohexane were arrived at by first measuring the hydrogen shift differences between 20 vol % TMS and 2 vol % cyclohexane in each solvent. Through knowledge of the intrinsic solvent shift, $\Delta\sigma_{H(TMS)}$, these measurements yielded intrinsic hydrogen shifts of cyclohexane relative to TMS. These shifts were rereferenced to the hydrogen resonance of 2% cyclohexane in TMS, at 0 ppm, by subtracting 1.44 ppm from the shifts referenced to TMS (1.44 ppm is the measured hydrogen shift difference between TMS and cyclohexane in a 2 vol % solution of cyclohexane in TMS). These intrinsic cyclohexane hydrogen shifts are designated $\Delta\sigma_{H(CHX)}$ in Table I.

Intrinsic carbon shifts for cyclohexane were obtained by first measuring the ^{13}C shift difference between cyclohexane and TMS in ternary solutions containing 2 vol % cyclohexane and 20 vol % TMS in each solvent for which values of $\Delta\sigma_{C(TMS)}$ were measured. By knowing the intrinsic carbon shift, $\Delta\sigma_{C(TMS)}$, of TMS (obtained as described above) we could at this point obtain intrinsic ^{13}C shifts of 2% cyclohexane in 20% TMS to 80% solvent, by simple addition. These shifts were in effect referenced to cyclohexane (2% in TMS as solvent) by subtracting the carbon shift difference of this mixture (−27.41 ppm, the minus sign indicating that cyclohexane is less shielded than TMS) from the observed cyclohexane (2%)–TMS (20%) shift differences in the various solvents. The resulting intrinsic cyclohexane ^{13}C solvent shifts, $\Delta\sigma_{C(CHX)}$, are tabulated in Table I. This approach to ^{13}C cyclohexane shifts is quite analogous to our route to ^{1}H cyclohexane shifts. It provides data that included the effect of 20% TMS in the solution.

An alternate approach to intrinsic ^{13}C shifts in cyclohexane makes use of the apparent carbon solvent shift (with respect to the cyclohexane proton resonances) in 20% solutions of cyclohexane in the solvents. This number is corrected for solvent effects on the cyclohexane protons by simply adding the latter to the apparent cyclohexane shifts, $\Delta\sigma^{a}{}_{C(CHX)}$. The intrinsic shift of the cyclohexane proton, $\Delta\sigma_{H(CHX)}$, was derived from $\Delta\sigma_{H(TMS)}$ as described above. This approach, completely analogous to the derivation of $\Delta\sigma_{C(TMS)}$, gives intrinsic shifts, $\Delta\sigma^{1}{}_{C(CHX)}$, which differ from the first approach described by a roughly constant 0.12–0.15 ppm (to higher shielding). This difference is associated with the fact that 20% TMS was present in the determination of $\Delta\sigma_{H(CHX)}$, but not in the determination of $\Delta\sigma^{a}{}_{C(CHX)}$; however, the exact origin of this difference is not known. The $\Delta\sigma^{1}{}_{C(CHX)}$ values depend on comparing apparent carbon shifts of 20% cyclohexane solutions in a particular solvent with hydrogen shifts of 2% cyclohexane solutions in 20% TMS–80% solvent; whereas $\Delta\sigma_{C(CHX)}$ depends *only* on 2% cyclohexane solutions in 20% TMS–80% solvent. This convention has the advantage of self-consistency, and for that reason we have chosen it over the other convention (leading to $\Delta\sigma^{1}{}_{C(CHX)}$), for the following discussion.

As indicated above, the intrinsic solvent shifts are referenced to pure TMS in the case of the TMS nuclides, or to 2 vol % cyclohexane in TMS for the cyclohexane shifts. Therefore, these shifts differ from "absolute" solvent shifts, relative to the gas phase at zero pressure, by constants which are different for each nucleus. While we cannot specify *absolute* solvent shifts involving different nuclei, it is, nevertheless, valid to discuss the data in terms of shift *differences*, for example, in assessing sensitivities to solvent changes or comparing shift ranges.

(2) General Trends. The "intrinsic" solvent shifts for the three nuclides of TMS and the two of cyclohexane are tabulated in Table I, along with the "apparent" ^{13}C shifts in these two solutes and the hydrogen and carbon shift differences between TMS and cyclohexane. Table I comprises halogenated benzenes and cyclohexanes and several other common solvents on which intrinsic solvent shifts were determined. The "corrected" or intrinsic ^{13}C shifts roughly parallel the apparent shifts in both TMS and cyclohexane. Apparent ^{13}C shifts of TMS and cyclohexane and TMS–cyclohexane ^{13}C shift differences in 54 additional aromatic and nonaromatic solvents are presented in Table II. The solvents of Table I represent a systematic series which we have characterized more fully, since they might be expected to reflect a certain few contributions to the observed solvent shifts, as discussed below.

The total range of ^{13}C TMS solvent shifts is about 4 ppm, with pure TMS nearly in the center of the range, at arbitrary zero. The ^{13}C shifts of cyclohexane span only roughly one-third that range, although they tend to parallel the TMS ^{13}C solvent shifts. Seemingly, cyclohexane is less sensitive to carbon solvent effects than TMS (however, see below). On the other hand, the protons of both solvents show about an equal sensitivity to solvent effects, the hydrogen shifts ranging over about 0.6 ppm. These shifts are also roughly parallel.

Plots of $\Delta\sigma_{C(TMS)}$ *vs.* $\Delta\sigma_{H(TMS)}$ (see Figure 1 of ref 17) and $\Delta\sigma_{C(CHX)}$ *vs.* $\Delta\sigma_{H(CHX)}$ (Figure 1 of this paper) for monohalobenzene (and benzene itself) and monohalocyclohexane (and cyclohexane itself) solvents suggest two distinct solvent shift correlations, one involving the aromatic solvents and the other cyclohexane solvents. (If the polyhalobenzenes were included, the correlation coefficient of the "correlation" associated with the monohalobenzenes would deteriorate, although the slope of this correlation would not be significantly altered.) An overall picture begins to emerge when a plot of $\Delta\sigma_{Si(TMS)}$ *vs.* $\Delta\sigma_{H(TMS)}$ (Figure 2 of ref 17) is also considered. Two distinct patterns are revealed: (1) $\Delta\sigma_{C(TMS)}$ is much more sensitive than the other four solvent shift quantities to the identity of the halogen X within a given solvent series RX (*i.e.*, for a given R, C_5H_5, or C_6H_{11}); and (2) $\Delta\sigma_{C(TMS)}$ is much less sensitive than the other nuclide shifts to the identity of R. Pattern 1 seems quite reasonable in the light of the greater responsiveness of ^{13}C and ^{29}Si shieldings than hydrogen shieldings to typical variations of electron distribution,[24,27,32,33] and the relative remoteness of silicon in TMS from the source of solvent–solute

(32) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(33) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I and II, Pergamon Press, Oxford, 1966.

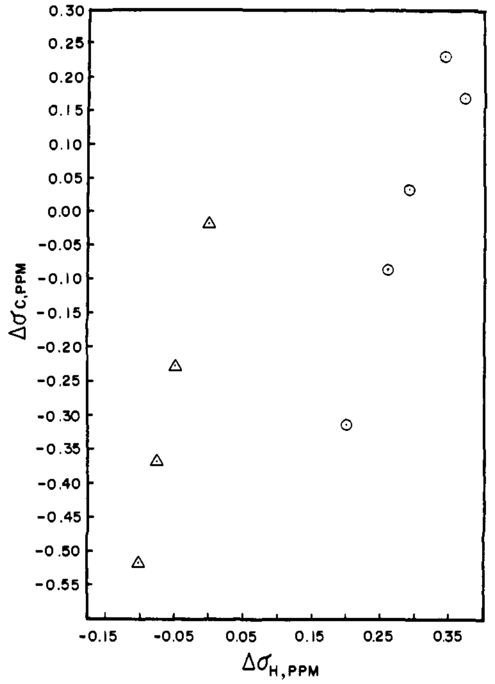

Figure 1. Plot of intrinsic carbon solvent shifts *vs.* intrinsic hydrogen solvent shifts of cyclohexane dissolved in iodocyclohexane, bromocyclohexane, chlorocyclohexane, and cyclohexane (these solvents are designated by △ in the figure and listed here in order of increasing $\Delta\sigma_{H(CHX)}$) and in iodobenzene, bromobenzene, chlorobenzene, benzene, and fluorobenzene (these solvents are designated by ⊙ in the figure and listed here in order of increasing $\Delta\sigma_{H(CHX)}$).

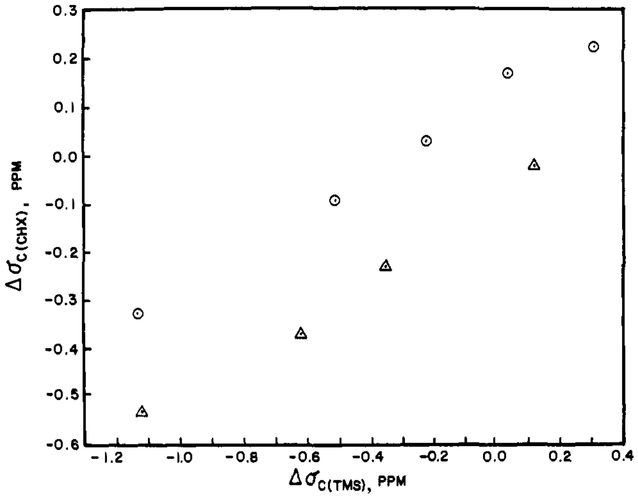

Figure 2. Plot of intrinsic carbon solvent shifts of cyclohexane *vs.* those of TMS dissolved in iodocyclohexane, bromocyclohexane, chlorocyclohexane, and cyclohexane (these solvents are designated by △ in the figure and listed here in order of increasing $\Delta\sigma_{C(CHX)}$) and in iodobenzene, bromobenzene, chlorobenzene, benzene, and fluorobenzene (these solvents are designated by ⊙ in the figure and listed here in order of increasing $\Delta\sigma_{C(CHX)}$).

Table II. Apparent Carbon-13 Solvent Shifts of TMS and Cyclohexane and Carbon-13 Chemical Shift Differences between TMS and Cyclohexane Dissolved in Various Organic Solvents[a]

Solvent	$\Delta\sigma^{a}{}_{C(TMS)}$[b]	$\Delta\sigma^{a}{}_{C(CHX)}$[c]	$\Delta\delta_{TMS-CHX}$[d]
Perfluorocyclohexane	1.45		28.49
Methanol	0.51	0.24	27.90
α,α,α-Trifluorotoluene	0.50		27.95
Acetic acid (glacial)	0.39		27.78
Nitroethane	0.41		27.77
Ethyl acetate	0.31		27.60
Acetonitrile	0.30	0.080	27.63
Ethanol (absolute)	0.28		27.51
n-Hexane	0.19		27.78
n-Propylamine	0.19		27.61
Tetrahydrofuran	0.15		27.64
Cyclohexene	0.14		27.64
2,2-Dimethylallene	0.12		
o-Fluorotoluene	0.067	0.028	27.50
Propionitrile	0.059		27.53
n-Heptane	0.049		27.58
m-Fluorotoluene	0.044	0.044	27.52
Triethylamine	0.020		27.45
2-Chloropropane	0.008		27.41
1,4-Dioxane	−0.072	0.14	27.39
m-Fluorochlorobenzene	−0.096		27.39
N,*N*-Dimethylformamide	−0.107		26.78
Nitrobenzene	−0.13	0.095	27.39
Cyclohexanone	−0.15		
Ethylbenzene	−0.18		27.35
Anisole	−0.21		27.30
1,2,3-Trimethylbenzene	−0.21	−0.088	27.36
sec-Butylbenzene	−0.24		
Indan	−0.27		27.29
Isopropylbenzene	−0.27		27.24
Norbornadiene	−0.27		27.11
p-Diisopropylbenzene	−0.30		27.14
Cyclopropylbenzene	−0.33		27.26
2-Bromopropane	−0.38		
tert-Butylbenzene	−0.39		
p-Fluorobromobenzene	−0.39		
2,4-Dichlorotoluene	−0.43		
Benzonitrile	−0.43	−0.088	27.11
Ethyl isothiocyanate	−0.45	−0.155	27.17
Benzaldehyde	−0.45	−0.068	27.00
N,*N*-Dimethylaniline	−0.47		27.15
Phenol	−0.48		27.08
Dimethylbenzyl alcohol	−0.53		26.96
Aniline	−0.62	−0.16	27.02
m-Bromotoluene	−0.63	−0.20	27.03
p-Bromotoluene	−0.63	−0.21	27.03
p-Fluoroiodobenzene	−0.88	−0.29	
Ethyl iodide	−0.92	−0.24	26.79
o-Dibromobenzene	−0.99	−0.37	26.84
o-Iodotoluene	−1.06	−0.36	26.75
Methyl iodide	−1.11	−0.42	26.84
m-Chloroiodobenzene	−1.26	−0.42	26.62
p-Chloroiodobenzene	−1.27	−0.39	26.63
o-Diiodobenzene	−1.95	−0.65	26.22

[a] Shifts in ppm with the resonance of the appropriate nuclide of the pure liquid (TMS or cyclohexane) at 0.00 ppm. [b] Apparent ^{13}C shift of TMS (20 vol %) obtained as described in the Experimental Section. [c] Apparent ^{13}C shift of cyclohexane (20 vol %) obtained as described in the Experimental Section. [d] ^{13}C shift difference between cyclohexane (2 vol %) and TMS (20 vol %) in the same sample.

interactions. The pattern of dependence of the solvent shifts on the identity of the halogen substituent in the solvent fits in with the findings of Spiesecke and Schneider[19] and Becconsall and Hampson[20] that solvents with heavier halogens (Br and I) strongly decrease the shielding of the carbon of the methyl iodide solute. Evans found similar effects in ^{19}F solvent shifts.[34] Pattern 2 appears to be consistent with an effect which operates much more strongly in one type of solvent (aromatic or saturated) than the other and which causes an increase in shielding of about 0.3 to 0.5 ppm for ^{1}H, ^{13}C, and ^{29}Si in these solutes when the solvent hydrocarbon skeleton is changed from cyclohexyl to phenyl. This observation is quite consistent with a solvent "ring current" diamagnetic anisotropy, which is believed to be prominent in aromatic systems.[3,4,32,33] This effect

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(34) D. F. Evans, *J. Chem. Soc.*, 877 (1960).

has been shown by Becconsall[35] and Rummens[36] to be constant at all points within the (approximately spherical) solute molecule and to be independent of the nuclide under consideration. (However, solvent anisotropy effects do depend on solute size.[35]) This roughly constant shielding effect by benzene-type solvents is not so clearly reflected in $\Delta\sigma_{C(TMS)}$ as it is in the other four groups of $\Delta\sigma$'s. Figure 2, a plot of $\Delta\sigma_{C(CHX)}$ *vs.* $\Delta\sigma_{C(TMS)}$, demonstrates this point. Whereas the cyclohexane carbon shielding increases by a roughly constant 0.27 ppm when R is changed from C_6H_{11} to C_6H_5, the TMS carbon shielding increases slightly (~0.11 ppm) for Cl and Br substituents, but *decreases* when X is H or I. This figure also dramatizes the nearly threefold higher overall sensitivity of the TMS carbon resonance, compared with the cyclohexane carbon resonance, to a change in X. The comparatively great sensitivity of cyclohexane to a change in solvent carbon framework suggests that TMS should be the better ^{13}C internal reference for studies involving different hydrocarbon frameworks, at least if both aromatic and saturated hydrocarbon skeletons are involved. Conversely, cyclohexane seems to have a marked superiority over TMS for substituent effect studies. In Figure 3 are plotted hydrogen shifts of cyclohexane *vs.* those of TMS. This distribution of points shows that the hydrogen resonances of the two solutes are about equally responsive to a change of X (note the nearly unity slope of the correlations), whereas, for a given substituent X, cyclohexane hydrogens show a slightly but significantly higher sensitivity than those of TMS to the identity of R; specifically, phenyl seems to increase the shielding of the hydrogens of cyclohexane relatively slightly more than those of TMS.

We find that halogen substituents on a given solvent framework tend to decrease the shielding of the hydrogens and carbons of TMS and cyclohexane and, less dramatically, the silicon of TMS as either (a) one progresses to the heavier halogens in RX as solvent (although substitution of fluorine for hydrogen on benzene gives an increased solvent shielding effect on the solute ^{13}C resonances), or (b) (again except for fluorine) more halogens of a given type are substituted. For example, in the halobenzenes, the hydrogen and carbon shieldings of the solute decrease monotonically from fluorobenzene to iodobenzene. Similarly, the shieldings decrease as the solvent is changed, *e.g.*, from methylene chloride to chloroform to carbon tetrachloride, or from chlorobenzene to *o*-dichlorobenzene to 1,3,4-trichlorobenzene. In short, the ^1H and ^{29}Si trends parallel the ^{13}C trends (although, as already shown, with rather less sensitivity) and are quite in accord with the findings of other workers.[2,11,13–15] Highly striking is the *shielding* effect bestowed on solute carbons by solvent fluorine substituents. The intrinsic ^{13}C shift of TMS in hexafluorobenzene is 2.08 ppm with respect to pure TMS, by far the largest carbon shielding effect we have observed. The comparable cyclohexane shielding is 0.52 ppm. Also, the relative (uncorrected) ^{13}C shift of TMS in perfluorocyclohexane is 1.45 ppm. Pronounced increases in shielding are also conferred by fluorinated solvents on ^{19}F shifts.[34] Note from Table II that fluorine substituents apparently do not increase the shielding of the hydrogens of TMS and cyclohexane as they do the carbons.

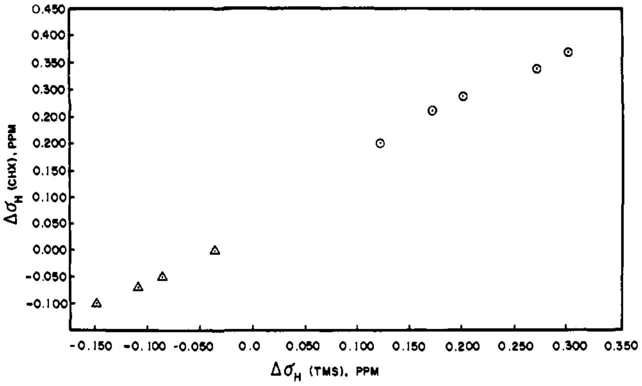

Figure 3. Plot of intrinsic hydrogen solvent shifts of cyclohexane *vs.* those of TMS dissolved in iodocyclohexane, bromocyclohexane, chlorocyclohexane, and cyclohexane (these solvents are designated by △ in the figure and listed here in order of increasing $\Delta\sigma_{C(CHX)}$) and in iodobenzene, bromobenzene, chlorobenzene, benzene, and fluorobenzene (these solvents are designated by ⊙ in the figure and listed here in order of increasing $\Delta\sigma_{H(CHX)}$).

Raynes[37] has found a pronounced additivity effect in the solvent shifts of methane dissolved in halogenated methane solvents. Our intrinsic solvent shifts also show a definite additivity. Subtracting the benzene solvent shift on a given solute nucleus from the solvent shift conferred by a monosubstituted benzene yields a localized (atomic or bond) parameter for that substituent which can be used to estimate the solvent shift in the di- and trihalobenzenes included in our study. That is, for the estimated shift in a disubstituted benzene

$$\Delta\sigma^{C_6H_4XY} = \Delta\sigma^{C_6H_5H} + (\Delta\sigma^{C_6H_5X} - \Delta\sigma^{C_6H_5H}) + (\Delta\sigma^{C_6H_5Y} - \Delta\sigma^{C_6H_5H}) \quad (7)$$

where $\Delta\sigma^{C_6H_5H}$, $\Delta\sigma^{C_6H_5X}$, and $\Delta\sigma^{C_6H_5Y}$ are the solvent shifts in benzene and in the two monosubstituted benzenes, respectively. An analogous expression holds for the trisubstituted case. Calculations based upon additivity equations yield results within 20% of the observed shifts in most cases. All of the observed trends are reflected in the additivity estimates, suggesting that, whatever effects are at the root of substituent contributions to the solvent shifts of this study, they are relatively nonspecific as to structural details of solute and solvent. The similarity of shifts in different isomers of a particular di- or trisubstituted benzene solvent (see Tables I and II) also supports this contention. Raynes[38] has characterized a similar additivity in solvent effects on spin–spin coupling constants.

Included in both Tables I and II are differences between observed apparent shifts of 20% TMS in a particular solvent and 20% cyclohexane in the same solvent (determined in separate binary solutions). A strong correlation should exist between this shift difference and the directly observed shift differences $\Delta\delta_{C(TMS-CHX)}$ for 20% TMS–2% cyclohexane ternary solutions, if our shift determinations are self-consistent, and in the absence of important specific binary or ternary interactions. Such a correlation is indeed manifested between these two sets of shift differences. It is not sur-

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(35) (a) J. K. Becconsall, *Mol. Phys.*, **15**, 129 (1968); (b) *ibid.*, **18**, 337 (1970).

(36) F. H. A. Rummens, *ibid.*, **19**, 423 (1970).

(37) W. T. Raynes, *J. Chem. Phys.*, **51**, 3138 (1969).

(38) W. T. Raynes, *Mol. Phys.*, **15**, 435 (1968).

prising that the correspondence is not perfectly monotonic, since the differences between apparent shifts include both hydrogen and carbon solvent effects, whereas $\Delta\delta_{C(TMS-CHX)}$ reflects only carbon solvent effects.

As is the case in Table I, the apparent carbon solvent shifts of cyclohexane in Table II display decidedly less overall sensitivity (in the solvents in which they were measured) than those of TMS. For those solvents in which carbon shifts of both solutes were measured, the TMS shifts span about 1.75 ppm, while the cyclohexane shifts cover approximately 0.90 ppm. Consistent with this greater TMS sensitivity to solvent is the observation that the measured ^{13}C shift differences between the two solutes are largest in those solvents in which the TMS carbon is apparently most shielded relative to a pure TMS reference (*e.g.*, 2-butyne or methanol; see hexafluorobenzene of Table II for a particularly striking example) and smallest in the solvents where TMS is least shielded relative to a pure TMS reference (methyl and ethyl iodide). That is, as the apparent TMS carbon shieldings decrease so do those of cyclohexane, although rather more slowly. The trends of the two solutes are monotonic; however, the excursion of apparent ^{13}C shifts of TMS is about twice that of cyclohexane.

Laszlo, *et al.*,[10] have carried out a study of hydrogen shifts of cyclohexane relative to TMS as an internal standard. As already indicated, these workers found relatively smaller shift differences between cyclohexane and TMS in aromatic solvents than in nonaromatic solvents. That is, cyclohexane moves to higher shielding (smaller shift difference) by about 0.07 ppm relative to TMS in substituted benzene solvents. We also observe a decrease in hydrogen shift difference of 0.07 ppm (see Table I). The data of Laszlo, *et al.*, do not permit one to pinpoint the origin of these decreased hydrogen shift differences, since the internal referencing procedure can only give solute (cyclohexane) shifts relative to the internal standard (TMS); nevertheless, it is plausible that the hydrogen shielding of TMS is relatively less in aromatic solvents than the hydrogen shielding of nonpolar hydrocarbon solutes, because TMS shows the same apparently decreased shielding with respect to all the hydrocarbon solutes, including cyclohexane, examined by Laszlo and coworkers.[10] It is believed that weak complexation of a small, nonpolar solute with an aromatic solvent slightly attenuates (by 0.05–0.10 ppm) the ring current-induced shielding on that solute.[3] Our results offer two pieces of evidence which are consistent with (but do not demand) the view[10] that TMS has a slight tendency to complex with aromatic solvents. One of these results is our observation that the hydrogen signal of TMS typically experiences a greater reduction of shielding in aromatic solvents (relative to nonaromatic solvents) than does cyclohexane (see Table II and Figure 3). The other observation involves some preliminary variable-temperature experiments in iodobenzene solvent, observing the *apparent* ^{13}C shift (*vide supra*), $\Delta\sigma^a{}_C$, of TMS and cyclohexane. While $\Delta\sigma^a{}_{C(TMS)}$ monotonically decreases with decreasing temperature (reflecting either a dominant increasing hydrogen or a decreasing ^{13}C shielding or both), $\Delta\sigma^a{}_{C(CHX)}$ remains constant within experimental error (± 0.02 ppm) over the entire temperature range (40 to $-50°$). Although an increasing TMS hydrogen shielding with temperature is consistent with the idea of complex formation,[3] the 0.25-ppm decrease observed is probably too large to be due solely to a change in hydrogen shielding. The very fact that $\Delta\sigma^a{}_{C(TMS)}$ has a significant temperature variation, whereas $\Delta\sigma^a{}_{C(CHX)}$ does not, suggests that the carbons of TMS are responding to a special situation, *e.g.*, complex formation.

(3) Dominant Solvent–Solute Interactions. The common belief[3,8,12] is that in solutions involving nonpolar, relatively unpolarizable solutes, such as the two employed in this study, the solvent effect observed by nmr is made up of two contributions: dispersion interaction and neighbor-molecule anisotropy. A third contribution, the polar effect arising from dipole-induced dipole interactions between solute and a polar solvent, could be present in the more polar solvents of Table I.[2,6,7,15,36] However, this effect is expected to be overshadowed by dispersion and anisotropy effects in halobenzenes and cyclohexanes. The present goal is to attempt to determine whether dispersion and anisotropy are, indeed, the dominant solvent effects between TMS or cyclohexane and the solvents of Table I. If so, we seek to ascertain the relative importance of these two solvent contributions in the various solvents of this study, and to gauge the relative responses to these contributions of the several nuclei in TMS and cyclohexane. Since we have solvent shift data for the several nuclei of these two particular solutes, we anticipate mapping the sensitivities of different regions of the solute molecules to the dominant solvent-shift influences in these systems.

A particularly appropriate avenue to these goals is a statistical technique called factor analysis.[9,15,39] This approach has been widely used by social scientists and statisticians for many decades to extract a small number of controlling trends from a large body of data, and from these trends to predict numbers missing from the data. Recently Malinowski and coworkers[9,15] have demonstrated the value of the formalism in analyzing solvent shifts for dominant contributions. The present work includes the application to our shift data (Table II) of a factor analysis scheme similar to that employed by Malinowski, *et al.*[9,15]

Essentially the use of factor analysis involves the following steps: (a) formation from the data matrix, **S**, of experimental data of a "correlation matrix," **C**, which cross-correlates the various elements of the data matrix to reflect the dominant trends in the data; (b) diagonalization of the correlation matrix and solution of the resulting eigenvalue problem to determine the significant eigenvectors (associated with "factors") which characterize the data; and (c) rotation of the eigenvectors into the arrays of elements believed to mirror the physically significant solvent–solute interactions expected to be dominant in determining shielding in the systems studied.

Couching the observed solvent shift in the terms introduced by BSS (eq 1) allows the use of factor analysis, provided that each term of the expansion can be written as a product of parameters, one depending only on solute characteristics and the other only on solvent properties. That is, each supposed contribution (dispersion, anisotropy, reaction field, etc.) to the total sol-

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[39] H. H. Harman, "Modern Factor Analysis," 2nd ed (Revised), University of Chicago Press, Chicago, Ill., 1967.

vent effect on shielding must be separable into two components: one hinging only on physical and chemical characteristics of the solvent, the other reflecting the response or sensitivity of the observed solute nuclide to the particular solvent property in question. Thus, we rewrite eq 1 as a sum of products of solute and solvent components

$$\mathbf{S}_{\alpha i} = \mathbf{V}_{\alpha 1}\mathbf{U}_{1i} + \mathbf{V}_{\alpha 2}\mathbf{U}_{2i} + \ldots + \mathbf{V}_{\alpha j}\mathbf{U}_{ji} + \ldots \quad (8)$$

where $\mathbf{V}_{\alpha j}$ is the jth influence of solvent α and $\mathbf{U}_{ji}$ is the "response" of the solute nucleus i to that (the jth) solvent influence. Coupling this with the BSS picture, each term can be identified with a specific kind of interaction (*e.g.*, the first with bulk susceptibility, the second with solvent anisotropy, the third with dispersion interaction, etc.). In matrix notation

$$\mathbf{S} = \mathbf{VU} \quad (9)$$

where **S** is the matrix of observed solvent shifts, **V** is the matrix of solvent contributions (hereafter referred to as the "solvent factor matrix"), and **U** is the matrix of solute nucleus responses (the "solute factor matrix").

The solvent shifts are arrayed in a $m \times n$ matrix, where m is the number of solvents included and n is the combined number of nuclides of TMS and cyclohexane (five if all nuclides are included, four if only ^{1}H and ^{13}C of the two solutes are included). Of the several ways of forming a correlation matrix,[39] we have chosen one of the simplest—multiplying the data matrix **S** by its transpose as follows.

$$\mathbf{C} = \mathbf{SS}^{t} \quad (10)$$

Equation 10 gives a correlation matrix, **C**, of dimension $m \times m$. The elements of **C** in eq 10 are each summed over all solute nuclei through the matrix multiplication process, and the m diagonal elements are each identifiable with a particular solvent. Each off-diagonal element is a sum of pairwise products of solvent effects for two solvents for all solute nuclei. An alternative correlation matrix could be formed according to the definition, $\mathbf{C} = \mathbf{S}^{t}\mathbf{S}$, in which case the diagonal elements are each identifiable with a particular solute. The next step in the approach that we have adopted is to find a matrix **B** which diagonalizes **C**

$$\mathbf{B}^{-1}\mathbf{CB} = [\lambda_j\delta_{jk}] \quad (11)$$

where δ_{jk} is a Kronecker delta and λ_j's are the eigenvalues of the (linear) matrix equation

$$\mathbf{CB}_{\cdot j} = \lambda_j\mathbf{B}_{\cdot j} \quad (12)$$

$\mathbf{B}_{\cdot j}$ is the jth eigenvector, the jth column of **B**. The elements of the diagonalized **C** are the eigenvalues, one associated with each eigenvector. A *factor* is customarily defined as simply a normalized eigenvector multiplied by the square root of the corresponding eigenvalue.[39] The eigenvectors which result from this diagonalization may be thought of as a set of orthonormal "solvent basis vectors," which span the solvent-effect space. They are the result of a transformation from real solvent basis functions, and are the vectors which, by means of a unitary transformation, we shall presently attempt to identify with particular types of solute–solvent interactions.

Formally, j runs from 1 to m. However, if factor analysis is to have any value in our problem, the data must be reproducible in terms of r factors (eigenvectors), where r is less than either m or n, corresponding to r dominant solvent influences on solute shielding. To define solvent and solute factor matrices and to set up the criterion for determining how many factors are necessary to reproduce the data matrix we write, from eq 10 and 11

$$\mathbf{B}^{-1}\mathbf{CB} = \mathbf{B}^{-1}\mathbf{SS}^{t}\mathbf{B} = \mathbf{B}^{t}\mathbf{SS}^{t}\mathbf{B} \quad (13)$$

since **B** is a unitary matrix. Then, the identification

$$\hat{\mathbf{U}} = \mathbf{B}^{t}\mathbf{S} \quad (14)$$

so that

$$\mathbf{B}^{-1}\mathbf{CB} = \hat{\mathbf{U}}\hat{\mathbf{U}}^{t} \text{ and } \mathbf{S} = \mathbf{B}\hat{\mathbf{U}} \quad (15)$$

leads to the identification

$$\mathbf{B} = \hat{\mathbf{V}} \quad (16)$$

in analogy with eq 9. Equation 15 suggests a criterion for reproducing **S** with the minimum number of factors. Let $\{\mathbf{B}\}$ be a "partial" eigenvector matrix having r columns, where r is less than m, the total number of eigenvectors (and the number of columns in **B**). Then, from eq 14 and 15

$$\{\hat{\mathbf{U}}\} = \{\mathbf{B}\}^{t}\mathbf{S} \quad (17)$$

$$\mathbf{S}_r = \{\mathbf{B}\}\{\hat{\mathbf{U}}\} = \{\mathbf{B}\}\{\mathbf{B}\}^{t}\mathbf{S} \quad (18)$$

The goal is to calculate $\mathbf{S}_r$ from eq 18 such that

$$\mathbf{S}_r \simeq \mathbf{S} \quad (19)$$

within experimental error of the observed solvent shifts or within some other arbitrary limits of reproducibility. $\mathbf{S}_r$ is the "approximate" shift matrix obtained by retaining only the r most important eigenvectors in **B**. The smallest r needed to accomplish this goal directly yields the number of factors necessary to account for the input data. The procedure is to start with a $\{\mathbf{B}\}$ that includes only the eigenvector associated with the largest eigenvalue, and obtain from eq 18 a $\mathbf{S}_1$ to be compared with the input **S**. We include an increasing number of successively less important eigenvectors in $\{\mathbf{B}\}$, one at a time, until we have reproduced **S**; *i.e.*, expression 19 holds. The number of eigenvectors necessary to render eq 19 true within our limits of reproducibility is the number of significant trends reflected by the array of solvent shifts, **S**.

Now that the number of controlling factors has been found, the final step in factor analysis is to perform a unitary transformation on $\{\mathbf{B}\}$ such that each significant eigenvector reflects a physically significant solvent-effect contribution. Here is where "chemical intuition" as well as additional scientific input enters for the first time Since the factor analysis calculations yielded only two significant eigenvectors (except for one solvent set), we had recourse to the two-dimensional vector rotator

$$\mathbf{R} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \quad (20)$$

The orthonormal pair of significant eigenvectors, which define a "plane" in the solvent-effect space, were simply rotated through all angles in steps of 5°, and criteria to be discussed below were used to attempt a choice of rotation angle for projecting eigenvectors of greatest

Table III. The Four Shift Matrices Employed in the Factor Analysis Calculations[a]

Solvent	$\Delta\sigma_{H(TMS)}$	$\Delta\sigma_{C(TMS)}$	$\Delta\sigma_{Si(TMS)}$	$\Delta\sigma_{H(CHX)}$	$\Delta\sigma_{C(CHX)}$
1. C_6H_6	0.30	0.04	0.49	0.37	0.17
2. C_6H_5F	0.27	0.31	0.32	0.34	0.23
3. C_6H_5Cl	0.20	−0.22	0.33	0.29	0.03
4. C_6H_5Br	0.17	−0.51	0.33	0.26	−0.09
5. C_6H_5I	0.11	−1.13	0.27	0.20	−0.32
6. *o*-$C_6H_4Cl_2$	0.15	−0.35	0.30	0.25	−0.07
7. 1,2,4-$C_6H_3Cl_3$	0.07	−0.52	0.18	0.15	−0.17
8. C_6H_{12}	−0.04	0.12	−0.05	0.00	−0.02
9. $C_6H_{11}Cl$	−0.08	−0.35	−0.10	−0.05	−0.23
10. $C_6H_{11}Br$	−0.11	−0.62	−0.11	−0.07	−0.37
11. $C_6H_{11}I$	−0.15	−1.12	−0.15	−0.10	−0.53
12. *m*-C_6H_4IBr	0.01	−1.49	0.11	0.09	−0.53
13. 1,2,4-$C_6H_3(CH_3)_3$	0.22	0.06	0.28	0.30	0.08
14. C_5H_5N	0.34	0.00	0.48	0.44	0.29
15. C_6F_6	0.33	2.08	0.38	0.37	0.52
16. *p*-$C_6H_4(CH_3)F$	0.22	0.28		0.20	0.22
17. $C_6H_5CH_3$	0.26	0.12		0.32	0.14
18. *o*-C_6H_4ClF	0.21	0.11		0.30	0.13
19. *p*-$C_6H_4(CH_3)_2$	0.24	0.11		0.30	0.15
20. *o*-$C_6H_4(CH_3)Cl$	0.20	−0.13		0.30	0.01
21. *m*-$C_6H_4(CH_3)Cl$	0.17	−0.16		0.26	0.03
22. *p*-$C_6H_4(CH_3)Cl$	0.17	−0.20		0.26	−0.02
23. *m*-C_6H_4BrF	0.14	−0.20		0.23	−0.01
24. 3,4-$[C_6H_3CH_3]Cl_2$	0.11	−0.35		0.20	−0.15
25. *o*-$C_6H_5(CH_3)F$	0.17	−0.45		0.26	−0.08
26. *m*-C_6H_4BrCl	0.08	−0.67		0.18	−0.21
27. *m*-C_6H_4IF	0.13	−0.77		0.23	−0.22
28. *m*-$C_6H_4Br_2$	0.04	−0.96		0.14	−0.33
29. *m*-$C_6H_4(CH_3)I$	0.09	−0.96		0.18	−0.30
30. 1,2,4-$C_6H_3Br_3$	0.04	−1.14		0.14	−0.32
31. *o*-C_6H_4ICl	0.08	−1.19		0.18	−0.41
32. *m*-$C_6H_4I_2$	0.00	−1.90		0.06	−0.73
33. 2-Butyne	−0.10	0.53		−0.04	−0.02
34. Acetone	0.03	−0.12		0.08	−0.01
35. CH_2Cl_2	−0.08	−0.26		−0.03	−0.25
36. $CHCl_3$	−0.14	−0.67		−0.09	−0.33
37. CCl_4	−0.16	−0.98		−0.14	−0.45
38. CS_2	−0.23	−1.00		−0.15	−1.02

[a] Shifts in ppm, taken from Table II. The first 11 solvents form solvent set 1; the first 14, solvent set 2; the first 15, solvent set 3; and all 38, solvent set 4. The solvents have been numbered for reference in the text and succeeding tables.

physical significance, *e.g.*, one embodying predominately dispersion and the other factor reflecting predominately anisotropy. The mathematical operation is simply

$$\{\mathbf{B}_{\cdot 1}\mathbf{B}_{\cdot 2}\}\mathbf{R} = \{\mathbf{B}_{\cdot 1,\mathrm{rot}}\,\mathbf{B}_{\cdot 2,\mathrm{rot}}\} \tag{21}$$

where $\{\mathbf{B}_{\cdot 1}\mathbf{B}_{\cdot 2}\}$ is the matrix of unrotated eigenvectors, $\mathbf{R}$ is given by eq 20, and $\{\mathbf{B}_{\cdot 1,\mathrm{rot}}\,\mathbf{B}_{\cdot 2,\mathrm{rot}}\}$ is the rotated matrix of the (still orthonormal) significant factors. Recalling the definition stated above for a factor, we can define solvent and nuclide factor matrices as follows

$$\mathbf{V} = \hat{\mathbf{V}}\boldsymbol{\Lambda}^{1/2} \tag{22}$$

and

$$\mathbf{U} = {}^{-}\boldsymbol{\Lambda}^{1/2}\hat{\mathbf{U}} \tag{23}$$

where $\boldsymbol{\Lambda}$ is a diagnal matrix consisting of the eigenvalues associated with the eigenvectors. For the case of two factors

$$\{\mathbf{V}\} = \{\hat{\mathbf{V}}\}\{\boldsymbol{\Lambda}\}^{1/2} \tag{24}$$

$$\{\mathbf{U}\} = \{\boldsymbol{\Lambda}\}^{-1/2}\{\hat{\mathbf{U}}\} \tag{25}$$

where $\{\mathbf{V}\}$ and $\{\mathbf{U}\}$ are $m \times 2$ and $2 \times n$ matrices, respectively, and

$$\{\boldsymbol{\Lambda}\} = \begin{bmatrix} \lambda_{I} & 0 \\ 0 & \lambda_{II} \end{bmatrix} \tag{26}$$

In eq 26, λ_I and λ_{II} are the eigenvalues associated with eigenvectors defining factors I and II, respectively.

The present study approaches the search for significant solvent and solute factors from the standpoint of a correlation matrix **C** formed by eq 10 and a set of significant nuclide factors determined from eq 17 and 23. Equations 16 and 22 show that the solvent factor matrix **V** contains orthogonal columns (factors), since **B** has orthonormal columns (eigenvectors).

It should be mentioned that our data matrix **S** is in the "transpose" of that used by Malinowski and coworkers[9,15] to arrive at solvent factor matrices directly; therefore our multiplication $\mathbf{SS}^t$ to form **C** corresponds directly to the multiplication $\mathbf{S}^t\mathbf{S}$ employed by Weiner and Malinowski. The form of the data matrix employed in the present work is largely a matter of programming convenience.

The discussion to follow essentially revolves around factor analysis calculations on four groups of solvents, specified in Table III. The smallest group, designated set 1, consists of cyclohexane, benzene, *o*-dichlorobenzene, and 1,2,4-trichlorobenzene; it includes di- and trisubstituted representatives. Set 2, containing 14 solvents, adds to the above solvents pyridine and two additional di- and trisubstituted benzenes. Set 3 consists of set 2 plus hexafluorobenzene, a curious solvent on which we shall comment below. Finally, set 4 in-

Table IV. Variation of Selected Vector Elements with Rotation of the Solvent Eigenvectors in 10° Steps[a]

Angle, deg	$V^{I}_{C_6H_{12}}$	$V^{I}_{C_6H_6}$	$V^{I}_{C_6H_5I}$	$V_{C_6H_{11}I}$	$V^{II}_{C_6H_{12}}$	$V^{II}_{C_6H_6}$	$V^{II}_{C_6H_5I}$	$V^{II}_{C_6H_{11}I}$	U^{I}_{H}	U^{I}_{C}	U^{I}_{Si}	U^{II}_{H}	U^{II}_{C}	U^{II}_{Si}
0	−0.03	−0.05	0.33	0.37	0.04	−0.41	−0.28	0.07	−0.27	−3.21	−0.18	−0.71	0.25	−1.11
10	−0.02	−0.12	0.28	0.37	0.05	−0.40	−0.33	0.01	−0.39	−3.12	−0.37	−0.66	0.81	−1.06
20	−0.01	−0.18	0.21	0.37	0.05	−0.37	−0.38	−0.06	−0.50	−2.93	−0.54	−0.58	1.34	−0.98
30	0.00	−0.25	0.13	0.35	0.05	−0.33	−0.40	−0.12	−0.59	−2.65	−0.70	−0.48	1.83	−0.87
40	0.00	−0.30	0.07	0.33	0.05	−0.28	−0.42	−0.18	−0.67	−2.30	−0.85	−0.37	2.26	−0.74
50	0.01	−0.34	0.00	0.29	0.05	−0.23	−0.43	−0.23	−0.72	−1.86	−0.96	−0.25	2.62	−0.57
60	0.02	−0.38	−0.08	0.25	0.05	−0.16	−0.43	−0.28	−0.76	−1.38	−1.04	−0.12	2.91	−0.40
70	0.03	−0.40	−0.15	0.20	0.04	−0.10	−0.41	−0.32	−0.76	−0.89	−1.10	0.01	3.10	−0.21
80	0.04	−0.41	−0.21	0.14	0.04	−0.02	−0.37	−0.35	−0.75	−0.30	−1.12	0.14	3.21	−0.02
90	0.04	−0.41	−0.28	0.07	0.03	0.05	−0.33	−0.37	−0.71	0.25	−1.11	0.27	3.21	0.18
100	0.05	−0.40	−0.33	0.01	0.02	0.12	−0.28	−0.37	−0.66	0.81	−1.06	0.39	3.12	0.37
110	0.05	−0.37	−0.38	−0.06	0.01	0.18	−0.22	−0.37	−0.58	1.34	−0.98	0.50	2.93	0.54
120	0.05	−0.33	−0.41	−0.12	0.00	0.25	−0.15	−0.35	−0.48	1.83	−0.87	0.59	2.65	0.70
130	0.05	−0.28	−0.43	−0.18	0.00	0.30	−0.07	−0.33	−0.37	2.26	−0.74	0.67	2.30	0.85
140	0.05	−0.23	−0.44	−0.23	−0.01	0.34	0.00	−0.29	−0.25	2.63	−0.58	0.72	1.87	0.96
150	0.05	−0.16	−0.43	−0.28	−0.02	0.38	0.08	−0.25	−0.12	2.91	−0.40	0.76	1.38	1.04
160	0.04	−0.10	−0.41	−0.32	−0.03	0.40	0.15	−0.20	0.01	3.11	−0.21	0.76	0.85	1.10
170	0.04	−0.02	−0.38	−0.35	−0.04	0.41	0.22	−0.14	0.15	3.21	−0.02	0.75	0.30	1.12
180	0.03	0.05	−0.33	−0.37	−0.04	0.41	0.28	−0.07	0.27	3.21	0.18	0.71	−0.26	1.11

[a] The vectors are taken from a factor analysis calculation on solvent set 3. The solvent eigenvectors V^{I}_{α} and V^{II}_{α} for solvent α were rotated as described in the text. Nucleus vectors U^{I}_{i} and U^{II}_{i} for nucleus i of TMS were obtained for each rotation angle as described in the text.

cludes all of the 38 solvents on which intrinsic shift data were obtained.

Not surprisingly, the two most important factors did not reproduce the input shifts of the set of 38 solvents quite so well as did the principal two factors associated with solvent sets 1, 2, and 3. For these latter three sets, the two principal factors were sufficient to reproduce the input shifts to within experimental error *via* eq 18. However, for the full set of 38 solvents, the inclusion of the eigenvector associated with the third largest eigenvalue was necessary to reproduce precisely the shift matrix, which suggests an additional solvent effect, such as a tenuous dipole-induced dipole interaction between solvent and solute. The finding that only two eigenvectors reproduce the data matrix for solvent sets 1, 2, and 3 may be taken as further evidence that the method of Becconsall and coworkers[16] for obtaining intrinsic hydrogen shifts does effectively eliminate the bulk susceptibility "factor." Other evidence for the success of this technique is outlined in the Experimental Section.

For the case of solvent set 4, checks were made to ascertain which solvent or solvents were principally responsible for enhancing the importance of the third factor. These checks were conducted by adding to a "base" set of 15 "innocent" solvents (halobenzenes and halocyclohexanes) one "suspicious" solvent, in a series of factor analysis calculations. This procedure revealed that hexafluorobenzene and carbon disulfide were the principal carriers of the third factor. Perhaps these two solvents, which have the highest and lowest factor II elements, respectively, over a range of rotation angles of special interest (see below), exert such potent influences that the above-postulated partitioning into solvent and solute factors is beginning to break down; *i.e.*, the dependence of the observed shift on the solvent influence reflected in factor II possibly becomes nonlinear at the two extremes. It seems at least possible that a third significant solvent influence, not directly connected with the solvent effect contributions associated with factors I and II, is at work here. It does seem clear that solvent polarity, an influence which might *a priori* be expected to manifest a third significant factor, is not important in these results, since the relatively polar solvents acetone and chloroform have no appreciable effect on the third eigenvalue. Nor do these solvents possess extreme factor II elements for the range of rotation angles discussed below.

Let us now consider the role of the solute in the present picture. The partitioning of properties between solvent and solute expressed in eq 8 yields a solute factor matrix **U** which in our view encompasses the responsiveness or sensitivity of the several solute nuclei to a "unit factor I or factor II influence" imposed on the nuclei. We can determine **U** by at least two equivalent routes, starting with a correlation matrix formed *via* eq 10: (a) obtain $\{\mathbf{U}\}$ from the expression $\{\mathbf{B}\}^{t}\{\mathbf{S}\}$ (eq 17) for the various rotated eigenvector pairs; and (b) perform a regression analysis on the set of equations

$$S_{\alpha i} = V^{I}_{\alpha}U^{I}_{i} + V^{II}_{\alpha}U^{II}_{i} \qquad (27)$$

for the shift of the ith nucleus due to the interaction with solvent α. The symbols U^{I}_{i} and U^{II}_{i} represent the sensitivities of nucleus i to factor I and factor II, respectively, and V^{I}_{α} and V^{II}_{α} are the factor I and factor II elements for the best solvent eigenvector rotation angle of solvent α. Since we have *m* equations in two unknowns, a multiple regression analysis[40] is appropriate for determining the nuclei sensitivities, U^{I}_{i} and U^{II}_{i}.

Identical sets of nuclei sensitivities have been computed by both approaches a and b above over the entire range of solvent–factor rotation angles, in 5° increments. The results of these rotations are summarized for both solvent and nuclei vectors in Table IV. These elements come from a factor analysis calculation on solvent shifts on all five nuclei of TMS and cyclohexane for a set of 15 halobenzene and halocyclohexane solvents. Of these solvents, eigenvector elements of cyclohexane, benzene, iodocyclohexane, and iodobenzene and nucleus vector elements of the three nuclei in TMS were taken as

[40] Program No. BMDO2R, Biomedical Computer Programs, University of California Publications in Automatic Computation, University of California Press, Berkeley, 1970.

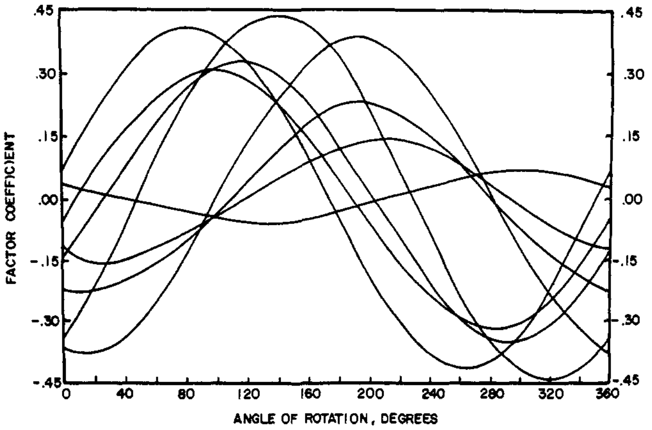

Figure 4. Angular dependence of solvent vector elements, $V^{I}{}_{\alpha}$, for the solvents of Table V from factor analysis of solvent set 3. In order of increasing value of zero-degree intercept, the solvents are iodocyclohexane, iodobenzene, bromocyclohexane, bromobenzene, chlorocyclohexane, chlorobenzene, cyclohexane, and benzene.

representative, for the purposes of the following discussion.

Our chief guidelines for attempting to find a narrow range of angles which turn the two pairs of solvent–solute vectors into dispersion and anisotropy interaction, as popularly conceived, are the following: (a) one of the rotated eigenvector pairs should reflect the main features of dispersion interaction as discussed below, (b) the other rotated eigenvector should display a substantial, and relatively constant difference between anisotropy effects of benzene or a halobenzene and cyclohexane or the corresponding halocyclohexane,[3,11] (c) intuitively, the halogen substituents should manifest a regular increment in the elements of the eigenvectors (assuming that both dispersion and anisotropy effects should show a relatively regular progression in the halogen series of the periodic table), and (d) a high degree of consistency of corresponding solute and solute vector elements should be maintained among the four solvent sets.

Relative dispersion effects for the solvents cyclohexane, benzene, and the monohalocyclohexanes and monohalobenzenes have been estimated according to available models, and are collected in Table V. The models used for these estimates are, arranged in roughly increasing order of sophistication (left to right in Table V): (a) correlation of dispersion interaction with the heat of vaporization of the solvent;[2] (b) the McRae term,[41] $\sigma_w = (n^2 - 1)/(2n^2 + 1)$, employed by Laszlo and Speert[42] to correlate proton coupling constants with dispersion interactions; (c) the dispersion model of Howard, Linder, and Emerson;[7] and (d) the model of Rummens, Raynes, and Bernstein[43] as employed by Malinowski and Weiner.[14] This last model is the only one which directly accounts for intermolecular interaction energy (through the Lennard-Jones potential). This model also stipulates that σ_w is directly proportional to the molecular polarizability and ionization potential of the solvent and inversely proportional to the molecular volume and three-halves power of the "distance of closest approach" of the solvent. Since Lennard-Jones potentials for halobenzenes and halocyclohexanes have not been tabulated, the Rummens–Raynes–Bernstein model was, unlike the other models, not applied to these solvents.

Table V. Relative Solvent Dispersion Interactions Calculated by Several Models, Normalized to Cyclohexane Solvent at 1.00[a,b]

Solvent	LS[c]	BSS[d]	HLE[e]	HLE[f]	RRB[g]
Cyclohexane	1.00	1.00	1.00	1.00	1.00
Benzene	1.13	0.997	1.09	1.03	1.18
Chlorocyclohexane	1.07	1.18	1.07		
Chlorobenzene	1.16	1.15	1.11		
Bromocyclohexane	1.12	1.25	1.09		
Bromobenzene	1.22	1.22	1.16		
Iodocyclohexane	1.19	1.29	1.12		
Iodobenzene	1.29	1.31	1.21		

[a] Dispersions were calculated for a hypothetical "unit" solute by setting all solute terms in the several dispersion expressions equal to unity. [b] The physical constants used in these calculations were obtained from the "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1970–1971. Where applicable, ionization potentials for the halocyclohexanes (not reported in the literature) were estimated from data on similar compounds. [c] Method of Laszlo and Speert,[42] using the Bayliss–McRae term, $\sigma_w = (n_D{}^2 - 1)/(2n_D{}^2 + 1)$. [d] Based on Trouton's rule as stated by Buckingham, Schaefer, and Schneider,[2] $\sigma_w = 17.0T_b + 0.009T_b{}^2$, where T_b is the normal boiling point of the pure solvent liquid. [e] Method of Howard, Linder, and Emerson.[7] Dispersions calculated from eq 11 and 12 of ref 7. [f] Method of Howard, Linder, and Emerson.[7] Dispersions calculated from eq 11 and 14 of ref 7. Molar diamagnetic susceptibilities not available for the halogenated solvents. [g] Method of Rummens, Raynes, and Bernstein (ref 43) as given in Malinowski and Weiner.[14] Dispersions calculated from eq 15 of ref 14 using parameters in the Lennard-Jones potentials as given in Figures 1 and 2 and Table VII of ref 21 for benzene and cyclohexane solvents. Parameters not available for the halogenated solvents.

All of the approaches predict: (a) that the solvent dispersion influence increases in regular fashion with change in substituent in the order H < Cl < Br < I for both monohalocyclohexanes and monohalobenzenes; and (b) (except for the empirical heat of vaporization criterion[2]) for a given substituent, a substituted benzene should have a stronger total dispersion interaction with the solute than the corresponding substituted cyclohexane. Plots were constructed of the angular dependence of solvent vector elements associated with benzene, cyclohexane, and the monosubstituted derivatives (the solvents in Table V) from each solvent set; one of these plots (from solvent set 3) is reproduced as Figure 4.

As previously indicated, for small, roughly spherical, noncomplexing solutes such as cyclohexane and TMS, the average secondary magnetic field due to the diamagnetic anisotropy of the solvent molecules has the same value at all points within the solute molecule[35,36] and confers a solvent shift contribution independent of the identity of the nucleus under consideration.[35] Since cyclohexane and TMS are of similar size,[35] all five nuclei of these solutes might be expected to show similar sensitivities to solvent anisotropy and the three TMS nuclei should show the same sensitivity. With this guideline for anisotropy effects a search was made for an eigenvector rotation angle which yields the most nearly equal solute vector (factor) elements. Table IV shows that 160° for solute vector II (or 70° for vector I) reflects similar responses, all well within a factor of two, of all five nuclides to changes in solvent influence.

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(41) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950); E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957); M. E. Baur and M. Nicol, *J. Chem. Phys.*, **44**, 3337 (1967).

(42) P. Laszlo and A. Speert, *J. Magn. Resonance*, **1**, 291 (1969).

(43) F. H. A. Rummens, W. T. Raynes, and H. J. Bernstein, *J. Phys. Chem.*, **72**, 2111 (1968).

From the accompanying solvent vectors (factors) for this rotation angle, it is found that benzene solvent increases a solute nuclide shielding by about 0.35 ppm relative to cyclohexane solvent (obtained by multiplying V^{II}_{α} by U^{II}_{i} as prescribed by eq 27). This effect is quite in line with estimated benzene-induced anisotropy shieldings.[14,15,43,44] Bringing into the picture the rest of the halobenzene and halocyclohexane solvents (see Figure 4) and cyclohexane solute in no way vitiates the above two points and adds the third point that the benzene-induced shielding for a particular halobenzene solvent is about 0.3 ppm relative to the corresponding halocyclohexane. Furthermore, factor analysis calculations on other groups of solvents in Table I, including the full set of 38 solvents (set 4 of Table III), yields rotation angles equally successful from the standpoint of magnetic anisotropy interactions. For only a small range of rotation angles (about 20°; see Table IV) does this picture prevail.

A similar search was conducted for an angle associated with solvent and nucleus vectors that could be considered consistent with the prevailing views of dispersion effects on shielding. Note that we require the two significant factors only to be linearly independent, not necessarily orthogonal. Specifically, the resonances of all solute nuclei should be displaced to lower shielding by a stronger dispersion interaction, meaning, for example, that the TMS nucleus vector elements in Table IV should all be one sign. Furthermore, overlooking the results of the BSS heat of vaporization dispersion approach in favor of the other four models represented in Table V, $\hat{V}_{C_6H_6}$ should be algebraically *less* than $\hat{V}_{C_6H_{12}}$ if the corresponding nucleus sensitivity elements are positive or algebraically *greater* than $\hat{V}_{C_6H_{12}}$ if the nuclide elements are negative. Similarly, $\hat{V}_{C_6H_5I}$ should be of such value that iodobenzene solvent is shown to confer a decreased shielding on all nuclei (reflecting stronger dispersion interaction) compared to benzene solvent. A similar statement applies to iodocyclohexane and cyclohexane. Inspection of Table IV shows that an angle around 180° for solvent and nucleus vectors I or 90° for vectors II comes closest to satisfying the above-mentioned dispersion interaction criteria, in that cyclohexane is predicted to confer only a marginally greater dispersion decrease in shielding than benzene (almost a negligible difference), while iodobenzene would manifest a much stronger dispersion interaction. Bringing into the picture the other halobenzene and halocyclohexane solvents shows that this rotation angle is consistent with the dispersion interaction guidelines stated above (except the BSS heat of vaporization rule) only if a particular halocyclohexane solvent were to be associated with a *stronger* dispersion interaction than the corresponding halobenzene. This situation would go against predictions of all of the dispersion models represented in Table V, except for the BSS heat of vaporization criterion. For none of the solvent groups considered in this study could a rotation angle be found for the solvent eigenvectors which gave results that conform for all nuclei to the dispersion interaction guidelines given above, although angles can be found which conform to the guidelines considering only the carbon resonances in TMS and cyclohexane. Specifically, a rotation angle of 160° for vector I (orthogonal to the vectors II associated with anisotropy above) or 70° for vector II (see Table V) is such an angle. For this rotation, however, inspection of the $\hat{U}$ elements shows that the hydrogen of TMS would reflect essentially no dispersion interaction and the silicon would be displaced to *increased* shielding by dispersion effects.

We mention in passing that eigenvector elements for all the rotation angles considered above show reasonably good additivities of solvent substituent effects of a sort analogous to the additivity model already discussed for observed intrinsic solvent shifts.

Thus, the evidence at our disposal supports a fairly strong case for identifying rotated factors with magnetic anisotropy interactions. Our criterion for this identification stems directly from previous results based upon classical magnetostatics[35,36] and the reasonable assumption that a solvent molecule (of no specified shape) reorients rapidly and randomly with respect to the solute sphere. This is a result of rather wide applicability and is free of dependence upon the crude simplifying assumptions on which models for dispersion interactions are typically based. By contrast with the anisotropy effect, neither significant factor in our analysis is totally consistent with presently held views of the contribution of dispersion interactions to the observed shift. Nor can either factor be reasonably identified with solvent polarity effects.

At hand, then, is a picture which appears to pose a challenge to currently popular models for those contributions to nmr solvent effects having *general* occurrence (*e.g.*, dispersion forces) rather than depending on the conditions of the nmr experiment (as magnetic anisotropy does). If one adheres to the view that the decrease in shielding due to dispersion interaction is greater for a (substituted) benzene solvent than for the corresponding cyclohexane, then there is no way of interpreting the factor analysis of our data in terms of a sort of "dispersion field" set up by the solvent, producing shifts of different magnitudes but the *same sign* for all solute nuclei. Or, if one adheres to the view that dispersion effects on shieldings have the same sign for all nuclei in a solute, then our results are not consistent with the benzene *vs.* cyclohexane relationship that is generally assumed.

Identification of a rotation angle with anisotropy shifts (160° for $\hat{V}^{II}\hat{U}^{II}$ or 70° for $\hat{V}^{I}\hat{U}^{I}$ in Table IV) allows a direct comparison of orders of anisotropic interaction with the results of Weiner and Malinowski.[15] This identification produces the rotated vectors shown in Table VI, based on solvent set 4. For the solvents at which their investigation overlaps with the present one, they found the following order of algebraically increasing σ_a: $CS_2 < CHCl_3 < CCl_4 < C_6H_{12} < CH_2Cl_2 < (CH_3)_2CO \ll C_6H_6 < C_6F_6$. This order was arrived at through considering only the hydrogen resonance of several nonpolar solutes, including TMS and cyclohexane.[15] The present investigation yields the following order for the four carbon and hydrogen resonances of TMS and cyclohexane: $CS_2 < CCl_4 < CHCl_3 < CH_2Cl_2 < (CH_3)_2CO \ll C_6H_6 < C_6F_6$, in qualitative agreement with the findings of Weiner and Malinowski.[15] Two points about these orders stand out: (a) both ascribe to CS_2 the algebraically lowest shielding effect, in qualitative agreement with the views

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(44) J. C. Schug, *J. Phys. Chem.*, 70, 1816 (1966).

Table VI. Identification of Rotated Solvent and Solute Vectors with Solvent Magnetic Anisotropy Interaction[a]

Solvent (α)[b]	$(V_{rot})^{II}_{\alpha}$ [c]	Solvent (α)[b]	$(V_{rot})^{II}_{\alpha}$ [c]
1	0.26	20	0.18
2	0.25	21	0.16
3	0.18	22	0.15
4	0.14	23	0.13
5	0.06	24	0.09
6	0.13	25	0.14
7	0.05	26	0.06
8	−0.01	27	0.09
9	−0.09	28	0.01
10	−0.12	29	0.05
11	−0.18	30	0.01
12	−0.05	31	0.02
13	0.20	32	−0.10
14	0.32	33	−0.05
15	0.33	34	0.04
16	0.18	35	−0.08
17	0.23	36	−0.13
18	0.20	37	−0.18
19	0.22	38	−0.31

Nucleus (i)	$^1H(TMS)$	$^{13}C(TMS)$	$^1H(CHX)$	$^{13}C(CHX)$
$(U^{II}_{rot})_i$	1.04	1.43	1.26	1.11

[a] The factor analysis is based on solvent set 4 of Table V, including ^1H and ^{13}C solvent shifts in all the solvents in Table II. [b] The numbering corresponds to solvents as listed in Table V. [c] Rotation angle for this particular solvent set is 200°.

of other workers;[2,35,36,44] and (b) both predict an even higher magnetic anisotropy shielding for hexafluorobenzene than for benzene itself. Finally, both the factor analysis results of Weiner and Malinowski[15] and the present findings suggest that halogen solvent substituents, particularly iodine, are associated with a sizable *negative* shielding anisotropy effect.

In the larger picture, perhaps significant is that our approach is a multinuclear investigation encompassing ^1H, ^{13}C, and ^{29}Si nuclides, each possessing characteristic responses to changes in environment. Every other systematic investigation into the nature of solvent effects in nmr has focused on only one nuclide, in almost every case hydrogen. The fact that carbon resonances in TMS and cyclohexane display a greater range of solvent shifts (four- or fivefold greater in TMS) than either hydrogen or silicon resonances raises the possibility that a single-nucleus investigation, such as that of Weiner and Malinowski on anisotropy interactions,[15] will not uncover the true complexity of nmr solvent shifts. It should be mentioned that Weiner and Malinowski did not explicitly consider solute factors; rather, they discussed solvent effects only in terms of solvent contributions and effectively assigned unity to the solute factors.

Conclusion

This study has focused on solvent effects observed on all three nuclides of TMS and both nuclides of cyclohexane, dissolved in a wide variety of solvents. The results found show that the solute resonances are by no means invariant, as has been frequently assumed, which together with other hydrogen evidence on small, nonpolar solutes should serve as a *caveat* to workers employing these solutes as internal references. Shift errors of up to several tenths of a ppm should be expected, particularly in ^{13}C shielding studies, although in many situations errors from a shifting internal reference will amount to less than a tenth of a ppm. TMS and cyclohexane emerge from the present investigation as about equally satisfactory hydrogen internal references. For carbon studies involving substituent changes on a particular (hydrocarbon) solvent framework, cyclohexane appears to be the superior choice, compared to TMS. On the other hand, for studies involving solvents having both saturated and aromatic carbon skeletons, TMS seems to be less sensitive to solvent effects. TMS has the additional advantages over cyclohexane (and most other saturated hydrocarbon references) of having a ^{13}C signal well removed from most other types of resonances (this comment also applies to hydrogen and ^{29}Si) and a high volatility, and the disadvantage of having a decoupled ^{13}C signal only about a third as strong as cyclohexane (for which Overhauser enhancement is stronger).[45]

Regarding the nature of solvent effects on TMS and cyclohexane, the factor analysis approach of the present work unequivocally demonstrates that, within the bounds of eq 8, for halobenzene and halocyclohexane solvents (including benzene and cyclohexane themselves) the solvent shift data are completely characterized by just two statistically significant solvent ininfluences. Attempts to transform these factors into the solvent contributions believed to be dominant[3,8,12,14,15,37] in the solute–solvent systems of this investigation show that, while a transformation consistent with prevalent views of solvent magnetic anisotropy[3,35] can be found, no transformation was found consistent with dispersion interaction, as presently envisaged.[2,8,12,14,42] This result suggests a need for a reexaming of the premises on which existing pictures of solvent effect contributions, particularly dispersion shifts, are based. Also needed is additional characterization of solvent effects on the several nuclei in structurally analogous solutes, and on gas-phase samples. Experiments directed to these aims are in progress.

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(45) K. F. Kuhlmann, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).