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Appendix

The proof of the inequalities used for van der Waals interactions, section V, is presented here.

(a) To show that $\Delta < 0$ in the low-temperature expansion (6), we recall that for any $x \neq y$

$$\exp(x^2) + \exp(y^2) - 2\exp(xy) > 2\exp(\tfrac{1}{2}x^2 + \tfrac{1}{2}y^2) > 0 \tag{A1}$$

where the convexity of the exponential function is used in (A1); the HEC inequality in (6) immediately follows.

(b) For case iv of section V, one of the α_i's is zero while the other two are positive. For example, $\alpha_A > \alpha_B > \alpha_C = 0$. Using the expression for Δ from (3) and (4) with

$$x^2 = \frac{M}{k_B T}\alpha_A{}^2 \qquad y^2 = \frac{M}{k_B T}\alpha_B{}^2$$

we get[36]

$$\Delta = e^{2xy} - e^{x^2+y^2} + e^{x^2} + e^{y^2} - 2e^{xy} = (e^{xy} - 1)^2 - (e^{x^2} - 1)(e^{y^2} - 1) \tag{A2}$$

since the function $f(u) = \log(e^{e^u} - 1)$ is convex

$$f(u_A) + f(u_B) > 2f(\tfrac{1}{2}u_A + \tfrac{1}{2}u_B) \tag{A3}$$

Substituting $u_A = 2\log(x)$, $u_B = 2\log(y)$, we have from (A3)

$$\log(e^{x^2} - 1) + \log(e^{y^2} - 1) > 2\log(e^{xy} - 1) \tag{A4}$$

Thus, $\Delta < 0$ in (A2).

(c) For case v of section V, α_B lies midway between α_A and α_C:

$$\alpha_B = \alpha_C + \delta = \alpha_A - \delta \tag{A5}$$

Define

$$u = \exp\left(\frac{M}{k_B T}\alpha_B\delta\right) \qquad v = \exp\left(\frac{M}{k_B T}\delta^2\right)$$

From (3)

$$\Delta = u^{-2}v^{-2}(v - 1)[2uv(v + 1) - 2uv^2 + 2u^3v(v + 1) - u^4v^2 - v^2 - u^2(1 + v + v^2 + v^3)] \tag{A6}$$

$P(u,v) = -\Delta u^2v^2/(v - 1)$ is a third-degree polynomial in v. A Taylor expansion around $v = 1$ contains four terms:

$$P(u,v) = P(u,1) + (v - 1)\frac{\partial P(u,1)}{\partial v} + \frac{1}{2}(v - 1)^2\frac{\partial^2 P(u,1)}{\partial v^2} + \frac{1}{6}(v - 1)^3\frac{\partial^3 P(u,1)}{\partial v^3} \tag{A7}$$

where

$$P(u,1) = (u - 1)^4 > 0 \tag{A8}$$

$$\frac{\partial P(u,1)}{\partial v} = 2(u - 1)^2(u^2 - u + 1) > 0 \tag{A9}$$

$$\frac{\partial^2 P(u,1)}{\partial v^2} = 2(u^4 - 2u^3 + 4u^2 - 2u + 1) > 0 \tag{A10}$$

$$\frac{\partial^3 P(u,1)}{\partial v^3} = 6u^2 > 0 \tag{A11}$$

Since $P^{(n)}(u,1) > 0$ for $3 \geq n \geq 0$, then $P(u,v) > 0$ for all $v > 1$. In other words, from (A7)–(A11), $\Delta < 0$ (HEC).

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(36) De Gennes, P.-G., private communication.

Relative Ring-Current Effects Based on a New Model for Aromatic-Solvent-Induced Shift[1]

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Abstract: A convenient method for measuring (relative to benzene) the above-plane ring-current effect of aromatic compounds is presented. The method is based on strictly linear relations $\Delta_{oi} = (\bar{a} + b)[D_o]_i$ between the induced upfield shift Δ_{oi} of an (externally referenced) ^{1}H NMR signal of a probe and the concentration $[D_o]_i$ of the aromatic D (solvent CCl_4). Δ_{oi} is the chemical shift relative to that of the solution where $[D_o]_i = 0$, and b is the necessary correction for the change in the susceptibility. A study of more than 30 compounds D (including the partial antiaromatic biphenylene) with 1-chloroisobutene as probe shows that its $\bar{a}$ values establish a relative scale of the above-plane ring-current effect. This relative scale generally displays a good agreement with a similar scale derived from diamagnetic exaltations. The probe behavior is explained by a simple model for ASIS (aromatic-solvent-induced shift) that divides ASIS into three components: upfield contributions from AUS effects (additional nonspecific shielding effects) and from complexation, counteracted by the downfield contribution through AUS effects on the customary internal reference. The AUS effect in its most simple mode depends linearly on the concentration $[D_o]_i$ of benzene (or other aromatic compounds). Prerequisites for the linear dependence are discussed.

Previous studies[2] of solvent (or cosolvent or cosolute) dependence of ^{1}H NMR chemical shifts δ have usually compared chemical shifts of the solute at a more or less constant concentration. In some studies the chemical shifts δ were extrapolated to zero solute concentration. To the best of our knowledge, however, a comparison of *slopes* of *linear* shift–concentration relations, obtained from constant solute concentration as a function of the much larger concentrations of a cosolvent or cosolute, have not yet been reported. Such linear relations over a large concentration range in high-precision experiments have seldom been observed before and never for a whole series of cosolvents or cosolutes. This paper reports now on such a unique behavior and on its relation to the so-called ring-current effect. An explanation of the observed linear relation is presented on the basis of a new model for ASIS, the

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(1) Dedicated to the memory of Professor Hans Musso.

(2) Laszlo, P. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, W., Feeney, J., Sutcliffe, L., Eds.; Pergamon Press: Oxford 1967; Vol. 3, Chapter 6, pp 231–402. Ronayne, J.; Williams, D. H. In *Annual Review of NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1969; Vol. 2, pp 83–124.

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aromatic-solvent-induced shifts.

Previous work has led to the development[3,4] and application[5–7] of a refined model for the ^{1}H NMR investigation of molecular complexes. This refinement (AUS concept, vide infra) is important for weak complexes of an acceptor A with an aromatic donor D. With stronger complexes of this type (and sufficiently large complex shifts Δ_{AD}), this refinement becomes progressively less significant, however, so that the classical model[8] is approached. Eventually the models become indistinguishable, since the contribution of the refinement to the total effect is then insignificant. In this case the classical model may even be superior because it is less sensitive to experimental scatter.

Both the classical[8] and the refined[3,4] model rely on the strong diamagnetic anisotropy of the aromatic D, usually ascribed to the ring-current effect (ring-current effect in the wider sense, vide infra). The complexation of A with D causes an upfield shift of A signals in both models. Under the usual experimental condition $[D_0] \gg [A_0]$ a plot of the observed change $\Delta_i = \delta_0 - \delta_i$ in chemical shift as a function of $[D_0]$ shows a downward curvature that is typical of the complexation. $[D_0]$ and $[A_0]$ are the formal concentrations of D and A, respectively. δ_0 is the chemical shift of A when $[D_0] = 0$. Subscript *i* refers to the *i*th solution of the experimental series.

While in most investigations of the classical type an internal reference is used for the measurements of δ_0 and δ_i, the refined model normally requires an external reference. The use of an internal reference is allowed only under very special premises.[4] If not otherwise stated, shifts δ in this paper are always relative to an external reference. Where necessary, one can make allowance for the change in the difference of the diamagnetic susceptibility between the probe solution and the external reference. This is done by subtracting $b[D_0]_i$ from Δ_i (see ref 4, 6, 7), where *b* is the susceptibility correction coefficient for the addition of $[D_0]_i$ to the solution of A in the respective nonpolar solvent, usually CCl_4.

It was recently reported[6] that 1-chloroisobutene (CLIB, 1-chloro-2-methylpropene) in CCl_4 shows a strictly linear shift dependence $\Delta_i = \bar{m}[D_0]_i = (\bar{a} + b)[D_0]_i$ on the benzene concentration for the signal of the methyl group ($CLIB_{cis}$) *cis to the chlorine atom*. The shift dependence (downward curvature) of the other methyl group ($CLIB_{trans}$) indicates the formation of a weak molecular complex (see Interpretation). Both signals coincide in CCl_4 ($[D_0] = 0$) and are shifted upfield when $[D_0] > 0$, the trans signal more so than the cis signal. In analogy to the generally accepted interpretation that the complex shift Δ_{AD} is induced on A by the ring current of D, the linear upfield shift of $CLIB_{cis}$ was ascribed to the ring current effect of benzene. The linearity indicated the absence of a complexation effect ($\Delta_{AD} = 0$) for $CLIB_{cis}$. The apparent paradox of the behavior of $CLIB_{cis}$ and $CLIB_{trans}$ is discussed in the Interpretation. On low resolution, the two methyl signals are (deceptive simple) doublets from which the allylic coupling constants $|^4J| = 1.46$ Hz for $CLIB_{cis}$ and $|^4J| = 0.97$ Hz for $CLIB_{trans}$ have been reported.[6] New measurements (250 MHz, C_6D_6) revealed a complication by methyl–methyl coupling that could be eliminated by decoupling yielding real doublets with $|^4J| = 1.40$ Hz for $CLIB_{cis}$ and $|^4J| = 1.51$ Hz for $CLIB_{trans}$. The previous[6] signal assignment finds strong support from a comparison of $CLIB_{cis}$ with its cyclic analogue *o*-chlorotoluene and of $CLIB_{trans}$ with *m*-chlorotoluene as will be discussed in the Interpretation.

The observed linear shift–concentration dependence has been explained on the basis of simple collision considerations implicating a time-averaged effect on the magnetic shielding.[6] Since discussion of collision effects may be misleading in light of the NMR time scale, one referee suggested that one should rather consider the average equilibrium distribution of the benzene molecules in the vicinity of the solute. This average equilibrium distribution changes with $[D_0]$: assuming no complexation, the probability of being a neighbor of a benzene molecule increases linearly with $[D_0]$ when $[D_0] \gg [\mathrm{CLIB}]$. A discussion of this hypothesis is given in the Interpretation.

Above-Plane Ring-Current Probe: Results

It was decided to test this hypothesis of a ring-current-dependent phenomenon. According to this hypothesis, other aromatic compounds D should also produce a linear shift–concentration relation $\Delta_i = \bar{m}[D_0]_i$ with $CLIB_{cis}$. The susceptibility corrected slope $\bar{a} = \bar{m} - b$ of this linear dependence should reflect the magnitude of the ring-current effect[9] *above* the aromatic plane[11] of the respective D.

As for the above-plane effect, a very different quantitative method has previously been described by Anet and Schenck.[12] A discussion of this method and of its fundamental shortcomings is given in the Interpretation. There are reasons to believe that the $CLIB_{cis}$ shift-concentration method provides a good quantitative measure of relative ring-current effects above the aromatic plane. More than 30 mono- and polycyclic condensed and noncondensed carbocycles and heterocycles as well as substituted benzenes have been studied so far. Except for the special case of hexafluorobenzene (see below), they always have given the unusual linear shift–concentration relation for $CLIB_{cis}$ over the total measureable range of $[D_0]_i$. Solubility or strong D signals too close to the small $CLIB_{cis}$ signal were the limiting factors for this range. Except for hexafluorobenzene, in all cases $CLIB_{trans}$ revealed greater upfield shifts and downwardly curved plots, indicating weak complexation. The low values of the formation constants *K* and of intercept/*K* (vide infra), often combined with unfavorable ranges of saturation fraction,[6,13] precluded a reliable determination of *K*. A casual remark[6] said that $K = 0.18$ L mol^{-1} for the benzene complex "could be computed from the data". There are various reasons that this value is too high. For instance, the simultaneously computed intercept/$K \approx \Delta_{AD}$ (see Interpretation) is too small (10 Hz at 90 MHz) in comparison to other benzene complexes.[4–7,14] Furthermore, under the assumption that the noncomplexing effects of $[D_0]$ on Δ_i are equal in size for $CLIB_{trans}$ and $CLIB_{cis}$ the shift difference method[4] ($\Delta_{i,\alpha} - \Delta_{i,\beta}$ where α and β refer to $CLIB_{trans}$ and $CLIB_{cis}$, respectively) yields $K =$ ca. 0.02 L mol^{-1} from the previous[6] as well as from new experimental data. The same procedure under the same premise gives *K* in the range 0.02–0.14 L mol^{-1} for the other D's of Table I except hexafluorobenzene and those cases in which the maximal shift difference was less than 7 Hz. The greatest values were obtained for fluoranthene and phenanthrene. It must be stressed that all these values can represent a rough estimate at best. In principle, one should be very skeptical about *K* values of this order unless they can be confirmed by additional independent findings (see also Interpretation).

The $CLIB_{cis}$ results are given in Table I. They confirm that $CLIB_{cis}$ is a quantitative probe of ring-current effects. The sequence of magnitudes in the derived relative scale is in most cases

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(3) Stamm, H.; Lamberty, W.; Stafe, J. *J. Am. Chem. Soc.* **1980**, *102*, 1529–1531.

(4) Lamberty, W.; Stamm, H.; Stafe, J. *J. Phys. Chem.* **1983**, *87*, 1589–1596. There is an error in this paper: the symbols "*o*-H" and "*m*-H" concerning *p*-nitrobenzaldehyde have to be interchanged.

(5) Stamm, H.; Lamberty, W. *Tetrahedron* **1981**, *37*, 565–568 (in English).

(6) Stamm, H.; Stafe, J. *Z. Naturforsch.* **1981**, *36b*, 1618–1627 (in English).

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(9) For the use of the term "ring current" compare footnote 17 in ref 10.

(10) Dauben, Jr., H. H.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. II, pp 167–206.

(11) ^{1}H NMR and the magnitude of ring-current magnetism have usually been connected by the chemical shifts of aromatic compounds (in-plane effects). Our approach is completely different and differs in essence even from a previous approach to above-plane effects.[12]

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(13) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167–170; Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044–4054.

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Table I. Ring-Current Effects $\bar{a}$ Exerted on $CLIB_{cis}$ by Aromatic Solutes D in CCl_4: Comparison of Relative Values with Relative Diamagnetic Exaltations

			rel scale	
solute D	$[D_o]_t$ range, mol L^{-1} (no. of data points)	$\bar{a}$,[a] ppm L mol^{-1}	this method	diamagnetic exaltation[b]
benzene[c]	0.50–10.82 (12)	0.069	1.00	1.00
tert-butylbenzene	0.07–0.45 (8)	0.070	1.02	0.88[d]
cumene	0.08–1.01 (12)	0.073	1.05	0.93[d]
toluene	0.67–9.13 (16)	0.078	1.13	0.93
o-xylene	0.31–2.12 (8)	0.081	1.17	0.91[d]
m-xylene	0.22–1.57 (8)	0.081	1.17	0.82[d]
p-xylene	0.43–2.06 (10)	0.082	1.19	0.84[d]
mesitylene	0.09–0.65 (8)	0.088	1.27	1.08[d]
chlorobenzene	1.26–9.52 (14)	0.060	0.87	0.81[d]
o-dichlorobenzene	1.76–8.61 (8)	0.053	0.76	0.69[d]
p-dichlorobenzene	0.28–2.27 (16)	0.040	0.57	0.56[d]
o-chlorotoluene	0.13–1.31 (10)	0.066	0.93	0.83[d]
p-chlorotoluene	0.17–1.47 (10)	0.057	0.82	0.69[d]
fluorobenzene	0.80–10.42 (12)	0.061	0.88	
hexafluorobenzene[e]	0.59–8.23 (12)	0.051[f]	0.73	
		0.052[g]	0.74	
anisole	0.53–5.05 (10)	0.069	1.00	1.08[d]
furan	1.20–13.59 (12)	0.042	0.60	0.65
thiophene	0.88–12.20 (16)	0.047	0.67	0.95
diphenylmethane	0.58–5.09 (14)	0.130	1.88	1.99[d]
biphenyl	0.29–1.81 (14)	0.132	1.90	1.91
fluorene	0.10–0.56 (14)	0.183	2.64	1.88, 2.05[d]
9,10-dihydrophenanthrene	0.15–1.11 (14)	0.131	1.88	1.96[d]
indene	1.32–7.97 (16)	0.104[e]	1.49	1.79[d]
biphenylene[h]	0.12–1.22 (8)	0.085	1.24	1.02
azulene	0.04–0.85 (15)	0.150	2.15	2.16, 1.93[d]
naphthalene	0.13–1.36 (13)	0.151	2.17	2.23, 2.12[d]
acenaphthene	0.10–1.17 (14)	0.143	2.06	1.96
acenaphthylene	0.14–1.61 (16)	0.159	2.29	2.87, 2.73[d]
fluoranthene[h]	0.05–0.68 (16)	0.232	3.34	3.07, 2.92[d]
phenanthrene	0.09–0.90 (14)	0.197	2.83	3.37, 2.92[d]
benzofuran	0.71–6.39 (12)	0.103[e]	1.49	1.72[d]
indole	0.14–1.10 (8)	0.115	1.66	1.99

[a] Standard deviation for $\bar{m}$ ($\bar{m} = \bar{a} + b$) between 0.0001 and 0.003 ppm L mol^{-1}. [b] Taken from ref 10 if not otherwise stated. [c] Taken from ref 6. There is an error in ref 6: b of benzene is 0.976 Hz L mol^{-1} at 90 MHz. [d] Calculated or recalculated according to Dauben's procedure[10] using increments taken from Haberditzl.[15] The required experimental susceptibilities were taken from ref 16. [e] Data from $CLIB_{trans}$. See text (Interpretation). [f] b calculated from Pascal constants[17] including the exaltation for delocalization. [g] Calculated from the susceptibilities of benzene and monofluorobenzene. [h] b of biphenylene (and fluoranthene) was calculated with the solution density of biphenylene (and fluoranthene): 1.08 g mL^{-1} from own measurements of both compounds. The known crystal densities are higher: 1.24 g mL^{-1} (1.25 g mL^{-1}). A comparable decrease of the density on destroying the crystal lattice is known from the reported[18] 11.3% volume expansion on fusion of the fluoranthene crystal (volume difference between crystal and melt).

as expected from simple structural considerations. A comparison with the relative scale of diamagnetic exaltations, as calculated by Dauben's group[10] (or calculated by us in the same way), is also informative. The agreement between the two scales is good to very good and thus supports the view of a neighborhood phenomenon exerted by the ring current of D molecules that surround $CLIB_{cis}$. We do not feel competent to assess the work of Dauben's group (or similar work from other groups). However,[10] the Pascal–Pacault–Haberditzl–Dauben method is based on certain assumptions, and its accuracy cannot be better than the accuracy of the estimation of the molecular susceptibility χ_m' from the Haberditzl increment system[15] for the nondelocalized molecular structure. For instance, the exaltations of naphthalene and azulene (relative values 2.23 and 2.16) are explicitly stated to be the same within experimental uncertainty.[10] Thus the relative accuracies of the values in Table I are at present unknown, although the large discrepancy for thiophene may be connected with the uncertainty[10] in the increments for the C–S–C part of the molecule. Contrary to the exaltation, our results place thiophene nearer furan than benzene. Generally, Dauben's group attested a larger uncertainty in χ_m' for heterocycles than for carbocycles. In some cases the estimation of χ_m' seems to be erroneous,[10] since on recalculation different numbers were obtained, possibly due to an error in counting atoms or bonds. One exaltation changed due to a different literature value for the experimental susceptibility.[16] The inaccuracy in the reported χ_m' is particularly important for phenanthrene, because the recalculated number agrees much better with the relative number of our method than the published exaltation does. In other cases the discrepancy between published and recalculated numbers is much smaller.

The large discrepancy for fluorene can be explained as follows. Since the anisotropy of a condensed ring system is usually close to the sum of the anisotropies of the individual rings,[10,19] the exaltation may give too low an estimate in this case. The diamagnetic exaltation of cyclopentadiene is significantly different from zero (47% of benzene; the authors considered the possibility of hyperconjugative π-electron delocalization[10]), which should cause a greater exaltation for fluorene than for biphenyl. Simple addition of the exaltations of biphenyl and cyclopentadiene gives 2.39 for fluorene. This value is closer to the number from our method (2.64) than to the reported or recalculated exaltation of fluorene. Similar considerations can explain the discrepancy for indene and indole; addition of the exaltations of benzene and cyclopentadiene or benzene and pyrrole give the numbers 1.47

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(17) Suhr, H. *Anwendungen der kernmagnetischen Resonanz in der organischen Chemie*; Springer-Verlag: Berlin, 1965; pp 24–27.

(18) McLaughlin, E.; Ubbelohde, A. R. *Trans. Faraday Soc.* **1957**, 628–634.

(19) Pacault, A. In *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israel Academy of Science and Humanities: Jerusalem, 1971; pp 39–46.

(indene) and 1.74 (indole), respectively. The exaltation for fluoranthene is in fair agreement both with our number and with the formal composition of the molecule from naphthalene and benzene. Since the relative exaltation of acenaphthylene has nearly the same value, one may assume that the exaltation is not a good measure of the ring-current effect of acenaphthylene, implying that our markedly lower relative number may be more reliable.

There are additional reasons to indicate that the method of linear shift-concentration relations can provide reliable relative numbers for planar D molecules. One peculiar result of Table I supports strongly the postulated linear relation between $\bar{a}$ and the magnitude of the diamagnetic ring-current effect (diatropism). The crucial structural difference between biphenylene and the other condensed compounds of Table I is the incorporation of an antiaromatic (paratropic) ring into biphenylene. The respective paramagnetic contribution essentially lowers the total diamagnetic ring current and leads indeed to a relative number (1.24) much lower than the naphthalene number. The biphenylene number agrees well with the number 1.18 that was recently calculated on a graph-theoretical basis in this journal.[20] Just as the other condensed compounds of Table I show the above-mentioned addition of the effects of the incorporated monocycles, in biphenylene the effect of one of the two benzene rings is nearly cancelled by the central cyclobutadiene.

Although the exaltation shows no systematic influence of increasing methylation of benzene, our method reveals a clear trend. A similar but inverse trend is observed for chlorination of benzene. One may indeed expect such a substituent influence. The agreement between the two scales is better for the five chlorinated benzenes of Table I including the positional influence with disubstitution. The influence of fluorination is as expected although, for reasons given below, the data for the perfluorinated benzene were obtained from $\mathrm{CLIB_{trans}}$. *tert*-Butylbenzene provided a lower relative number on our scale than did toluene. This finding may reflect a larger average distance between $\mathrm{CLIB_{cis}}$ of a CLIB molecule and a neighboring D molecule due to a steric hindrance of collisions, although hyperconjugation in toluene may provide another explanation. *tert*-Butylbenzene was actually selected to test the steric hindrance required from our model. Steric hindrance predicts a similar but smaller effect for cumene, as was indeed found. For the same reason the relative number for diphenylmethane may be somewhat low.

As a whole, the agreement between the two relative scales in Table I is remarkable when one considers that the diamagnetic exaltation is assumed to reflect the true ring-current effect (ring current effect in the narrower sense) while $\bar{a}$ should reflect the total magnetic anisotropy, i.e., the ring-current-induced anisotropy plus the anisotropy of the (hypothetical) nondelocalized molecule. To verify this hypothesis, the two cyclohexadienes were studied. Both isomers yielded $\bar{a} = 0.011$ ppm L mol^{-1} (relative scale number 0.16) from 5 data points ($[\mathrm{D_o}]_i$ 0.18–0.58 mol L^{-1}) for the 1,3 isomer and from 10 data points ($[\mathrm{D_o}]_i$ 0.07–0.60 mol L^{-1}) for the 1,4 isomer. The accuracy of these two results (maximum Δ_i about 2 Hz) is definitely not as good as that of the results in Table I (maximum Δ_i usually an order of magnitude greater), but even an unlikely error of 10% would be irrelevant for the present discussion. The relative exaltation numbers are −0.05 for the 1,3 isomer and +0.01 for the 1,4 isomer.[10] These numbers are smaller than the inherent error of the estimation and have been considered to be indistinguishable from zero.[10] Thus there is a small but fundamental difference between the two relative scales in Table I. A substantial part of this difference is, however, compensated for by referring the relative scale of $\bar{a}$ to the total diamagnetic anisotropy of benzene and the relative exaltation scale to the ring-current anisotropy of benzene. It seems relevant to note here that this difference between the pure ring-current effect and the total anisotropy is often not recognized in calculations of a proton site in a complex or in a molecule.

The large difference in $\bar{a}$ between the two nonaromatic cyclohexadienes on one hand and the compounds of Table I on the other hand would be difficult to explain unless by the difference in diamagnetic anisotropy. Thus, in addition to the good agreement of most of our numbers with the relative exaltation numbers in Table I, the cyclohexadiene and biphenylene results may be regarded as evidence for the proposed linear relationship between $\bar{a}$ and the diamagnetic anisotropy (ring-current effect in the wider sense) of a planar D that allows a tight vicinity to $\mathrm{CLIB_{cis}}$ (i.e., a D without steric hindrance of collisions between $\mathrm{CLIB_{cis}}$ and the plane of D). For acenaphthylene one can add a further argument in favor of $\bar{a}$, since this is only slightly greater than the $\bar{a}$ of acenaphthene or naphthalene. By comparison with the cyclohexadiene $\bar{a}$ the respective differences (0.23 and 0.12 in the relative scale) appear compatible in size with the extra double bond present in acenaphthylene.

This new method provides a means to obtain directly, with commonly available equipment, in a short time and with a very simple technique, relative values of the ring-current magnetism of many aromatic compounds. Apart from planarity of D the only prerequisite would appear to be sufficient solubility in $\mathrm{CCl_4}$. The possibility to perform the measurements at elevated temperatures to improve solubility has not yet been tested.

Interpretation of Probe Behavior: AUS Concept and ASIS

The results in Table I are clearly associated with the particular solvent effects usually called ASIS, when the applied technique is analyzed in terms of molecular complexes. An explanation of Table I is presented that fuses both aspects. Although other explanations may be found, our model seems to be very useful and compatible with many results. It emerges from (a) the AUS concept as published in this journal[3] and developed further in ref 4 and from (b) the first observation of a linear shift–concentration relation[6] that was found by chance during the pursuit of another concept. Indeed, this explanation was implicitly contained in and logically derived from the said papers. Our next two examples of linear behavior (CLIB with naphthalene and phenanthrene)[21] were studied to examine how much a complex shift is "allowed" to increase when D in AD changes from benzene to naphthalene and to phenanthrene.

According to theory (compare, e.g., ref 22) the influence of a solvent on the chemical shift δ_s relative to the chemical shift δ_g in the gaseous state of the "solute" is composed of contributions from bulk diamagnetic effects, from magnetic anisotropy of solvent molecules, from polar effects (electric field effects), from van der Waals effects, and from specific interactions between solute and solvent molecules (i.e., complexation effects). The first contribution can be either rather accurately determined or eliminated by internal referencing. The problems of the latter technique are known[23] and will be discussed later. The sum of the remaining contributions may be termed local solvent effects.[23] The magnitude of any single component of the local effects is difficult to estimate either theoretically or experimentally unless the component in question strongly predominates. The latter condition is more easily achieved when—as in Table I—the chemical shifts of a solute in two solvents are compared. This is particular so when both solvents (and their molecules) have similar properties with the exception of one, which is important for the effect to be studied. Predominance of specific effects is the basic principle for classic NMR studies of molecular complexes. This predominance is highlighted by the experimental fact that there is a gradual change in the (mixed) solvent and that both components of the solvent are usually nonpolar, thus keeping the influence of the polar effect small if not negligible.

Insufficient predominance of the specific effect was probably responsible for many problems in the determination of formation constants *K* of molecular complexes where data reduction was

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(21) Presented at the Gordon Research Conference on Electron Donor–Acceptor Interactions, 1984. H.S. thanks Professors William Herndon and Heinz Staab for the discussion at this conference and for the encouragement received in this way.

(22) Buckingham, A. D.; Schaefer, T.; Schneider, W. G. *J. Chem. Phys.* **1960**, *32*, 1227–1233.

(23) Becconsall, J. K.; Daves Jr., G. D.; Anderson Jr., W. R. *J. Am. Chem. Soc.* **1970**, *92*, 430–432.

restricted to the pioneering work in this field (e.g., ref 8). These problems are (a) nucleus dependence of K and/or (b) nonlinearity of Scatchard–Foster–Fyfe plots or Hanna–Ashbaugh plots.[8] It was precisely these problems that led to the mentioned refinement of the model and of the data reduction by taking into account the change in nonspecific local effects (AUS effects) when part of the inert solvent (CCl_4 in our case) is replaced by D. This change seems to be significant for an aromatic D only, due mainly to the anisotropy of D.

So, for the determination of formation constants K of weak 1:1 molecular complexes AD from ^1H NMR shifts the classical model and the classical kind of data reduction have been refined by the concept of additional unspecific shielding (AUS[3,4]) of free (A) and complexed (AD) acceptor molecules by noncomplexing aromatic donor molecules D in the vicinity of A or AD, respectively. Under the usual experimental conditions, i.e., $[D_o]_i \gg [A_o]$, the additional chemical shift is in most cases at least approximately given by $a_1[D_o]_i$ for A and by $a_2[D_o]_i$ for AD. The magnitudes of the AUS coefficients a_1 and a_2 are assumed to depend on the molecular site of the observed proton. Reduction of data according to a modified[3,4] Scatchard–Foster–Fyfe equation (eq 1) provides K from the chemical shifts Δ_{oi} of an A signal measured relative to the same signal in the absence of D.

$$\frac{\Delta_{oi} - m_2[D_o]_i}{[D_o]_i} = -K(\Delta_{oi} - m_2[D_o]_i) + \text{intercept} \qquad (1)$$

$$\text{intercept} = K\Delta_{AD,\infty} + m_1 - m_2$$

$$m_1 = a_1 + b \qquad m_2 = a_2 + b$$

$\Delta_{AD,\infty}$ is the true complex shift, i.e., the shift of the complexed A relative to the shift of the free A, and b is the susceptibility correction for the strongly recommended[3,4] external reference. The meaning of the indices is the same as in ref 3 and 4.

Applying this refined model in combination with high-precision experiments, a study of more than 20 A/D systems[4–7,14] in CCl_4 provided K values in the range of 0.1–3.4 L mol^{-1}. In this study a strong emphasis was placed on efforts to reach an optimal range of saturation fraction $[AD]/[A_o]$.[13] The K values obtained are much higher than the reliability limit given by Person[13] for photometric determinations of K. The relative experimental error in Δ_{oi} is not greater than that assumed by Person for photometry, at least when $\Delta_{AD,\infty}$ or intercept/K is large (e.g., >1 ppm). Prue[24] gave a limit of 0.2 L mol^{-1} for photometric determinations which was deduced by consideration of the nonspecific effect (Orgel and Mulliken[25]). Prue's deduction was based on two premises that do not hold for the NMR technique: the measurable effect was assumed to be equal in size for real complexes and for contact complexes (encounters) and to be independent of the arrangement of the interacting molecules relative to each other. One of the most important aims of the said study was to confirm the reliability of the obtained K's. The least-squares sums were low, there was a good agreement between the results from different kinds of data reduction, and there was a good agreement with results from the shift difference method.[4] The crucial test, however, was the independence of the obtained K from the observed nuclei of A. A was usually selected so that it provided at least two independent NMR signals, usually three or four. It is considered good evidence for the reliability of K when one obtains the same K from three or four different signals. This agreement in K was always found, with the exception of one system where most probably a 1:2 complex is formed in addition to the 1:1 complex.[7,26] The values of K obtained depended quite reasonably on D and on A. Steric hindrance was observed in the complexation of a planar A with a planar D when a substituent was introduced in A that protruded from the molecular plane.[14]

So, by considering K (and intercept/K) the results obtained with the AUS concept appear to be sound. As for the two AUS coefficients, a_1 cannot be determined experimentally, while a_2 varied as expected with the molecular site in A (and so also in AD). One referee pointed out that Becconsall's derivation[27] that there is no site specificity in the anisotropy effect of benzene on a spherical solute molecule might be incompatible with the observed site specificity. The main result of Becconsall's theory was, however, the dependence of the anisotropy effect on the diameter of the solute molecule. Following Becconsall's experimental test for his theory (Table 1 in ref 27), the differences in local shielding effects $\sigma_{loc}(\text{benzene}) - \sigma_{loc}(CCl_4) = \Sigma_{loc}$ were measured (250 MHz) for the four proton sites in 2-methylbutane and were found to be (in ppm) 0.712 for the methine proton, 0.683 for the methylene protons, 0.668 for the single methyl group (Me), and 0.655 for CMe_2. The same trend was observed with 2,3-dimethylbutane, 2,2-dimethylbutane, and 3,3-dimethylpentane and can be expressed (maximum deviation 0.007 ppm) by the empirical equation $\Sigma_{loc}(\text{methine}) = \Sigma_{loc}(\text{methylene}) + 0.027\ \text{ppm} = \Sigma_{loc}(\text{single Me}) + 0.040\ \text{ppm} = \Sigma_{loc}(CMe_2) + 0.049\ \text{ppm} = \Sigma_{loc}(CMe_3) + 0.052$ ppm. This is a remarkable site specificity where probably only differences in anisotropy and van der Waals effects are involved. Rummens[28] has provided evidence that both effects can contribute to a site specificity of the magnetic shielding by a nonpolar solvent. Thus, also the AUS effect can be expected to show a site specificity, in particular when one considers the nonspherical shape of A molecules and AD complexes and the influence of polar effects in A (and AD) on the relative orientation of surrounding D molecules. It is important to state here that the core of the AUS concept is not necessarily connected with the site specific anisotropy effect depending exclusively on molecular shape. Furthermore, the AUS effect on A or AD is presumed to be caused predominantly but not at all exclusively, by an anisotropy effect. For example, van der Waals effects may increase or decrease the site specificity when they differ for the aromatic D and the isotropic solvent molecules (CCl_4 in our case). Site specificity of van der Waals effects can be taken for granted.[29]

A logical extension of the AUS concept is its application to ASIS, a phenomenon that has been used and analyzed in many papers (compare, e.g., ref 2, 30–33, 36). From the AUS concept it follows immediately that ASIS, $\delta_{CCl_4} - \delta_{\text{benzene}}$ (or $\delta_{\text{cyclohexane}} - \delta_{\text{benzene}}$[36]), for a solute A is composed essentially of three contributions: {1} AUS with corresponding upfield shifts is always operative; {2} complexation-induced shifts may vary from zero to dominant upfield shift contributions according to eq 1 or in a more complex manner if the pure 1:1 model does not hold or self-association is involved; {3} apparent downfield shifts caused by upfield migration of the internal reference signal counteracting {1} and {2} or apparent upfield shifts caused by downfield migration of the internal reference signal.

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(33) Leupold, I.; Musso, H.; Vicar, J. *Chem. Ber.* **1971**, *104*, 40–49. To avoid an influence of the (internal) reference shifts on ASIS, the proposed use of an "absolute" external reference is not necessary. For this purpose any external reference dissolved in any solvent will do, since the "influence" of eternal referencing comes only through the difference $\chi_{CCl} - \chi_{\text{benzene}}$ (assuming an identical shape factor), i.e., through the change in volume susceptibility when going from CCl_4 to benzene. This independence of "absolute" ASIS on the choice of an external reference has already been stated by Rummens and Krystynak.[34] For solvent effects on internal references see also Laszlo et al.[35]

(34) Rummens, F. H.; Krystynak, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 6914–6921.

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According to ref 4 and 6, the contribution from AUS may include a small term quadratic in the benzene concentration $[D_o]_i$ if the solute signal originates from two or more proton groups in A with an intramolecular distance large enough to allow simultaneous noncomplexing but (on the average of time) magnetically effective collisions with more than one benzene molecule. In terms of the average equilibrium distribution of benzene molecules in the vicinity of the solute one has to consider "more than one vicinity" for such a solute signal. As one referee pointed out, such quadratic may also (in part) be due to a quadratic term in the χ_v for the mixed solvent. On changing the solvent stepwise from pure CCl_4 to nearly pure benzene, noncomplexing solutes of this type, e.g., TMS or cyclohexane, show[6] $\Delta_{oi} = q[D_o]_i^2 + r[D_o]_i$ with $r = 0.054$ ppm L mol^{-1} and q in the range 0.000 40–0.000 61 ppm L^2 mol^{-2}. When the vicinity of such a solute, or rather the vicinity of all its equivalent proton groups, contains only one benzene molecule (second term), this benzene molecule will essentially shield or deshield only one of these equivalent groups. Therefore, this r is smaller ("partial shielding"[4]) than r for a signal derived from a single proton group in A ($\bar{a}$ of benzene in Table I).

The second contribution to ASIS, the complexation-induced shift, $\Delta_{AD,\infty}[AD]/[A_o]$, needs no comment. The third contribution arises from the use of an external reference in ASIS experiments as was recently demonstrated by Jutila[37] and already discussed previously by Musso et al.[33] and by Rummens and Krystynak.[34] Like any solute, the internal reference is liable to an AUS effect that may be nonlinear for one of the common references[6] (see above). The combined equidirectional contributions to ASIS by the first two contributions are reduced by the third and may even be dominated by it, resulting in a negative ASIS.[33] For the ASIS $\delta_{CDCl_3} - \delta_{benzene}$ the interaction of $CDCl_3$ with A may contribute to ASIS. In principle, the three components of $\delta_{CCl_4} - \delta_{benzene}$ can be separated, depending on the precision obtainable in K and $\Delta_{AD,\infty}$ (for which intercept/K is an approximation). Thus, according to the published[4] complex parameters and according to the AUS of internal TMS (concentration <0.2%),[6] the ASIS of *p*-dinitrobenzene (1.03 ppm from the figure in ref 30a, 1.07 ppm from our own measurement) is composed of 1.102 ppm from the complexation (assuming $[A_o] = 0.1$ mol L^{-1}), about 0.689 ppm from AUS (in the approximation $m_1 = m_2$), and −0.673 ppm (−0.62 ppm is given by Jutila) for internal TMS, amounting to a total of 1.12 ppm. The true, reference-independent ASIS (Becconsall et al.[23] proposed the notation $\bar{\Delta}_{C_6H_6}^{CCl_4}$ for this quantity; Rummens and Krystynak[34] have shown how it can be obtained experimentally) is 1.67 ppm as calculated from complexation and AUS, diminished by the susceptibility correction of 0.122 ppm. It should be noted, however, that such calculations may suffer from various inaccuracies that may occur in the susceptibility correction, in the approximations $m_1 = m_2$ and $\Delta_{AD,\infty}$ = intercept/K, and in the parameters of the complex.

The simultaneous but separate consideration of specific (complexation) and nonspecific effects, as quantified by eq 1 for the most simple and probably most frequent case, is the crucial point in the novel AUS model of ASIS. Former attempts to understand ASIS can be classified into three groups: pure complexation, pure nonspecific effects, and some kind of merging of both of these effects in a cluster model.[32] The latter constitutes the electronically favored part of the AUS effect. It ignores more or less the entropic average equilibrium distribution of solvent molecules D in the vicinity of a solute molecule A which must result even without electrostatic interactions. In contrast, the AUS coefficients a_1 and a_2 may include van der Waals as well as electrostatic contributions such as attraction or repulsion of the π-electron cloud of D.

According to the discussion above and in ref 4 there are three formally simple requirements if a reference A is to provide an easily measurable signal with a strictly linear shift dependence on the concentration $[D_o]_i$ of benzene or another aromatic compound sufficiently soluble in CCl_4: (1) The signal should originate from a molecular area of A too small to be shielded magnetically by two of these aromatic molecules simultaneously. (2) The signal should be free of complexation effects (specific effects). (3) The signal should be sharp and not too weak. Requirement (1) is met when the signal arises from a single proton, a single methylene, or a single methyl group; (2) is met with certainty when A does not complex at all; (3) is best met by a methyl singlet. How does the $CLIB_{cis}$ fulfill these requirements, in particular (2), since (1) and (3) are obviously fulfilled, although (3) not optimally (but one can easily determine the chemical shift of the center of the apparent doublet)? Simple molecular considerations have led to a T-shaped topology (Figure 1) for the benzene complex,[6] being governed by the polar nature of CLIB, so that the complexing benzene molecule "touches" $CLIB_{trans}$ and leaves $CLIB_{cis}$ outside the influence of the specific effects of this complexing benzene molecule ($\Delta_{AD,\infty} = 0$ for $CLIB_{cis}$). Thus, being measured with an external reference, the upfield shift Δ_{oi} of $CLIB_{cis}$ is caused by the AUS effect in its linear form and by the linear susceptibility contribution $b[D_o]_i$. This means that $\Delta_{oi} - b[D_o]_i$ is a weighted (i.e., K and $[D_o]_i$ dependent) average of $a_1[D_o]_i$ and $a_2[D_o]_i$. Since in principle one can only speculate about the magnitude of a_1, an estimation of the difference between a_1 and a_2 is difficult at best. For $CLIB_{cis}$, however, a_1 and a_2 will not differ much, if any, since all local nonspecific effects on $CLIB_{cis}$ will be insignificantly changed when going from free CLIB to complexed CLIB. The T-shaped topology of the complex leaves $CLIB_{cis}$ in a rather free position. So, the relative difference $2(a_1 - a_2)/(a_1 + a_2)$ can be expected to be small (absolute value), reducing eq 1, in the limits of experimental precision, to $\Delta_{oi} = m_2[D_o]_i = (a_2 + b)[D_o]_i$. Hence requirement (2) is sufficiently met because $\Delta_{AD,\infty} = 0$ and the absolute value of $2(a_1 - a_2)/(a_1 + a_2)$ is sufficiently small so that $\Delta_{oi} = \bar{m}[D_o]_i = (\bar{a} + b)[D_o]_i$, where $\bar{m}$ and $\bar{a}$ can be taken as a constant average of m_1 and m_2 and of a_1 and a_2, respectively.

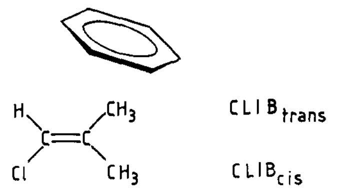

Figure 1. Benzene complex.

The explanation presented for the behavior of $CLIB_{cis}$ toward aromatic D (except hexafluorobenzene) finds further support from the following results. According to the above explanation, other probe substances should exist that fulfill the three requirements set up for a linear shift–concentration dependence. Toluene was considered to be a candidate for a second anisotropy probe. Its methyl signal showed indeed the expected linear behavior (except with hexafluorobenzene, which produced a downward curvature) in the hitherto investigated cases: benzene, *tert*-butylbenzene, anisole, diphenylmethane, fluorene, 9,10-dihydrophenanthrene, indene, biphenylene, azulene, fluoranthene, acenaphthylene, phenanthrene, and benzofuran. These measurements yielded a relative scale whose numbers were equal to within ±4% (two exceptions, see below) with the corresponding numbers of the $CLIB_{cis}$ scale. The $\bar{a}$ of benzene (0.067 ppm L mol^{-1}) comes very close to $\bar{a}$ from $CLIB_{cis}$. *tert*-Butylbenzene had a deviation (relative scale) of +5%. This may lie within the precision of the method, but it would also be compatible with a greater minimum distance (i.e., a more efficient steric hindrance of collisions) between *tert*-butylbenzene and $CLIB_{cis}$ than between *tert*-butylbenzene and the methyl group of toluene. The other exception was azulene (+8%). If this is a significant deviation, it may be connected with the electric dipoles of the molecules involved, which will lead to prolonged duration of the encounter (by Coulomb attraction increased AUS effect). More information about this and other questions may come from future work. To give the methyl group of toluene a molecular environment very similar to $CLIB_{cis}$, *o*-chlorotoluene was investigated as a third probe with several D's. For benzene, chlorobenzene, thiophene, naphthalene, phenanthrene, and fluoranthene $\bar{a}$ was identical to within ±2% with the corresponding $\bar{a}$ of Table I. Conversion to a relative scale was

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[37] Jutila, M. *Acta Chem. Scand.* **1981**, *35B*, 503–506.

not necessary for the comparison of the two probes since $\bar{a}$ (0.070 ppm L mol^{-1}) was practically identical with that of CLIB$_{cis}$. In these experiments *m*-chlorotoluene was simultaneously studied. Its methyl signal showed a behavior similar to that of CLIB$_{trans}$. The maximum discrepancy (for the highest concentration of fluoranthene) was $\Delta_{oi} = 21.00$ Hz as compared with 19.72 Hz for CLIB$_{trans}$. At low concentrations $[D_o]_i$ the Δ_{oi}'s were identical within the precision of the shift measurements (0.12 Hz). These comparisons of CLIB with the two chlorotoluenes support the signal assignment[38] for CLIB as well as the complex topology as shown in Figure 1.

The behavior of hexafluorobenzene contrasts sharply with that of the other aromatic compounds D. Both methyl signals of CLIB are shifted upfield by hexafluorobenzene but that of CLIB$_{cis}$ more so than that of CLIB$_{trans}$. This reversed behavior is unequivocally demonstrated by the crossing of the two methyl signals of CLIB when a solution of CLIB in pure benzene is stepwise changed to a solution in pure hexafluorobenzene. The hexafluorobenzene data in Table I are derived from CLIB$_{trans}$, which shows a linear dependence on $[D_o]_i$, while CLIB$_{cis}$ shows a nonlinear dependence with an upward curvature. Thus, in the above general interpretation the two methyl signals of CLIB have to be interchanged for hexafluorobenzene with the modification that the complexation behavior of hexafluorobenzene, in particular the topology of this complex, is not yet understood. The complexation must induce a downfield shift ($\Delta_{AD,\infty} < 0$) on CLIB$_{cis}$. Very recent unpublished results[14] point analogously to an "abnormal" topology or other abnormal effects in the complexation of hexafluorobenzene with caffeine and tetramethyluric acid but not in the complexation of caffeine with fluorobenzene.[14] The linear shift–concentration relation of CLIB$_{trans}$/hexafluorobenzene, however, indicates a pure ring-current effect. The respective $\bar{a}$ of hexafluorobenzene that is obtained from CLIB$_{trans}$ can be assumed to be at least a good approximation for the hypothetical $\bar{a}$ from CLIB$_{cis}$. Considering the basis of the relative scale, for benzene the hypothetical $\bar{a}$ of CLIB$_{trans}$ will come very close to $\bar{a}$ of CLIB$_{cis}$. The behavior of *m*-chlorotoluene toward hexafluorobenzene is identical with that of CLIB$_{trans}$ (identical $\bar{a}$), while the behavior of *o*-chlorotoluene resembles that of CLIB$_{cis}$. The methyl signal of toluene gives a downward curvature. An "abnormal" influence of hexafluorobenzene (as compared to the influence of benzene) on chemical shifts of solutes is known from previous work[30] on ASIS$_{C_6F_6}$, $\delta_{CCl_4} - \delta_{C_6F_6}$. The three contributions to ASIS$_{benzene}$, $\delta_{CCl_4} - \delta_{benzene}$, as discussed above will be found here too, but the contribution from complexation to ASIS$_{C_6F_6}$ seems to be complex and opposite in direction (downfield). The crucial point for the present discussion, however, is again the linear concentration dependence of the contribution from AUS.

As mentioned above, our method might be compared with a previous attempt to measure above-plane ring-current effects.[12] That attempt used acetonitrile as a probe and applied a completely different technique for the estimation of relative solvent shifts *S*: the change in chemical shift of acetonitrile relative to internal cyclohexane was measured when going from the solvent cyclohexane to the solvent X. No linear shift–concentration relation guaranteed the absence of complexation effects. *S* is a kind of ASIS with cyclohexane as internal reference. According to the explanation for ASIS, these *S* values are composed of the three contributions to ASIS. Similar to the example of dinitrobenzene analyzed above, the main contribution will be the complexation effect $\Delta_{AD,\infty}[AD]/[A_o]$. That means *S* depends mainly on the formation constant *K* of the acetonitrile complex, on the respective complex shift $\Delta_{AD,\infty}$, and on the concentration $[D_o]_{neat}$ of neat D, where the authors used the symbol X in place of D. While in our method the linear shift dependence $\Delta_{oi} = \bar{a}[D_o]_i$ comes exclusively from the AUS effect on CLIB$_{cis}$, the contribution to *S* from the AUS effect on acetonitrile is counterbalanced more or less by the AUS effect on the internal reference cyclohexane. The authors assume K to be nearly constant for various X, so that *S* would roughly be proportional to $\Delta_{AD,\infty}$. This does not necessarily hold. On going from D (or X) = benzene to D (or X) = phenanthrene, the increase in *K* amounted to a factor of 7 for tetracyanoethane,[39] of 5 for caffeine,[14] and of 12 for tetramethyluric acid[7] and fervenulin.[14] A comparison of the *S* values with the numbers of both relative scales in Table I, as far as possible, shows that in accordance with the authors *S* can be considered a qualitative measure only: *S* = 1.00 for benzene, *S* = 0.75 for thiophene, *S* = 0.42 for furan, *S* = 0.45 for biphenylene, and *S* = 1.35 for (methylated) naphthalene. A further (and perhaps more important) consideration is the fact that acetonitrile has an extremely high electric dipole moment, which will lead to an orientation-specific interaction of the type dipole–induced dipole. This interaction depends on the polarizability of D. Thus, even the anisotropy of the polarizability may play a major role here.

Experimental Section

Chemical shift measurements (precision better than ±0.122 Hz) were performed in the PFT mode on a Bruker HX 90-E spectrometer (90 MHz), using external $Me_3SiCD_2CD_2CO_2Na/D_2O$ contained in a precisely centered capillary. For each D investigated a set of solutions (number given in Table I) with varying $[D_o]_i$ was prepared by mixing appropriate volumes of two stock solutions, one with $[D_o]_i = 0$ (pure CCl_4) and the second with $[D_o]_i$ very near the highest possible concentration. The two volumes of stock solutions and their mixing were checked by weighing. The concentration of CLIB was the same in both stock solutions of a set and was in the range 0.005–0.010 mol L^{-1} except for the following sets (same units): mesitylene and *o*-chlorotoluene (0.0142), dihydrophenanthrene (0.0166), indene (0.0129), phenanthrene (0.0138), fluoranthene (0.0119), benzofuran (0.0118), and indole (0.0138). For each solution of a set the chemical shift was measured at least twice. The benzene data were taken from ref 6. Benzene and toluene were deuterated. The stock solution of biphenylene crystallized at low room temperature. Slight warming (ca. 25 °C) provided again a homogeneous solution.

Molar susceptibilities, χ_m, were taken from the literature.[15] The susceptibility correction in ppm can be calculated according to

$$\Delta_{i,\mathrm{corr}} = \Delta_i + {}^2\!/_3(\chi_{v,CCl_4} - \chi_{v,\mathrm{soln}\,i})$$

$\chi_{v,\mathrm{soln}\,i}$ was calculated by applying Wiedemann's law for the additivity of the susceptibilities of mixtures. The second term of the above equation is equal to $-b[D_o]_i$.

The 250-MHz spectra were obtained with a Bruker W 250 spectrometer.

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Note Added in Proof. Recent results with pyridine indicate that the CLIB complex with such a polar base differs from that shown in Figure 1: the shift dependence on $[D_o]$ is nonlinear with an upward curvature for both methyl signals of CLIB.

Supplementary Material Available: Tables providing $[D_o]_i$, Δ_{oi}, probe concentration, and susceptibility correction *b* for the systems investigated (21 pages). Ordering information is given on any current masthead page.

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[38] NOE experiments with CLIB in C_6D_6 (250 MHz, 500 MHz) were unsuccessful.

[39] Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: London, 1968; p 202.