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Linear Solvation Energy Relationships. 22. Some Further Examples of the Importance of the *d*δ Term

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Examples are shown of attempts at correlation of solvent effects by the LSER equations (a) $XYZ = XYZ_0 + s\pi^*$ and (b) $XYZ = XYZ_0 + s(\pi^* + d\delta)$. Where the absolute magnitude of the *d* term is relatively small, correlations by equation a may appear to succeed, even though equation b is the more correct equation. For larger *d* values, however, correlations are apt to fail unless equation b is used. Examples described are the ^{77}Se NMR shifts of dimethyl selenide, the ^{125}Te NMR shifts of dimethyl telluride, and the lowest energy band in the electronic spectrum of tungsten tetracarbonyl 1,10-phenanthroline.

We have shown earlier[2] that, when hydrogen-bonding interactions are excluded by a judicious choice of solvents and reactants or indicators, correlations of many types of reactivity parameters and physicochemical properties can take either of two forms: (a) For all electronic spectral transitions so far considered which are shifted bathochromically with increasing solvent dipolarity, with all solvents considered together, and for other properties if families of solvents with similar polarizability characteristics are treated separately (e.g., only non-chlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents), the form of the linear solvation energy relationship (LSER) is given by eq 1, where

$$XYZ = XYZ_0 + s\pi^* \qquad (1)$$

π^* is a dipolarity/polarizability parameter that measures the solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect.[3] (b) For the other types of properties, if all solvents need to be considered together, the preferred from of the LSER becomes eq 2, where δ, a "polarizability

$$XYZ = XYZ_0 + s(\pi^* + d\delta) \qquad (2)$$

correction term", is 0.0 for non-chlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.

Where type A hydrogen bonding (solvent donor/solute acceptor) also influences the XYZ term, the relationships corresponding to eq 1 and 2 are given by eq 3 and 4. Where

$$XYZ = XYZ_0 + s\pi^* + a\alpha \qquad (3)$$

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha \qquad (4)$$

$$XYZ = XYZ_0 + s\pi^* + b\beta \qquad (5)$$

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + b\beta \qquad (6)$$

type B hydrogen bonding (solute donor/solvent acceptor) plays a part, the corresponding equations are eq 5 and 6, where α is a measure of solvent HBD (hydrogen bond donor) acidity[2a,4] and β a measure of solvent HBA (hydrogen bond acceptor) basicity.[2a,5] The XYZ's that have been correlated by eq 1–6 include positions and/or intensities of maximal absorption in IR, UV/visible, ESR, and NMR spectra, NMR coupling constants, free energies of solution or of transfer between solvents of dipolar solutes, and logarithms of reaction rate and equilibrium constants and fluorescence lifetimes.

Frequently, although eq 2, 4, or 6 is the statistically favored form of the LSER, correlations of type (b) properties by eq 1, 3, or 5 have still shown seemingly acceptable statistical measures of goodness of fit (i.e., correlation coefficients, *r*, greater than 0.95). This is usually the case where the *d* value in eq 2, 4, or 6 is relatively small ($d < 0.15$) and the spread of the XYZ values relatively large. Thus, we have reported[6] that, although eq 2 is, indeed, the preferred form of the LSER, solvent shifts of most infrared spectral bands are adequately correlated by eq 1 (of *r* values for 25 correlations, all were greater than 0.90, 23 were greater than 0.95, and 21 were greater than 0.97). Where the "polarizability correction term" is larger ($d > 0.30$) and the XYZ spread relatively smaller, however, attempts at fitting experimental data to eq 1, 3, or 5 have sometimes resulted in seeming lack of correlation.

^{77}Se NMR Shifts of Dimethyl Selenide

As an example of the latter type of experience, Valeev, Kalabin, and Kushnarev[7] have reported poor correlations of solvent effects on the ^{77}Se NMR shifts of $(CH_3)_2Se$ with the solvatochromic parameters π^*, α, and β. Insufficient α values were said to be available for a correlation according to eq 3 (the Russian workers were evidently not aware that non-HBD solvents have α values of zero), and the multiple-parameter correlation with π^* and β according to eq 5 had a correlation coefficient of 0.502 ($n = 13$). We wish now to demonstrate the salutary effect of including a $d\delta$ term in such correlations.

^{77}Se NMR $\Delta\delta$ values have been obtained for 5 mol % solutions of Me_2Se in 19 solvents for which the solvatochromic parameters are known.[7] The shifts are given relative to neat Me_2Se as an external reference, and the authors have shown that the contributions to these shifts from the volume diamagnetic susceptibilities and the magnetic anisotropies of the solvents are no more than 1–2 ppm (i.e., differences in these contributions are negligibly small). The results are assembled with solvent π^* and α values in Table I and plotted against π^* in Figure 1. It is seen in the plot that, if all solvents are considered equally, linear correlation is, indeed, quite poor. However, when the aliphatic and aromatic solvents are considered separately, reasonably good linear progressions become evident. Further, the data points for the aliphatic HBD solvents nitromethane (**32**), methanol (**105**), and acetic acid (**201**) appear to be collinear with those for the non-hydrogen-bonding aliphatic solvents, suggesting that the ^{77}Se NMR shifts are little, if at all, influenced by type A hydrogen bonding by these proton donors.

The least-squares linear regression equations are (a) for ten non-chlorinated HBD and non-HBD aliphatic solvents eq 7,

$$\Delta\delta(^{77}\text{Se NMR}) = 3.2 - 17.5\pi^*\ \text{ppm}^{8} \qquad (7)$$

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(1) (a) University of California. (b) White Oak Laboratory.

(2) (a) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1080. (b) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.

(3) For most non-chlorinated aliphatic solvents (specifically excluding dioxane and hexamethylphosphoramide) π^* values are very nearly proportional to molecular dipole moments: Abboud, J.-L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 8327.

(4) Taft, R. W.; Kamlet, M. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1723; *J. Am. Chem. Soc.* **1976**, *98*, 2886.

(5) (a) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 342. (b) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377.

(6) Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans 2* **1979**, 337.

(7) Valeev, R. B.; Kalabin, G. A.; Kushnarev, D. F. *Zh. Org. Khim.* **1980**, *16*, 2482.

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Table I. Solvent Effects on Properties Studied

no.[a]	solvent	π^*	α	NMR shifts, ppm		$10^{-3}\nu_{\max}(\mathrm{I})$, cm^{-1}
				^{77}Se	^{125}Te	
2	cyclohexane	0.0	0.0	4.5		
3	triethylamine	0.14	0.0	0.4	5.9	
6	carbon tetrachloride	0.29	0.0	2.1	0.9	
7	diethyl ether	0.27	0.0	−2.8	−0.2	19.05
8	toluene	0.54	0.0		0.0	
14	benzene	0.59	0.0	−3.2	−3.1	19.23
15	chlorobenzene	0.71	0.0			19.57
16	2-butanone	0.67	0.05			20.62
17	anisole	0.73	0.0			20.00
18	acetone	0.71	0.09	−9.8	−12.7	21.05
20	1,2-dichloroethane	0.81	0.0			20.80
21	methylene chloride	0.83	0.25	−7.2	−14.9	20.08
23	dimethylformamide	0.88	0.0	−11.9	−18.6	21.46
24	pyridine	0.87	0.0	−5.5	−9.8	
26	hexamethylphosphoramide	0.88	0.0	−9.4		
29	dimethyl sulfoxide	1.00	0.0	−14.9	−26.4	21.83
30	chloroform	0.58	0.35	−7.6	−6.3	19.49
31	nitrobenzene	1.01	0.0	−5.4	−7.1	20.75
32	nitromethane	0.85	0.23	−13.4	−20.6	21.65
41	cyclohexanone	0.76	0.0			20.45
53	mesitylene	0.41	0.0	0.3	5.8	
57	phenylacetonitrile	0.99	nyd[b]	−7.0		
58	acetophenone	0.90	nyd[b]			20.70
61	1,2-dimethoxyethane	0.53	0.0			20.34
63	*N,N*-dimethylaniline	0.90	0.0	−4.2		
90	cumene	0.41	0.0		1.2	
97	fluorobenzene	0.62	0.0		−5.9	
104	ethanol	0.54	0.86			20.20
105	methanol	0.60	0.98	−8.3	−11.2	20.79
109	benzyl alcohol	0.98	0.43			20.70
201	acetic acid	0.64	1.01	−6.7		

[a] Solvent numbering is the same in all papers of this series. [b] Not yet determined.

with r = 0.975 and sd (the standard deviation) = 1.5 ppm, and (b) for six aromatic solvents eq 8, with r = 0.927 and sd = 1.1 ppm. From eq 7 and 8, the d term in eq 2 is calculated to be −0.42,[9] and the "all-solvents" correlation for the 18 solvents of Table I (excluding chloroform)[10,11] is given by eq 9, with r = 0.959[10] and sd = 2.1 ppm. A plot of $\Delta\delta$(exptl) against $\pi^* - 0.42\delta$ is shown in Figure 2, where it is seen that, in contrast with the poor correlations reported by Valeev and co-workers, inclusion of the $d\delta$ term leads to a quite acceptable linear regression equation. The correlation equations indicate, rather convincingly, that solvent effects in the ^{77}Se NMR shifts of dimethyl selenide are influenced primarily (or exclusively) by dipolarity and little, if at all, by HBD acidity (except possibly in the case of chloroform)[11] or polarizability (vide infra).

$$\Delta\delta(^{77}\mathrm{Se\ NMR}) = 3.6 - 9.8\pi^*\ \mathrm{ppm} \quad (8)$$

$$\Delta\delta(^{77}\mathrm{Se\ NMR}) = 2.2 - 15.9(\pi^* - 0.42\delta)\ \mathrm{ppm} \quad (9)$$

When it is taken with eq 7 and 9, the $\Delta\delta$ value of 0.0 for neat Me_2Se suggests that the π^* value of this compound is 0.14–0.18, i.e., about like that for triethylamine (π^* = 0.14), and somewhat less dipolar than diethyl ether (π^* = 0.27).

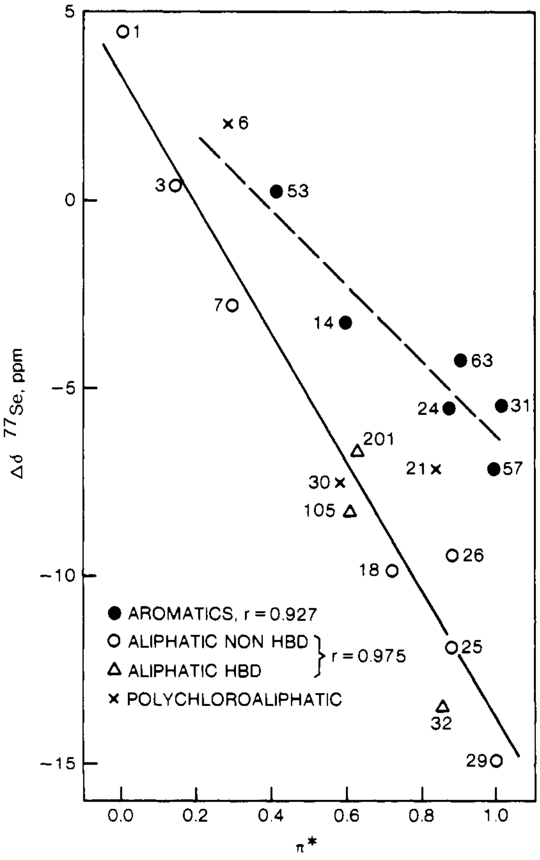

Figure 1. ^{77}Se NMR shifts of dimethyl selenide plotted against solvent π^* values.

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(8) The multiple linear regression equation with π^* and α is $\Delta\delta = 3.22 - 17.5\pi^* - 0.002\alpha$, with r = 0.974, which confirms that effects of type A hydrogen bonding by these aliphatic HBD solvents are negligible.

(9) The d term is estimated through the equation $d = 2(\Delta XYZ)/[s(\mathrm{al}) + s(\mathrm{ar})]$, where ΔXYZ is the difference between values calculated through the aliphatic and aromatic regression equations at π^* = 0.7 and s(al) and s(ar) are the slopes of those regression equations.

(10) If the result for $CHCl_3$ is included, r becomes 0.942.

(11) We have commented earlier[4] on the frequently observed seeming anomaly where weaker HBD solvents like $CHCl_3$ form hydrogen bonds to weak HBA solutes; while stronger HBD solvents like MeOH or AcOH do not. The rationale is in the fact that the latter amphiprotic solvents are stronger HBA bases than the solute and achieve greater stability by remaining self-associated rather than by hydrogen bonding to the solute.

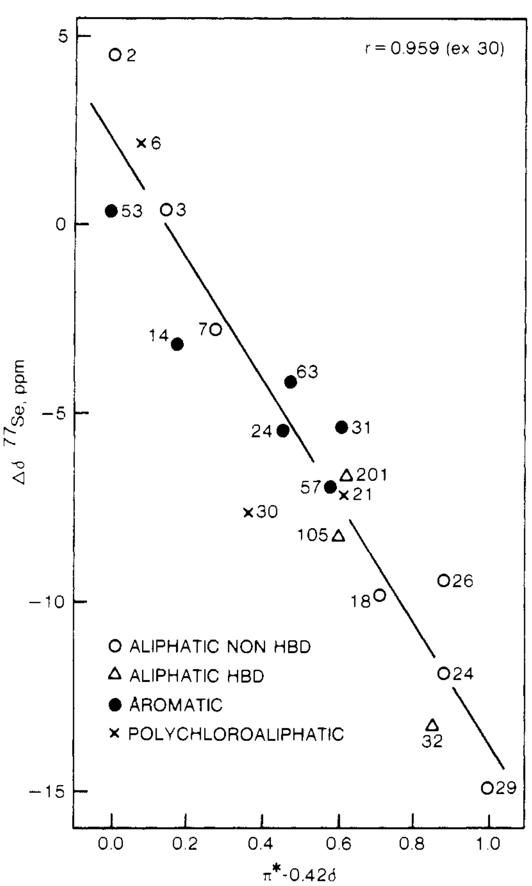

Figure 2. ^{77}Se NMR shifts plotted against $\pi^* - 0.42\delta$.

Further, we have shown earlier[2a,12] that the *d* term in eq 2 is related to the dipolarity/polarizability blend in the solvent effect on XYZ (expressed in terms of functions of the solvent refractive index and the bulk dielectric constant or molecular dipole moment), with *d* becoming more negative as the contribution of the polarizability term became smaller. The *d* value of −0.42 in eq 9 is among the largest negative values which we have yet encountered, which is consistent with the very weakly dipolar solute, Me_2Se, causing relatively little polarization in cybotactic solvent molecules. These observations are in accord with the findings of Valeev *et al.*, who, despite their failures at correlation, concluded that the predominating role is played by the polarity of the solvent.

^{125}Te NMR Shifts of Dimethyl Telluride

The same Russian workers have also reported solvent effects on the ^{125}Te NMR shifts of $(CH_3)_2Te$, again in 5 mol % solutions and against neat Me_2Te as an external standard.[13] Their results in 17 solvents for which the solvatochromic parameters are known are also assembled in Table I.

We have carried out the same types of correlations as above and, as before, the result for chloroform (solvent **30**) was out of line.[11] Also out of line in this case, for reasons that are not now evident to us, was the result for nitrobenzene (**31**). The other 15 solvents fit eq 1 and 2 rather well. As before, a plot against π^* clearly showed the data points for the nonchlorinated aliphatic HBD and non-HBD solvents to be collinear, again indicating that type A hydrogen-bonding effects were negligible. The regression equation for the aliphatics is given by eq 10, with $n = 7$, $r = 0.991$, and sd = 1.6 ppm. For

$$\Delta\delta(^{125}\text{Te NMR}) = 10.5 - 35.5\pi^* \text{ ppm} \qquad (10)$$

the six aromatic solvents (excl **31**), the regression is given by eq 11, with $r = 0.931$ and sd = 2.2 ppm. From eq 10 and 11,

$$\Delta\delta(^{125}\text{Te NMR}) = 15.4 - 30.2\pi^* \text{ ppm} \qquad (11)$$

the *d* term was calculated to be −0.26,[9] and the all-solvents correlation with $\pi^* - 0.26\delta$ is given by eq 12, with $n = 15$ (excl

$$\Delta\delta(^{125}\text{Te NMR}) = 8.4 - 32.6(\pi^* - 0.26\delta) \text{ ppm} \qquad (12)$$

31 and **32**), $r = 0.984$,[14] and sd = 1.9 ppm. A plot of Δδ(exptl) against $\pi^* - 0.26\delta$ is shown in Figure 3.

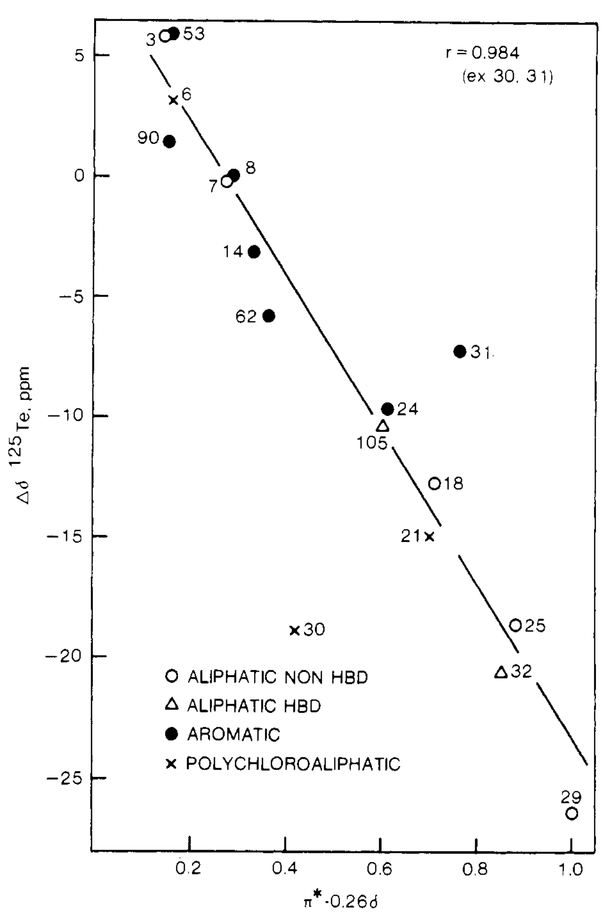

Figure 3. ^{125}Te NMR shifts of dimethyl telluride plotted against $\pi^* - 0.26\delta$.

From eq 10 and 12 and the Δδ value of 0.0 for neat Me_2Te, the π^* value for dimethyl telluride, acting as solvent, is calculated to be 0.26–0.30, i.e., about as dipolar as diethyl ether. The greater dipolarity of Me_2Te compared with that of Me_2Se is consistant with the smaller $-d$ value in eq 12 compared with that in eq 9. The more dipolar solute, Me_2Te, induces the greater solvent polarizability contribution to the dipolarity/polarizability blend.

That NMR spectra of $(CH_3)_2Se$ and $(CH_3)_2Te$ are not influenced by the HBD acidity of most protic solvents[11] indicates that they are very weak HBA bases. In a continuation of the progression from $\beta = 0.47$ for diethyl ether,[2,5] and $\beta = 0.25$–0.29 for diethyl sulfide (estimated from $pK_{HB} = 0.11$ and the 4-fluorophenol ^{19}F NMR value $\Delta = 1.10$ ppm[15] and equations relating these properties to β^{5b}), such weak HBA basicity properties for dialkyl selenides and tellurides are not unexpected.

UV/Visible Spectrum of $W(CO)_4$(phen)

Solvatochromic behavior remarkably similar to that above (i.e., a large $-d\delta$ term and an insignificant dependence on the

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[12] Abboud, J-L, M.; Kamlet, M. J.; Taft, R. W., submitted for publication in *J. Am. Chem. Soc.*

[13] Kalabin, G. A.; Valeev, R. B.; Kushnarev, D. F. *Zh. Org. Khim.* **1981**, *17*, 947.

[14] If the result for nitrobenzene is included, the *r* value becomes 0.952; if the $CHCl_3$ result is also included, $r = 0.904$.

[15] Gurka, D.; Taft, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4794.

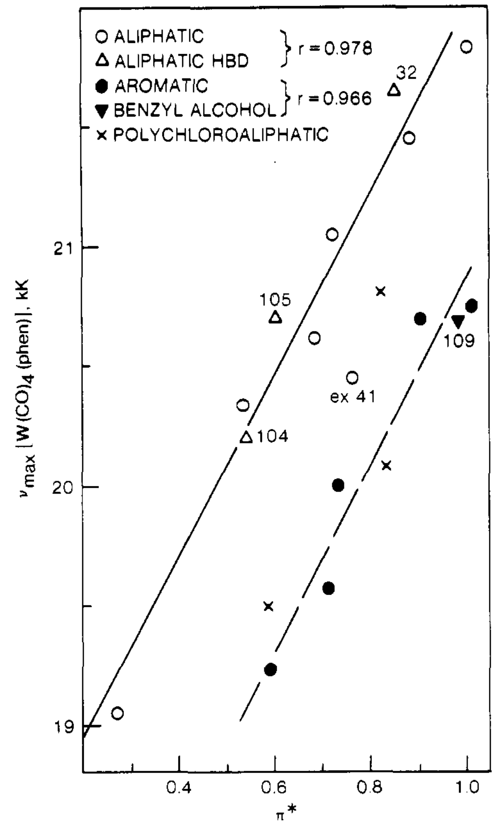

Figure 4. $\nu_{\max}$(I) plotted against solvent π^* values.

α value of self-associated HBD solvents) is shown by a completely unrelated property, the metal → ligand band in the electronic spectrum of tungsten tetracarbonyl 1,10-phenanthroline (I), W(CO)$_4$(phen). Values of $\nu_{\max}$(I) reported by Burgess, Chambers, and Haines[16] in the 18 solvents for which the solvatochromic parameters are known are included in Table I. All correlations discussed below will exclude an obviously out-of-line point for cyclohexanone (solvent **41**). A plot of $\nu_{\max}$(I) against π^* is shown in Figure 4.

It is seen in the figure that, as with the earlier examples, linear correlation is quite poor if all solvents are considered together (the r value is 0.706). If, however, the aliphatic and aromatic solvents are considered separately, good linear regressions are observed for the individual families. It is also seen that the data points for nitromethane (**32**), ethanol (**104**), and methanol (**105**) are collinear with those for the aliphatic non-HBD solvents and the data point for benzyl alcohol (**109**) is collinear with those for the aromatic non-HBD solvents, which is strong evidence that these HBD solvents do not hydrogen bond to I (or, far less likely, that they do hydrogen bond but the hydrogen bonding does not affect the spectrum).

The correlation for the non-chlorinated HBD and non-HBD aliphatic solvents is given by eq 13, with $n = 9$, $r = 0.978$,[17]

$$\nu_{\max}(\mathrm{I}) = 10^3(18.21 + 3.82\pi^*)\ \mathrm{cm}^{-1} \qquad (13)$$

and sd = 0.17×10^3 cm^{-1}. The correlation for the aromatic solvents, including benzyl alcohol, is given by eq 14, with n

$$\nu_{\max}(\mathrm{I}) = 10^3(17.05 + 3.78\pi^*)\ \mathrm{cm}^{-1} \qquad (14)$$

$= 6$, $r = 0.966$, and sd = 0.21×10^3 cm^{-1}. From eq 13 and 14, the d term is calculated to be -0.30,[9] and the all-solvents correlation according to eq 2 (excl CH$_2$Cl$_2$ and CHCl$_3$, which probably hydrogen bond weakly to I) is given by eq 15, with

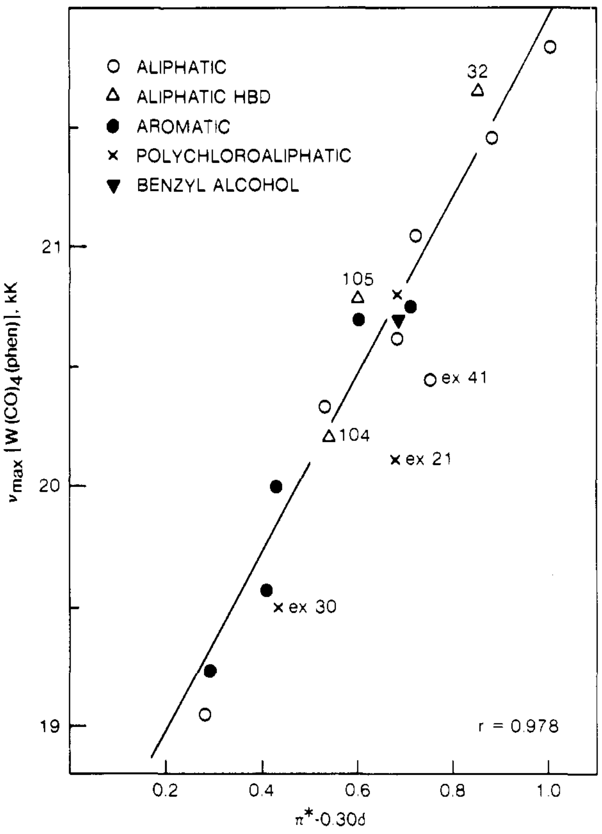

Figure 5. $\nu_{\max}$(I) plotted against $\pi^* - 0.30\delta$.

$$\nu_{\max}(\mathrm{I}) = 10^3[18.18 + 3.85(\pi^* - 0.30\delta)]\ \mathrm{cm}^{-1} \qquad (15)$$

$n = 15$, $r = 0.978$,[17] and sd = 0.17×10^3 cm^{-1}. A plot of $\nu_{\max}$(I) against $\pi^* - 0.30\delta$ is shown in Figure 5, where can be seen the weak bathochromic effect of hydrogen bonding by CH$_2$Cl$_2$ (**21**) and CHCl$_3$ (**30**) (probably to the C=O ligands)[18] and the satisfactory linear regression for the other solvents.

We have recently discussed the problems involved in determining π^* values of HBD solvents (primarily because of difficulties in finding non-HBA indicators that allow us to unravel dipolarity/polarizability from hydrogen-bonding effects).[19] For this reason eq 14 and 15 are of particular interest to us in that they are the first independent confirmation of the π^* value of benzyl alcohol.

Concluding Remarks

We have now carried out sufficient correlations according to eq 2, 4, and 6 to arrive at some very rough preliminary generalizations regarding the sign and magnitude of the d coefficient. Thus, the d value of 0.0 for $\pi \rightarrow \pi^*$ transitions of uncharged indicators (all of which are shifted bathochromically with increasing solvent dipolarity) appears very nearly to represent a limiting condition. We have encountered only one unambiguous example of a positive d term, the fluorescence spectrum of the merocyanine II, for which $d = +0.08$.[20]

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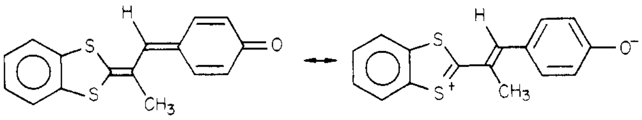
[16] Burgess, J.; Chambers, J. C.; Haines, R. I. *Transition Met. Chem.* (*Weinheim, Ger.*) **1981**, *6*, 145.

[17] If the result for cyclohexanone is included, r becomes 0.960 for eq 13 and 0.955 for eq 15. If CH$_2$Cl$_2$ and CHCl$_3$ are included, r becomes 0.952 for eq 15.

[18] We are very hesitant in suggesting this rationale because of the uncertainty of the δ value of 0.5 for the polychloro aliphatic solvents. The results could also be rationalized by a larger δ. Further, hydrogen bonding to carbonyl should withdraw electrons and hence destabilize the excited state in a metal → ligand transition. This should lead to a hypsochromic effect of hydrogen bonding rather than the observed bathochromic effect.

[19] Chawla, B.; Pollack, S. K.; Lebrilla, C. B.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 6924.

[20] Kamlet, M. J.; Taft, R. W. *Pol. J. Chem.*, in press.



IIa IIb

Electronic $\pi \rightarrow \pi^*$ transitions of charged indicators, which are shifted bathochromically (e.g., 4-nitrophenoxide ion),[21] and all electronic spectra, which are shifted hypsochromically (i.e., all spectra wherein the magnitude of the dipole decreases in the electronic excitation) have relatively large negative *d* terms; we have encountered values ranging from −0.15 to −0.40. The same applies to ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{29}Si, and ^{119}Sn NMR shifts and coupling constants (as well as the ^{77}Se and ^{125}Te shifts reported here). As has been mentioned, values of *d* have generally been lower for infrared $\bar{\nu}$ results, generally ranging from −0.05 to −0.15.

In sharp contrast with the trend reported here for the NMR results, −*d* values for free energies of transfer between solvents seem to decrease with decreasing solute dipolarity. We have reported[22] values near *nil* for toluene and dioxane solutes, −0.09 for the 2-butanone solute, −0.20 for the nitromethane solute, and −0.17 for the $Et_4N^+I^-$ ion pair. As concerns reaction rates, we have encountered *d* values of −0.09 to −0.17 for various types of Menschutkin reactions, but we have been unable to relate *d* to transition-state dipolarity or structure. Thus, we have encountered both larger and smaller −*d* values for reactions with less dipolar transition states.

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Registry No. I, 14729-20-5; ^{77}Se, 14681-72-2; Me_2Se, 593-79-3; ^{125}Te, 14390-73-9; Mn_2Te, 593-80-6.

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(21) Abboud, J. L. M.; Taft, R. W.; Kamlet, M. J. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 603.

(22) Kamlet, M. J.; Carr, P. W.; Taft, R. W.; Abraham, M. H. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1689.

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Murray Hill, New Jersey 07974

Electronic Structure and Bonding in the Disulfur and Diselenium Complexes $[M(X_2)(PH_3)_4]^+$ (M = Rh, Ir; X = S, Se)

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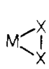
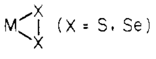
SCF–Xα–SW calculations have been carried out on the model compounds $[M(X_2)(PH_3)_4]^+$ (M = Rh, Ir; X = S, Se) in order to investigate the electronic structure and bonding in complexes of side-on-bonded disulfur and diselenium. In agreement with experiment, the calculations predict an X–X bond order of about 1 and reveal that the M–X_2 covalent interaction increases along the sequence $RhSe_2 < IrSe_2 < RhS_2 < IrS_2$. Relativistic effects partly account for the increase in interaction from Rh to Ir. The side-on-bonded S_2 and Se_2 groups are best described as molecules with excited configuration $...(p\sigma)^2(\pi)^3(\pi^*)^3$. The M–$S_2$ or M–Se_2 bond consists of in-plane π overlap of an S_2 or Se_2 $\pi_{\parallel}^*$ orbital with a metal $p_x + d_{xz}$ hybrid of predominantly p_x character and of σ overlap of a metal $d_{z^2} + p_z$ hybrid with S_2 or Se_2 $\pi_{\parallel}$ and $p\sigma$ orbitals. Optical spectra of $[M(X_2)(dppe)_2]^+$ in EPA glasses at liquid-nitrogen temperature are reported for the 300–800-nm region. All bands are assigned, and acceptable agreement is found between observed and calculated transition energies. The HOMO → LUMO transition occurs as a weak band in the 530–700-nm region; it is primarily intraligand (S_2 or Se_2) in character. The lowest energy strong band is associated with the transition from the M–X_2 π-bonding orbital to the LUMO; it shifts to higher energy from M = Rh to M = Ir on account of the increase in M–X_2 interaction.

Introduction

Disulfur and diselenium can bond to metals in a variety of bridging geometries and also as terminal groups in the side-on manner[2]



Side-on-bonded S_2 and Se_2 complexes are, of course, analogues of the well-known side-on-bonded dioxygen complexes, but unlike the case of the dioxygen complexes, their chemistry has been relatively little studied, and there is no reliable information on their electronic structure. Recent work, especially the preparation of novel new disulfur complexes[3] and the discovery of the addition of low-valent-metal complexes across the S–S and Se–Se bond,[4-6] indicates that further studies on the chemistry of side-on-bonded S_2 and Se_2 are likely to yield interesting results. As a guide for future work, and for interpretation of experimental results, it would be valuable to have detailed information about the electronic structure and bonding in the



group. This paper provides such information from an SCF–Xα–SW investigation of the electronic structure of the complexes $[M(X_2)(PH_3)_4]^+$ (M = Rh, Ir; X = S, Se).

The complexes $[M(X_2)(PH_3)_4]^+$ are models for the compounds $[M(X_2)(L\text{–}L)_2]^+$ (M = Rh, Ir; X = S, Se; L–L = dppe, dmpe), and the calculations are in good agrement with

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(2) For a summary of types of metal–disulfur geometries see A. Müller and M. Jagermann, *Inorg. Chem.*, **18**, 2631 (1979).

(3) Examples: $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$ by A. Müller, W. Nolte, and B. Krebs *Angew. Chem., Int. Ed. Engl.*, **17**, 279 (1978); $(NH_4)_2[Mo_3S(S_2)_6]$ by A. Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl, and M. Dartmann, *ibid.*, **17**, 535 (1978); $[(CH_3)_4N]_2[Mo_2O_2S_2(S_2)_2]$ by W. Rittner, A. Müller, A. Neumann, W. Bather, and R. C. Sharma, *ibid.*, **18**, 530 (1979).

(4) D. Seyferth, R. S. Henderson, and M. K. Gallagher, *J. Organomet. Chem.* **193**, C75 (1980).

(5) D. A. Lesch and T. B. Rauchfuss, *J. Organomet. Chem.*, **199**, C6 (1980).

(6) A. P. Ginsberg, W. E. Lindsell, C. R. Sprinkle, K. W. West, and R. L. Cohen, *Inorg. Chem.*, **21**, 3666 (1982).

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