Solvent and Free-Radical Effects on the ^{13}C NMR Spectra of Hydrocarbons

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Abstract: The proton-decoupled ^{13}C NMR spectra of benzene, naphthalene, azulene, acenaphthylene, fluoranthene, phenanthrene, and 6,6-pentamethylenefulvene have been obtained in dilute solutions in cyclohexane, triethylamine, di-*n*-butyl ether, diisopropyl ether, diethyl carbonate, tetrahydrofuran, butyronitrile, γ-butyrolactone, propylene carbonate, dimethyl sulfoxide, benzene, toluene, fluorobenzene, anisole, acetophenone, benzonitrile, and nitrobenzene. It has been found that (1) the chemical shifts (relative to an external reference) of both alternant and nonalternant hydrocarbons are sensitive to solvent dipolarity-polarizability effects. (2) In the case of "select solvents" (aliphatic, monofunctional compound with one single dominant bond moment) there is a generally good correlation between the solvent-induced chemical shifts (SICS) and the π^* scale of solent dipolarity–polarizability. (3) Aromatic solvent induced shifts (ASIS) and specific interactions are significant in aromatic solvents, although dipolarity-polarizability contributions are still very important. (4) With very few exceptions, SICS (relative to cyclohexane solvent) are downfield, and the results are not in favor of the simple reaction field model. (5) For aromatic hydrocarbons, there is a clear proportionality between the SICS and the paramagnetic shifts induced by the stable free-radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). (6) There is no simple relationship between the SICS and the calculated electronic charge distribution of the solute molecules. These results show the important role played by quadrupoles and higher multipoles in determining solvent–solute interactions involving aromatic solutes. They also suggest that these medium effects involve both a "general dielectric effect" and a more localized noncontinuum action of the peripheral solvent atoms on the peripheral solute atoms.

The sensitivity of ^{19}F, ^{13}C, ^{131}Xe, and ^{129}Xe NMR[4-6] spectra to the molecular environment of solutes has lead to their widespread use for the quantitative analysis of solvent effects.

In most cases (with the exception of Xe), these studies have dealt with strongly polar solutes, particular, substituted benzenes and fluorobenzenes.

Here, we examine the ^{13}C NMR spectra of unsubstituted hydrocarbons (mostly aromatic) in different aprotic aliphatic and aromatic solvents.

The reasons for this choice are as follows: (i) These molecules are free from conformational problems, and their geometries are generally well known. (ii) In the case of substituted benzenes and fluorobenzenes, the hydrocarbon moiety plays a relatively minor role in determining the total dipole moment of the molecule, which is largely dependent on the bond moment(s) of the substituent(s). In the present case, some molecules are devoid of a permanent dipole moment and their electrostatic interactions are determined by higher multipoles. Even in the case of the weakly polar nonalternant hydrocarbons, there are no strong local bond moments. (iii) The ^{13}C NMR spectra of a number of these compounds have been carefully analyzed and all the transitions assigned.[7,8] One can then evaluate the individual response of each carbon to changes in the molecular environment. (iv) The effect of aromatic solvents on the physico-chemical properties of aliphatic solutes is well documented[9] and is included in some empirical treatments of medium effects.[10]

We feel that this work might provide complementary information leading to a better understanding of this kind of solvent–solute interactions.

Experimental Results

We have obtained the ^{13}C NMR spectra of naphthalene (A), azulene (B), acenaphthylene (C), fluoranthene (D), phenanthrene (E), and 6,6-pentamethylenefulvene (F) in the following solvents: cyclohexane (**1**), triethylamine (**2**), di-*n*-butyl ether (**3**), diisopropyl ether (**4**), diethyl carbonate (**5**), tetrahydrofuran (**6**), butyronitrile (**7**), γ-butyrolactone (**8**), propylene carbonate (**9**), dimethyl sulfoxide (**10**), benzene (**11**), toluene (**12**), fluorobenzene (**13**), anisole (**14**), acetophenone (**15**), benzonitrile (**16**), and nitrobenzene (**17**).

The experimental results are given in Tables I and II.

The chemical shifts given therein are taken with reference to the resonance frequency of benzene in the same solvents (benzene has been used as the internal reference). This technique has been used in many cases and is mostly intended to eliminate "bulk" effects.[4a,5a-b] The symbol $(\int^{C_i}_{C_6H_6})_S$ stands for the chemical shift of the *i*th carbon of a given molecule, relative to the chemical shift of benzene in the same solvent.

Cyclohexane was chosen as the reference solvent. $\delta_{S_4C_6H_{12}}\int^{C_i}_{C_6H_6}$ stands for the difference $(\int^{C_i}_{C_6H_6})_S - (\int^{C_i}_{C_6H_6})_{C_6H_{12}}$.

External referencing of the chemical shifts is important.[11] Thus, we have determined the chemical shifts of benzene disolved in solvents **1–17** relative to that of benzene in a dilute cyclohexane solution (external reference). These experimental shifts Δ_s, corrected for bulk susceptibility effects, are shown in Table III (see also the Experimental Section).

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[11] We are grateful to a referee for this and other suggestions and for valuable comments.

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Table I. Relative Solvent Shifts[a,b] $(\int^{C_i}_{C_6H_6})_S$ of Various Hydrocarbons in "Select" Solvents

hydrocarbon	C_i	solvent									
		$c\text{-}C_6H_{12}$	$(C_2H_5)_3N$	$(n\text{-}C_4H_9)_2O$	$(i\text{-}C_3H_7)_2O$	$OC(OC_2H_5)_2$	$(CH_2)_4O$	$n\text{-}C_3H_7CN$	$OCOCH(CH_3)CH_2O$	$OC(CH_2)_3O$	$(CH_3)_2SO$
benzene	1	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
naphthalene	1, 4, 5, 8	−0.36	−0.36	−0.36	−0.36	−0.44	−0.44	−0.52	−0.58	−0.57	−0.58
	2, 3, 6, 7	−2.64	−2.61	−2.59	−2.55	−2.52	−2.54	−2.43	−2.38	−2.35	−2.38
	9, 10	5.88	5.77	5.76	5.69	5.54	5.67	5.32	5.10	5.10	4.71
azulene	1, 3	−9.91	−10.04	−10.02	−10.08	−10.21	−10.27	−10.33	−10.43	−10.39	−10.48
	5, 7	−6.03	−5.87	−5.85	−5.79	−5.71	−5.66	−5.53	−5.47	−5.44	5.41
	4, 8	7.79	7.92	7.94	7.97	8.11	8.08	8.18	8.29	8.27	8.39
	6	8.20	8.42	8.44	8.55	8.56	8.44	8.49	8.50	8.52	8.51
	2	8.79	8.68	8.69	8.67	8.75	8.79	9.03	9.20	9.21	9.35
	9, 10	12.58	12.47	12.44	12.39	12.27	12.32	12.00	11.76	11.82	11.42
acenaphthylene	3, 8	−4.69	−4.51	−4.50	−4.44	−4.24	−4.32	−4.08	−3.90	−3.90	−3.79
	5, 6	−1.25	−1.18	−1.17	−1.17	−1.14	−1.16	−1.11	−1.16	−1.09	−1.04
	4, 7	−0.90	0.81	−0.78	−0.73	−0.63	−0.66	−0.50	−0.42	−0.39	−0.42
	1, 2	0.93	0.98	0.98	1.02	0.98	0.95	0.98	1.00	0.92	1.07
	9, 10	12.16	11.95	11.96	11.91	11.70	11.79	11.44	11.19	11.28	11.79
	11	0.82	0.68	0.63	0.42	0.20	0.34	0.00	−0.25	−0.48	−0.57
	12	0.38	0.29	0.29	0.24	0.12	0.20	0.00	−0.42	−0.58	−0.76
fluoranthene	7, 10	−8.72	−8.54	−8.49	−8.45	−8.18	−8.23	−8.00	−7.86	−7.82	−7.57
	1, 6	−6.9	−6.87	−6.84	−6.82	−6.73	−6.76	−6.66	−6.66	−6.62	−6.43
	3, 4	−1.84	−1.73	−1.71	−1.66	−1.61	−1.63	−1.56	−1.53	−1.51	−1.46
	8, 9	−0.89	−0.81	−0.76	−0.71	−0.67	−0.71	−0.55	−0.51	−0.47	−0.53
	2, 5	−0.57	−0.46	−0.41	−0.35	−0.25	−0.26	−0.10	0.00	0.00	0.00
	15	2.33	2.24	2.25	2.19	2.06	2.00	1.88	1.68	1.70	1.30
	16	4.88	4.68	4.65	4.55	4.21	3.03	3.87	3.52	3.54	3.12
	13	9.41	9.24	9.22	9.12	8.84	8.87	8.54	8.19	8.25	7.84
	11	11.77	11.64	11.62	11.54	11.34	11.32	11.05	10.79	10.83	10.40
phenanthrene	4, 5	−5.66	−5.56	−5.60	−5.57	−5.56	−5.53	−5.61	−5.67	−5.62	−5.45
	2, 3, 6, 7	−1.92	−1.85	−1.80	−1.76	−1.69	−1.72	−1.56	−1.49	−1.45	−1.52
	9, 10	−1.37	−1.34	−1.33	−1.34	−1.38	−1.40	−1.45	−1.49	−1.45	−1.52
	1, 8	0.29	0.31	0.32	0.33	0.30	0.27	0.24	0.20	0.20	0.16
	12, 13	2.70	2.56	2.53	2.46	2.23	2.39	1.94	1.72	1.76	1.42
	11, 14	4.40	4.25	4.23	4.16	4.05	4.17	3.84	3.64	3.68	3.28
6,6-pentamethylenefulvene	1, 4	−8.50	−8.46	−8.45	−8.41	−8.44	−8.42	−8.35	−8.37	−8.39	−8.24
	2, 5	2.59	2.50	2.46	2.43	2.25	2.10	2.09	2.07	2.02	2.00
	5	12.47	12.23	12.19	12.10	11.90	11.87	11.41	11.06	11.20	10.79
	6	25.40	25.81	26.14	26.15	26.91	27.73	29.03	28.77	30.02	30.88

[a] Defined in the text. [b] In ppm. Positive values are downfield.

Table II. Relative Solvent Shifts $(\int^{C_i}_{C_6H_6})_S$ of Selected Hydrocarbons[a,b] in Aromatic Solvents

hydrocarbon	C_i	C_6H_6	$C_6H_5CH_3$	C_6H_5F	$C_6H_5OCH_3$	$C_6H_5COCH_3$	C_6H_5CN	$C_6H_5NO_2$
benzene	1	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
naphthalene	1, 4, 5, 8	−0.34	−0.29	−0.37	−0.38	−0.42	−0.48	−0.46
	2, 3, 6, 7	−2.54	−2.54	−2.53	−2.48	−2.44	−2.48	−0.46
azulene	9, 10	5.54	5.66	5.51	5.43	5.23	5.16	5.24
	1, 3	−9.94	−9.91	−10.02	−10.03	−10.06	−10.15	−10.13
	5, 7	−5.81	−5.82	−5.78	−5.72	−5.54	−5.59	−5.54
	4, 8	8.10	8.09	8.08	8.12	8.23	8.17	8.18
	6	8.45	8.46	8.58	8.66	8.66	8.61	8.56
	2	8.81	8.76	8.71	8.72	8.85	8.86	8.88
	9, 10	12.19	12.28	12.22	12.07	11.92	11.78	11.93
acenaphthylene	3, 8	−4.25	−4.28	−4.23	−4.16	−4.04	−4.07	−4.08
	5, 6	−1.12	−1.18	−1.15	−1.10	−1.06	−1.08	−1.10
	4, 7	−0.68	−0.73	−0.69	−0.61	−0.53	−0.59	−0.55
	1, 2	1.06	1.06	0.99	1.13	1.10	0.99	0.97
	9, 10	11.69	11.79	11.73	11.59	11.43	11.29	11.42
	11[c]							
	12[c]							
fluoranthene	7, 10	−8.27	−8.30	−8.40	−8.18	−8.04	−8.09	−8.23
	1, 6	−6.69	−6.71	−6.83	−6.72	−6.66	−6.70	−6.81
	3, 4	−1.71	−1.69	−1.71	−1.64	−1.59	−1.65	−1.67
	8, 9	−0.77	−0.76	−0.75	−0.65	−0.65	−0.73	−0.71
	2, 5	−0.38	−0.39	−0.40	−0.25	−0.18	−0.25	−0.30
	15[c]							
	16[c]							
	13	8.94	9.04	8.91	8.73	8.51	8.40	8.52
	11	11.44	11.55	11.38	11.27	11.05	10.94	11.05
phenanthrene	4, 5	−5.49	−5.46	−5.67	−5.58	−5.54	−5.65	−5.73
	2, 3, 6, 7	−1.81	−1.83	−1.78	−1.69	−1.65	−1.69	−1.72
	9, 10	−1.33	−1.42	−1.37	−1.36	−1.35	−1.45	−1.43
	1, 8	*c*	0.34	0.30	0.29	0.20	0.21	0.23
	12, 13	2.34	2.44	2.31	2.19	2.00	1.82	2.01
	11, 14	4.03	4.12	4.07	3.95	3.77	3.61	3.76
6,6-pentamethylenefulvene	1, 4	−8.15	−8.13	−8.17	−8.19	−8.16	−8.16	−8.26
	2, 3	2.62	2.62	2.46	2.42	2.31	2.31	2.26
	5	11.97	12.06	11.84	11.71	11.52	11.40	11.50
	6	27.55	27.30	28.09	28.33	28.71	29.08	29.04

[a] Defined in the text. [b] In ppm. Positive values are downfield. [c] Interference with solvent peaks.

Table III. "Absolute" Chemical Shifts, Δ_s, of Benzene in Various Solvents[a]

solvent	$\Delta_s{}^b$ (ppm)	solvent	$\Delta_s{}^b$ (ppm)
c-C_6H_{12}	(0.00)	$(CH_3)_2SO$	1.19
$(C_2H_5)_3N$	0.13	C_6H_6	0.06
$(n\text{-}C_4H_9)_2O$	0.12	$C_6H_5CH_3$	−0.02
$(i\text{-}C_3H_7)_2O$	0.17	C_6H_5F	0.07
$OC(OC_2H_5)_2$	0.24	$C_6H_5OCH_3$	0.16
$(CH_2)_4O$	0.32	$C_6H_5COCH_3$	0.35
$n\text{-}C_3H_7CN$	0.45	C_6H_5CN	0.38
$OCOCH(CH_3)CH_2O$	0.69	$C_6H_5NO_2$	0.26
$OC(CH_2)_3O$	0.63		

[a] Referred to a 0.3% v/v solution of benzene in cyclohexane (external reference). [b] ±0.03 ppm (see text).

Since it is known[12] that the ^1H NMR shifts of nonalternant hydrocarbons in "inert" solvents are concentration-dependent we have used the lowest possible solute concentration, typically in the mole fraction range 7×10^{-3}–1×10^{-2} for the hydrocarbon and 3×10^{-3} for benzene. A classical example of concentration dependence is that of azulene. Thus, we have obtained its ^{13}C NMR spectrum in cyclohexane solutions at mole fractions 1.0×10^{-3}, 3.0×10^{-3}, 5×10^{-3}, 1.0×10^{-2}, and 2.0×10^{-2} and found that the chemical shifts of the various atoms remain constant throughout this concentration range. It seems reasonable to assume that if any concentration effects are still present, they must be small, of the order of the experimental reproducibility 0.01 ppm.

Discussion

I. Differential Solvent Shifts. A. The Role of the "Select Solvents". Inspection of Table I shows that the chemical shifts of most of the carbons of the molecules herein are sensitive to medium effects.

The signs of the $\delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6}$ are either positive or negative, depending on the molecules and on the position of the C_i's within each of them. Their usual range of variation is −1.4 to 1.0 ppm.

As a first approximation, the $\delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6}$ for most of the different C_i's are proportional, whether the atoms belong to the same or to different molecules. Figure 1 provides representative examples.

It follows that these differential shifts must be proportional to some quantitative measure of medium effects.

Perusal of Table I shows that the importance of these effects increases with the permament dipole moment of the solvent. Thus, it seems appropriate to attempt a correlation with the π^* scale of solvent dipolarity-polarizability,[10] for it has been shown that this scale is an approximately linear function of the solvent's dipole moment (this holds particularly for "select solvents", that is, aliphatic, nonpolyhalogenated molecules, devoid of hydrogen-bonding acidity, with one single dominant bond moment.[13] The solvents used in this work are all members of the "select solvent set").

We have summarized in Table IV the results of these correlations. It appears that, to a reasonably good approximation, the relative chemical shifts follow eq 1.

$$\delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6} = I + s\pi^* \qquad (1)$$

The intercept of eq 1, I, is generally very small, pratically nil within the limits of experimental error. This indicates essentially direct proportionality. Figure 2 illustrates these points.

Of the 36 regressions given in Table IV, two have correlation coefficients (r) higher or equal than 0.99, 20 are in the range

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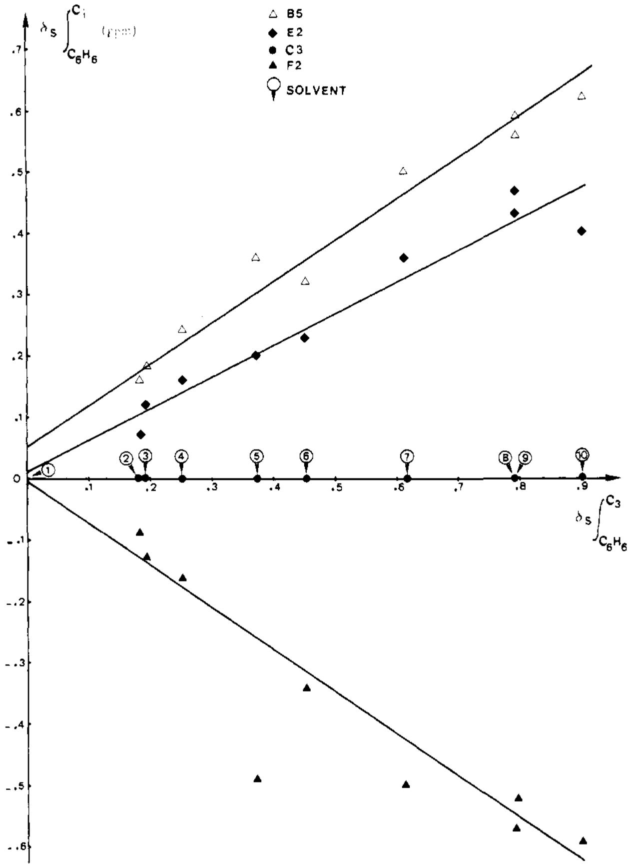

Figure 1. Solvent-induced differential shifts for carbons B5 (azulene), E2 (phenanthrene), and F2 (6,6-pentamethylene fulvene) vs. solvent-induced differential shifts for C3 (acenaphtylene).

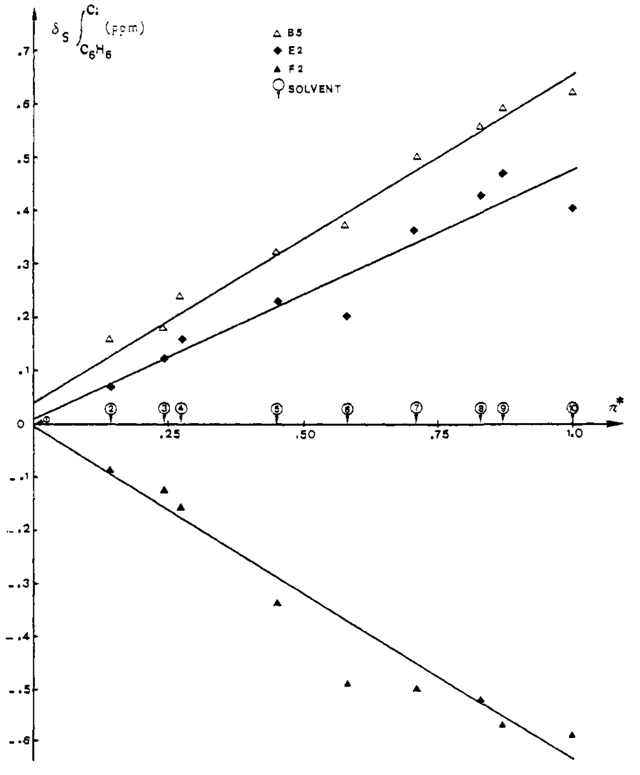

Figure 2. Solvent-induced differential shifts for carbon B5, E2, and F2 vs. the empirical dipolarity-polarizability parameter π^*.

0.95–0.99, and seven in the range 0.90–0.95.

Of the seven regressions with correlation coefficients lower than 0.90, five belong to carbons displaying very low sensitivity to medium effects ($|s| < 0.2$). These are carbons B6 (see later), C1, E1, E4, and F1. That is, r is small because the $\delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6}$ vary, seemingly at random, within very narrow limits. Figure 3 shows the behavior of carbon 1 of acenaphthylene, a typical example.

It can be seen that in eight cases, corresponding to C_i = A9, B2, B9, C10, C11, C12, D16, and E11, the correlations are significantly improved if the THF 6 datum is excluded from the regression. The corresponding coefficients I', s', and r' are given in Table V. It is clear that the deletion of this datum has very little effect on the slopes and intercepts of the correlations. These points shall be considered later, in connection with the structural influence of the solute.

Table IV. Correlation of Differential Solvent Shifts with π^* Values[a] ("Select" Solvents)

hydrocarbon	C_i	s^b (ppm)	I^b (ppm)	r^b
benzene	1	(0.0)	(0.0)	
naphthalene (A)	1, 4, 5, 8	−0.27 ± 0.02	0.04 ± 0.01	0.962
	2, 3, 6, 7	0.30 ± 0.02	−0.01 ± 0.01	0.961
	9, 10	−1.03 ± 0.10	0.10 ± 0.06	0.933
azulene (B)	1, 3	−0.57 ± 0.02	−0.02 ± 0.01	0.991
	5, 7	0.61 ± 0.02	0.04 ± 0.01	0.991
	4, 8	0.56 ± 0.02	0.02 ± 0.01	0.987
	6	0.18 ± 0.06	0.17 ± 0.03	0.593
	2	0.67 ± 0.09	−0.22 ± 0.05	0.893
	9, 10	−1.05 ± 0.09	0.10 ± 0.05	0.947
acenaphthylene (C)	3, 8	0.88 ± 0.04	0.03 ± 0.02	0.982
	5, 6	0.16 ± 0.01	0.03 ± 0.01	0.948
	4, 7	0.52 ± 0.03	0.01 ± 0.02	0.978
	1, 2	0.05 ± 0.03	0.03 ± 0.01	0.398
	9, 10	−1.20 ± 0.10	0.07 ± 0.06	0.952
	12	−1.09 ± 0.12	0.15 ± 0.07	0.911
	11	−1.39 ± 0.09	0.07 ± 0.05	0.969
fluoranthene	7, 10	1.07 ± 0.04	−0.01 ± 0.02	0.987
	1, 6	0.41 ± 0.04	0.02 ± 0.02	0.947
	3, 4	0.33 ± 0.02	0.05 ± 0.01	0.972
	2, 5	0.60 ± 0.03	0.02 ± 0.01	0.984
	8, 9	0.39 ± 0.03	0.03 ± 0.02	0.951
	15	−0.91 ± 0.07	0.09 ± 0.04	0.953
	16	−1.78 ± 0.23	0.03 ± 0.13	0.891
	13, 14	−1.51 ± 0.08	0.11 ± 0.05	0.976
	11, 12	−1.27 ± 0.08	0.11 ± 0.04	0.971
phenanthrene (E)	4, 5	0.05 ± 0.05	0.05 ± 0.02	0.268
	2, 3, 7, 6	0.46 ± 0.03	0.01 ± 0.01	0.963
	9, 10	−0.18 ± 0.02	0.05 ± 0.01	0.912
	1, 8	−0.16 ± 0.02	0.05 ± 0.01	0.898
	12, 13	−1.23 ± 0.09	0.09 ± 0.05	0.961
	11, 14	−0.96 ± 0.09	0.05 ± 0.05	0.935
6,6-pentamethylene-fulvene	1, 4	0.1 ± 0.03	0.004 ± 0.02	0.862
	2, 3	−0.64 ± 0.04	0.01 ± 0.02	0.977
	5	−1.63 ± 0.09	0.08 ± 0.05	0.977
	6	5.45 ± 0.31	−0.49 ± 0.18	0.976

[a] These correlations involve the complete set of ten "select" solvents used in this work. [b] Defined in the text and in eq 1.

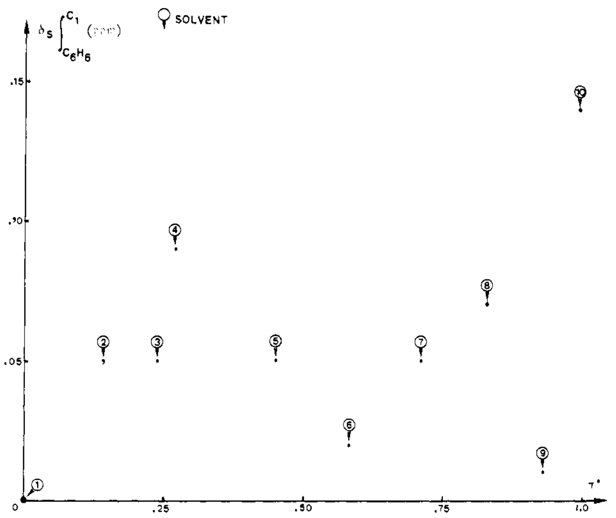

Figure 3. Solvent-induced differential shifts for acenaphtylene carbon C1 vs. the π^* parameter.

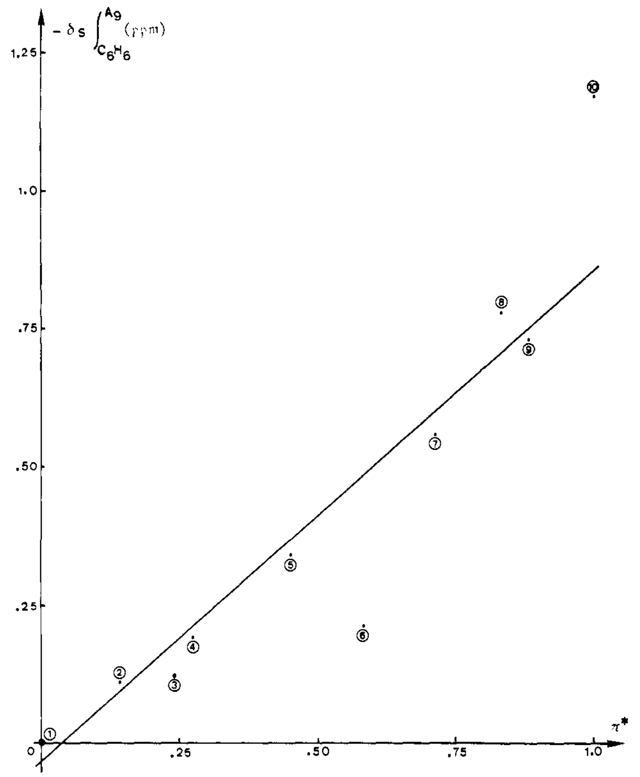

Figure 4. Solvent-induced differential shifts for naphthalene carbon A9 vs. the π^* parameter.

A fundamental implication of eq 1 is that the leading contribution to the differential shifts originates in electrostatic interactions.

We must consider, however, that the π^* scale is a blend of electrostatic and dispersive interactions[14] (heavily weighed in favor of the former). Therefore, London forces[15] are likely to be significant contributors to these effects.[16] Indeed, the $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ for propylene carbonate (solvent **9**) are generally smaller (in absolute value) than $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ for Me_2SO (solvent **10**) in spite of the fact that the dipole moment (4.9 D) and the dielectric constant (65.1) for **9** are higher than those for **10** (3.9 D). The latter solvent, however, is substantially more polarizable (the respective refractive indexes for **9** and **10** are 1.4212 and 1.4773). In the case of the quaternary carbons of all these solutes, the effect is even more important than what it can be expected on the basis of the π^*_{10} value. The case of A9 is illustrated in Figure 4.

Triethylamine (**2**) is known to be a fairly strong hydrogen bonding (HB) base ($\beta = 0.71$; β is a quantitative measure of HB basicity[17]) endowed with a low dipolarity–polarizability ($\pi^*2 = 0.14$).

In all cases, the differential shifts induced by **2** are smaller (in absolute value) than those produced by **3** a much weaker base ($\beta = 0.46$) with a slightly higher dipolarity–polarizability ($\pi^* = 0.24$). This, together with the satisfactory correlations involving π^* *alone*, strongly argue against the differential shifts being a consequence of weak HB interactions.

The slopes, *s*, in eq 1 have a simple physical meaning: they measure the sensitivity of the various chemical shifts to dipolarity–polarizability interactions. Within the family of solvents studied herein, the polarizability varies very little (except for Me_2SO, **10**), and as a first approximation the *s* terms represent the sensitivity of the chemical shifts to dipolarity effects.

Table V. Influence of the THF Datum on the Correlation of Differential Solvent Shifts with π^* Values

hydrocarbon	C_i	s'^a (ppm)	I'^a (pmm)	r'^a	r (Table IV)
naphthalene (A)	9	−1.03 ± 0.05	0.04 ± 0.01	0.971	0.933
azulene (B)	2	0.69 ± 0.08	−0.20 ± 0.04	0.921	0.893
	9	−1.07 ± 0.07	0.08 ± 0.04	0.974	0.947
acenaphtylene (C)	10	−1.22 ± 0.08	0.05 ± 0.05	0.975	0.952
	11	−1.41 ± 0.06	0.05 ± 0.04	0.987	0.969
	12	−1.12 ± 0.10	0.13 ± 0.06	0.945	0.911
fluoranthene (D)	16	−1.71 ± 0.06	0.09 ± 0.03	0.991	0.891
phenanthrene (E)	11	−0.98 ± 0.06	0.03 ± 0.03	0.972	0.935

[a] Defined in the text.

The π^* scale has been obtained through the study of rather polar solvatochromic indicators,[10] their ground-state dipole moments being generally in the range 4–6 D (in their lowest singlet excited state they possibly reach 15 D). The solutes considered in this work have permanent dipoles ranging from nil (A and E) to less than 1 D (all others). The broad range of applicability of the π^* scale is particularly striking and suggests an essentially constant solvation mechanism, irrespective of the solute dipolarity.

Furthermore, the *s* values for alternant and nonalternant hydrocarbons are of quite the same size (see Table V). Since the alternant hydrocarbons are devoid of permanent dipole moment, these results provide information on interactions controlled by higher multipoles. As seen above, the relative chemical shifts of these compounds show satisfactory adherence to eq 1. On quantitative grounds, these effects are quite comparable to those found in studies involving relatively polar solutes. For instance, the solvent-induced chemical shifts of the para carbons of a wide variety of substituted benzenes, C_6H_5–X, closely follow eq 1 with *s* values ranging from −1.12 (X = NMe_2) to +1.70 (X = NO_2).[5b]

On a formal basis, Buckingham[18] and Musher's[19] extensions of the reaction field theory (RF)[20] provide a rationale for these findings. In these models, the solvent-induced NMR shifts of a given nucleus are proportional to the components of the RF acting on the bonds originating in this nucleus (vide infra). In the extended Onsager model of the RF, the solute is assimilated to a polarizable sphere of radius *a* with a charge distribution in its center. Let n_1, α and μ, respectively, stand for the refractive index, the polarizability and the permanent dipole moment of the solute; ϵ is the dielectric constant of the solvent.

The modulus, *R*, of the reaction field is given[18] by

$$R = [2(\epsilon - 1)/(n_1^2 - 1)/3(2\epsilon + n_1^2)](\mu/\alpha) \qquad (2)$$

A reasonable value of n_1 for many solutes is $n_1 \approx 2^{1/2}$. This allows a simplification of eq 2

$$R \approx \frac{4(\epsilon - 1)}{3(\epsilon + 1)}(\mu/a^3) \qquad (3)$$

R is a measure of the response of the solvent to the electric field created by the dipole (permanent and induced) of the solute.

If the solute is also endowed with a quadrupole moment, θ, a field gradient, *R'*, is also present

$$R' = [6(\epsilon - 1)/(3\epsilon + 2)](\theta/a^5) \qquad (4)$$

According to Buckinghan,[18] the solvent contribution to the screening constant of a given nucleus, X, is proportional to both *R* and *R'*. Obviously, the proportionality constants depend on the number and kind of the atoms bound to X as well as on their relative spatial orientations and the polarizability of the bonds; these points have been analyzed by Batchelor.[21] What is most important for our present purposes is the fact that for $\epsilon > 2$ (that

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(14) (a) Abboud, J.-L. M.; Guihêneuf, F.; Essefar, M.; Taft, R. W.; Kamlet, M. J. *J. Phys. Chem.* **1984**, *88*, 4414. (b) Brady, J. E.; Carr, P. W. *J. Phys. Chem.* **1982**, *86*, 3053. (c) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1080.

(15) (a) London, F. *Z. Phys.* **1930**, *63*, 245. (b) London, F. *Z. J. Phys. Chem.* **1942**, *46*, 305.

(16) (a) Buckingham, A. D.; Schaefer, T.; Schneider, W. G.; *J. Chem. Phys.* **1960**, *32*, 1227. (b) Howard, B. B.; Linder, B.; Emerson, M. T. *J. Chem. Phys.* **1962**, *36*, 485. (c) de Montgolfier, P. *J. Chim. Phys.* **1969**, *66*, 639, 1969, *66*, 685. (d) Homer, J.; Percival, C. C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1. Abundant experimental evidence regarding dispersion effects on NMR shifts can be found in ref 5c, 5f, and 6a.

(17) See, e.g.: ref 4b and 10a.

(18) Buckingham, A. D. *Can. J. Chem.* **1960**, *38*, 300.

(19) Musher, J. I. *J. Chem. Phys.* **1962**, *37*, 34.

(20) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

(21) Batchelor, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 3410.

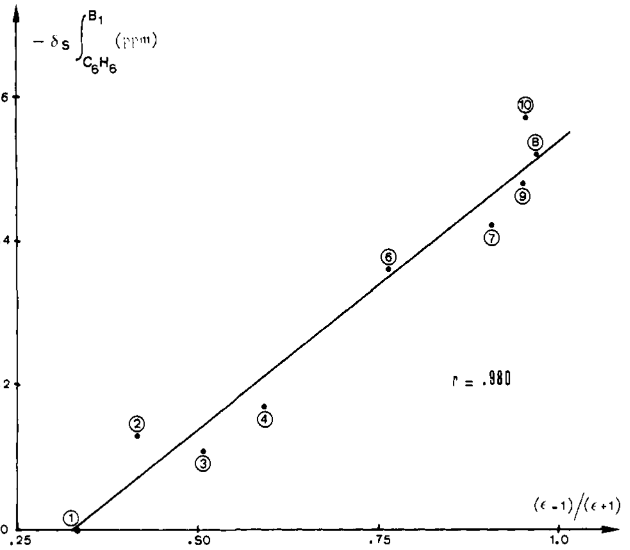

Figure 5. Correlation of the solvent-induced differential shifts for azulene carbon B1 with the $(\epsilon - 1)/(\epsilon + 1)$ dielectric function.

is, for the majority of the solvents), the solvent dependent term in eq 4, namely $(\epsilon - 1)/(3\epsilon + 2)$ is very nearly proportional to $(\epsilon - 1)/(\epsilon + 1)$, the solvent-dependent part of eq 3. It follows that as far as the electrostatic contributions are concerned, dipoles, quadrupoles, and the combinations thereof should display the same kind of solvent dependence.[22]

This is precisely what we have found. Furthermore, these equations also predict a linear relationship between the $\delta_S \int^{C_i}_{C_6H_6}$ and the $(\epsilon - 1)/(\epsilon + 1)$ function. Most of our experimental results are indeed compatible with such an expectation: as an example, Figure 5 shows results for B1.

As mentioned above, the solutes used in this work have a low (or nil) dipolarity, and dielectric saturation effects are unlikely to appear in the solutions studied herein. We also notice that the Onsager model does not include saturation effects. Now, the π^* scale has been determined in and applied to systems where some degree of dielectric saturation is likely to occur. Thus, several authors[23] have successfully correlated a number of physical and chemical reactivity data (including the π^* scale) with Block and Walker's dielectric function,[24] $\theta(\epsilon)$, defined as

$$\theta(\epsilon) = 3\epsilon \mathrm{Ln}\epsilon/(\epsilon \mathrm{Ln}\epsilon - \epsilon + 1) - (6/\mathrm{Ln}\epsilon) - 2 \qquad (5)$$

This function assumes a very strong dielectric saturation around the solute. As expected from eq 1, the differential shifts are linear functions of $\theta(\epsilon)$. Figure 6 is a plot of $\delta_{S,C_6H_{12}} \int^{C_i}_{C_6H_6}$ vs. $\theta(\epsilon)$ for B1.

The correlations with $(\epsilon - 1)/(\epsilon + 1)$ and with $\theta(\epsilon)$ are seen to be of essentially the same quality. This is a general result, which highlights the difficulties inherent to the choice of a mathematical model for the representation of the electrostatic contribution to medium effects, on the sole grounds of the "goodness of fit".

The models envisaged above assimilate the solvent to a continuous dielectric. This is an oversimplification, as shown by the following two examples.

(1) We find that 27 out of 36 $\delta_{THF,C_6H_{12}} \int^{C_i}_{C_6H_6}$ values determined in this work are substantially smaller (in absolute value) than predicted by eq 1. This is striking, because, in general, 6 is a particularly well-behaved solvent. On the other hand, we know that in correlations between the π^* scale and the permanent dipole moments (or dielectric functions) of the "select solvents", the dipolarity–polarizability of THF seems slightly "too high": the experimental π^* value for THF is 0.58, while the calculated ones are in the range 0.46–0.49.

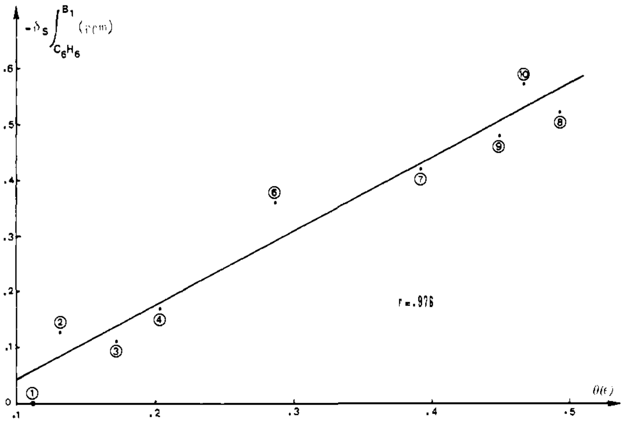

Figure 6. Correlation of the solvent-induced differential shifts for azulene carbon B1 with the $\theta(\epsilon)$ dielectric function.

This has been rationalized[13] in terms of the small steric crowding around the C–O–C moiety, which makes possible a closer approach of the polar terminus of 6 toward the solute. If we back-calculate π^*_{THF} from the set of the 27 experimental differential shifts and eq 1, we find an average of 0.42 ± 0.06 for the 16 tertiary carbons and 0.36 ± 0.10 for the 11 quaternary. This would suggest that in these systems, 6 behaves more nearly as a "continuous dielectric". A likely explanation is that the very small net charges on most of the atoms (vide infra) are unable to "sort out" the polar termini of the THF molecules. This sorting out would amount to a lowering of the average solvent–solute distance and an enhancement of the local RF. This might be supported by the finding that $\delta_{THF,C_6H_{12}} \int^{C_i}_{C_6H_6}$ for B1, B5, F1, and F6 are well described by eq 1 with $\pi^*_{THF} = 0.58$. Now, these atoms are precisely among those endowed with the largest net charges.[25]

The difference between the averages of the calculated π^*'s for tertiary and quaternary carbons is small, but it is noteworthy that the latter, individual values as low as 0.27 are found in A, B, and E. At this point, we have no rationale for this fact.

(2) The standard π^* value for diethyl carbonate (**5**), 0.45, nicely accounts for the experimental differential shifts $\delta_{5,C_6H_{12}} \int^{C_i}_{C_6H_6}$. This standard value is nearly twice as large as the one calculated by means of the correlations between π^* and the dipole moment or dielectric functions of the solvents.

Analogous behavior has been reported for the acyclic esters methyl formate and methyl and ethyl acetates. This fact was explained on the basis of the very low steric requirements around the ester functionality.[13] The results for 6 and the fact that solvents such as **2** (very hindered functionality) and **9** (very exposed one) are "well-behaved" suggest the need for a different explanation.

We tentatively suggest that, in general, **5** does not behave as a "continuous dielectric" and the various bond moments of this molecule tend to act as separate entities.

B. The Role of Aromatic Solvents. From the data given in Table II, it can be deduced that most $\delta_{S,C_6H_{12}} \int^{C_i}_{C_6H_6}$ for aromatic solvents range between −0.5 and +0.5 ppm. Application of eq 1 to these differential solvent shifts leads to the results given in Table VI.

It appears that, for all the quaternary carbons as well as for A1, B5, E1, F2, and F5, the slopes of the linear regressions are close to those found in the correlations involving "select solvents", *thusly suggesting a similar pattern of solvent–solute interactions.* In the present cases, however, the correlation coefficients (0.91–0.98), are somewhat lower, the main reasons being the following: (i) the smaller range of variation of the π^* parameter and (ii) the particular behavior of acetophenone (**15**), benzonitrile (**16**), and nitrobenzene (**17**). Thus, while the π^* values for these compounds are respectively equal to 0.90, 0.90, and 1.01, the shifts induced by **15** and **16** are frequently different and larger (in

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[22] It follows that the study of solvent effects on the properties of a solute only provides an estimate of the *overall* electrostatic contributions to solvent–solute interactions. Further information is thus necessary in order to unravel the contributions from dipoles and higher multipoles.

[23] See, e.g.: (a) Brady, J. E.; Carr, P. W. *J. Phys. Chem.* **1982**, *86*, 3053. Abboud, J.-L. M.; Taft, R. W. *J. Phys. Chem.* **1979**, *83*, 412.

[24] Block, M.; Walker, S. M. *Chem. Phys. Lett.* **1973**, *19*, 363.

[25] According to CNDO/2 and MNDO calculations.

Table VI. Correlation of Differential Solvent Shifts, $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$, with the π^* Values for Aromatic Solvents[a]

hydrocarbon	C_i	s^b (ppm)	I^b (ppm)	r^b
benzene	1	(0.0)	(0.0)	
naphthalene (A)	1, 4, 5, 8	−0.34 ± 0.06	0.01 ± 0.04	0.928
	2, 3, 6, 7	0.17 ± 0.05	0.02 ± 0.04	0.795
	9, 10	−0.98 ± 0.14	0.01 ± 0.11	0.947
azulene (B)	1, 3	−0.45 ± 0.07	−0.04 ± 0.05	0.941
	5, 7	0.68 ± 0.06	0.01 ± 0.04	0.981
	4, 8	0.23 ± 0.04	−0.03 ± 0.03	0.915
	6	0.28 ± 0.16	−0.06 ± 0.12	0.596
	2	0.29 ± 0.10	−0.04 ± 0.08	0.759
	9, 10	−0.93 ± 0.17	0.01 ± 0.13	0.911
acenaphthylene (C)	3, 8	0.51 ± 0.07	0.01 ± 0.05	0.953
	5, 6	0.18 ± 0.06	0.02 ± 0.04	0.801
	4, 7	0.39 ± 0.06	−0.01 ± 0.04	0.942
	1, 2	−0.10 ± 0.13	0.08 ± 0.10	0.292
	9, 10	−0.95 ± 0.16	0.04 ± 0.13	0.922
	12[c]			
	11[c]			
fluoranthene (D)	7, 10	0.46 ± 0.21	−0.02 ± 0.16	0.672
	1, 6	−0.03 ± 0.15	−0.04 ± 0.11	0.081
	3, 4	0.15 ± 0.08	0.02 ± 0.06	0.636
	2, 5	0.35 ± 0.13	0.08 ± 0.07	0.746
	8, 9	0.15 ± 0.09	0.01 ± 0.07	0.557
	11, 12	−1.20 ± 0.17	0.00 ± 0.13	0.947
	13, 14	−1.30 ± 0.18	0.00 ± 0.14	0.949
	15[c]			
	16[c]			
phenanthrene (E)	4, 5	−0.36 ± 0.17	−0.04 ± 0.13	0.655
	2, 3, 6, 7	0.30 ± 0.09	0.02 ± 0.07	0.808
	9, 10	−0.10 ± 0.10	0.00 ± 0.07	0.400
	1, 8	−0.28 ± 0.06	−0.03 ± 0.05	0.916
	12, 13	−1.11 ± 0.21	0.00 ± 0.16	0.909
	11, 14	−0.95 ± 0.18	0.04 ± 0.14	0.911
6,6-pentamethylene-fulvene (F)	1,4	−0.10 ± 0.07	−0.06 ± 0.08	0.508
	2, 3	−0.77 ± 0.10	−0.06 ± 0.08	0.954
	5	−1.31 ± 0.18	−0.01 ± 0.06	0.947
	6	3.65 ± 0.49	0.14 ± 0.14	0.952

[a] These correlations involve the complete set of seven aromatic solvents used in this study. [b] Defined in the text and in eq 1. [c] Not determined.

Table VII. Calculated "$\pi^*_{11}(C_i)$" Parameter for Benzene[a]

hydrocarbon	C_i	"$\pi^*_{11}(C_i)$"
naphthalene (A)	1, 4, 5, 8	−0.07
	2, 3, 6, 7	0.30
	9, 10	0.43
azulene (B)	1, 3	−0.05
	2	0[b]
	6	0.05[b]
	5, 7	0.30
	4, 8	0.52
	9, 10	0.47
acenaphthylene (C)	3, 8	0.50
	5, 6	0.63
	4, 7	0.40
	9, 10	0.54
fluoranthene (D)	7, 10	0.44
	1, 6	0.61
	3, 4	0.24
	2, 5	0.28
	8, 9	0.23
	13	0.38
	11	0.35
phenanthrene (E)	2, 3, 6, 7	0.22
	9, 10	−0.05
	11, 14	0.44
	12, 13	0.38
6,6-pentamethylenefulvene (F)	2, 3	−0.06
	5	0.21
	6	0.41

[a] Defined in the text. Calculations have been carried out whenever the correlation coefficient for eq 1, as applied to "select solvents" was higher than 0.90. [b] Estimated from the π^*'s of solvents giving close $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ values.

absolute value) than those induced by **17**. A plausible explanation is the existence of weak electron donor–acceptor interactions between the solutes and **16** or **17**. A substantial reduction of the slopes (relative to those obtained in the case of "select solvents") is found for A2, B1, B4, C3, C4, D1, D2, D3, D7, D8, E2, and E9. Furthermore, A2, D1, D2, D3, D7, D8, E2, and E9 also show low correlation coefficients. D7 is a good example, for in the correlations involving "select solvents" we had $s = 1.07 \pm 0.04$ and $r = 0.987$, while now, $s = 0.46 \pm 0.21$ and $r = 0.672$. This obviously indicates a very significant change in the mechanism of solvent–solute interactions. It is important to show that in the case of aromatic solvents we are not witnessing "random" variations of the solvent-induced shifts. Thus, within a molecule, say that of fluoranthene, we find that the differential solvent shifts for most of the various tertiary carbons are linearly related, with standard deviations of fit of, generally, 0.01–0.03 ppm, comparable to the combined experimental uncertainties.

The reduction of the slopes of the correlations of $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ vs. π^* can be explained by the time average cybotactic environment of the C_i's being more benzenelike. This would imply that the interactions of (at least a part of) the solute with the aromatic moiety of the solvent (Ph–X) molecules strongly compete with those involving the more polar terminus, X.

A quantitative comparison of $(\int_{C_6H_6}^{C_i})_{C_6H_6}$ and $(\int_{C_6H_6}^{C_i})_{\text{select solvents}}$ is carried out as follows: we define a parameter, "π^*_{11} (C_i)" equal to the hypothetical π^* value for benzene (**11**) that would apply to this solvent, were it "select". From this definition is follows that, for each C_i, "$\pi_{11}(C_i)$" can be calculated through eq 6

$$\text{“}\pi^*_{11}(C_i)\text{”} = \left[\left(\int_{C_6H_6}^{C_i}\right)_{C_6H_6} - \left(\int_{C_6H_6}^{C_i}\right)_{C_6H_{12}} + I\right] \Big/ s \quad (6)$$

Where I and s pertain to correlations involving "select solvents" and are given in Table IV. The calculated "$\pi^*_{11}(C_i)$" are collected in Table VII.

The "$\pi^*_{11}(C_i)$" values vary between −0.07 and +0.63, an impressive range corresponding to the difference between cyclohexane and butyronitrile. It is well-knonw that correlations involving *both* "select" *and* aromatic solvents often require that the π^* values for the latter be corrected by adding a constant correction term.[10a] This term is characteristic of the solute and/or the property being studied and generally lies between 0 and −0.30, the standard value for π^*_{11} being 0.59. In this case, the most remarkable fact is that widely different "$\pi^*_{11}(C_i)$" are found for carbons belonging to the same molecule. This indicates a general ASIS-type effect[9] between benzene and the various solutes. It has been shown[23] that the standard π^* value for **11** is higher than expected on the basis of its dielectric constant and refractive index (depending on the models,[23b] the calculated values are in the range 0.1–0.2). We have suggested that effects such as the anisotropic polarizability and the high quadrupole moment of this molecule may well be responsible for this enhancement of π^*_{11}. Indeed, Nikki and co-workers[26] have quantitatively shown that ASIS effects can be rationalized in terms of dipole (solute)–dipole (solvent) and dipole (solute)–quadrupole (solvent) interactions.

On a semiquantitative basis it is possible to rank the "$\pi^*_{11}(C_i)$" values found for the different carbons of azulene (B) by using the calculated MNDO or CNDO/2 charges for these atoms and considering the possible time-averaged orientations of the benzene ring with respect to the molecular plane of B.

These calculations, inspired in work by Nikki,[26] Mallion,[27] and their co-workers cannot be pursued in exactly the same way, for we known that here, the local charges are very small and have to compete with strong dispersive interactions. We are presently involved[28] in the quantitative determination of the energetics of such solvent–solute interactions as a necessary condition for the treatment of these ASIS effects.

II. The Role of the Solute. The absence of a single highly localized strong dipole in the various molecules examined herein

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(26) Nikki, K.; Nakagawa, N. *J. Magn. Reson.* **1985**, *23*, 432 and references therein.

(27) Haigh, C. W.; Mallion, R. B. *J. Mol. Spectrosc.* **1970**, *35*, 491.

(28) Abboud, J.-L. M.; Rico, M., work in progress.

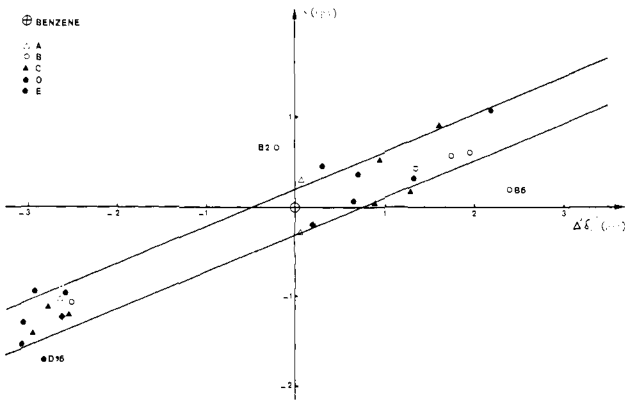

Figure 7. Solvent-induced differential shifts vs. differential free-radical paramagnetic shifts for aromatic hydrocarbons.

explains our lack of success at correlating the *s* values with the positions of the different carbon atoms within each of the solute molecules.

Clearly, the method successfully applied by Buckingham to solvent effects on the ^1H chemical shifts of nitrobenzene need to be replaced here by an approach incorporating more "microscopic information" about the molecular structure of the solute. Work is currently under way in order to apply Pople's[29] theoretical treatment of semiempirical molecular orbital methods (CNDO/2 and INDO/S) into which some measure of "dielectric effects" can be introduced.[30]

"Polarity effects" are important for both "select" and aromatic solvents, although for the latter, other phenomena (discussed in I.B) are significant. At this point, it seems that the "polarity effects" described above can be attributed to two main factors: (i) the "purely dielectric", which should favor the separation of charges within the solute molecules (even if they are devoid of a permanent dipole moment) and (ii) a transient or "pseudocontact" interaction between the solvent molecules and the various carbon atoms of the solute. The relevance of the first factor follows from the correlations between the $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ and π^* seen above. The contribution of the second factor is also apparent from the results of the previous sections.

Relevant additional proofs are as follows.

(1) Grant and co-workers[31] have recently published an important study dealing with the influence of the free-radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) on the ^{13}C NMR spectra of a number of hydrocarbons. The latter were dissolved in carbon tetrachloride, and the experiments involved the determination of the ^{13}C chemical shifts at various TEmPO concentrations, up to about 1.2 M. In all cases, the differences between the shifts in the presence of TEMPO and in the pure solvent varied linearly with the concentration of the free radical. The average molar value of these shifts, that is, the slopes of these lines, corrected for the bulk magnetic susceptibilities of the solutions and the effect of TEMPO on the chemical shift of the internal reference are noted $\overline{\Delta\delta}_f$. Grant and co-workers have obtained $\overline{\Delta\delta}_f$ values for 22 hydrocarbons, including benzene and compounds A to E. We define $(\Delta'\delta_f^{int})_{C_i} = (\overline{\Delta\delta}_f)_{C_i} - (\overline{\Delta\delta}_f)_{C_6H_6}$. That is, $(\Delta'\delta_f^{int})_{C_i}$ is a measure of the TEMPO-induced paramagnetic shift of the *i*th carbon of a given molecule, relative to the paramagnetic shift of benzene.

Figure 7 is a plot of *s* (for correlations involving "select" solvents) vs. $(\Delta'\delta_f^{int})_{C_i}$ for these molecules. Although both sets of values are not strictly linearly related, they display an unequivocal trend of proportionality. More precisely, with only three exceptions all the *s* values are within 0.25 ppm of a line encompassing both tertiary and quaternary carbons and passing through the origin (C_6H_6). Of the three exceptions, the most conspicuous are those of B2 and B6. Going back to Tables IV and V we notice that their correlation coefficients through eq 1 are low while the slopes are sizable. That this is a sign of an anomaly is confirmed by the relatively large absolute values of the intercepts. Let us examine next the $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ vs. π^* plots for B2 and B6 (Figure 8). They show a clear pattern; for the low π^* values, the differential shifts vary approximately linearly with π^*, the respective slopes, s_i, being -0.41 and +1.1 for B2 and B6. Then, as π^* increases, there seems to appear a new phenomenon that tends to oppose this variation. In the case of B2 this leads to an inversion of the sign of the slope and, for B6, to an almost complete levelling of the solvent effect. Although the s_i's are only crude estimates it is significant that, if they were used instead of the "average" *s* values, the points for B2 and B6 would display a "normal behavior".

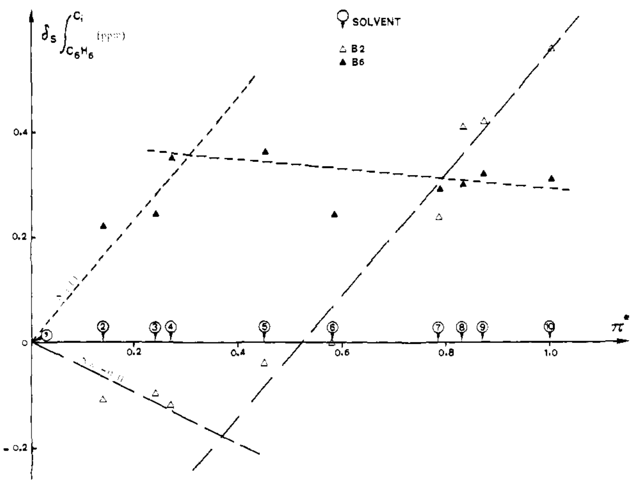

Figure 8. Solvent-induced differential shifts for azulene carbons B2 and B6 vs. the π^* parameter.

Table VIII. Free Radical Effect on the ^{13}C NMR Spectrum of 6,6-Pentamethylenefulvene

carbon C_i	$(\Delta'\delta_f^{int})_{C_i}$ [a,b]
1, 4	-0.54
2, 3	-0.36
5	-2.57
6	-2.26

[a] In ppm. [b] Defined in the text.

If we follow Grant and Poindexter in their pseudo-contact model for the paramagnetic shifts, we have to consider main contributiors to the size of the $(\Delta'\delta_f^{int})_{C_i}$: (i) the individual sensitivity of each carbon and (ii) the relative stability of the transient complexes. Now, the largest spin density is to be found on the N-O group, the polar teminus of the TEMPO molecule. Factor (ii), therefore, should be determined by the effective electric field in the immediate neighborhood of each carbon atom. This mechanism should also be important in determining the $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ and $(\Delta'\delta_f^{int})$ values and we suggest that this is the main reason for the approximate proportionality between the differential solvent shifts and the differential paramagnetic shifts. Given the relatively small concentrations of TEMPO used by Grant and co-workers, the bulk dielectric constants of the solutions were certainly low, and the electronic structure of the solute molecules were not significantly perturbed by dielectric effects. On the light of the results of section I as well as from the studies by other workers it seems that, in general, local and dielectric effects remain proportional to each other. In the case of B2 and B6 we find that, as long as the dielectric constants of the solvents remain low, the proportionality between $\delta_{S,C_6H_{12}}\int_{C_6H_6}^{C_i}$ and $(\Delta'\delta_f^{int})_{C_i}$ holds indeed.

The "kinks" in the *s* vs. π^* plots might reflect a breakdown on the proportionality between "local" and "dielectric" effects. Such

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[29] Pople, J. A. *J. Chem. Phys.* **1962**, *37*, 53, **1962**, *37*, 60.

[30] (a) Ando, I.; Kato, Y.; Kondo, M.; Nishioka, A. *Makromol. Chem.* **1977**, *178*, 803. (b) Jallali-Heravi, M.; Webb, A. G. *Org. Magn. Reson.* **1980**, *13*, 116. (c) Ando, I.; Nishioka, A.; Kondo, M. *J. Magn. Reson.* **1976**, *21*, 429. (d) Jallali-Heravi, M.; Na Lamphun, B.; Webb, G. A.; Ando, I.; Kondo, M.; Watanabe, S. *Org. Magn. Reson.* **1980, 14**, 92. (e) Tiffon, B.; Ancian, B. *Org. Magn. Reson.* **1981**, *16*, 247.

[31] Zu Wen Quin; Grant, D. M.; Pugmire, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 2747.

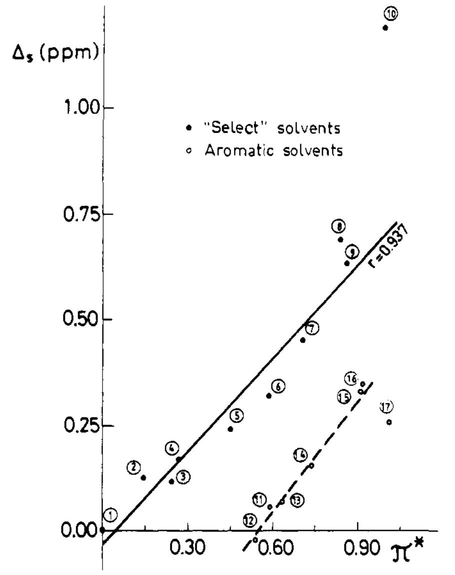
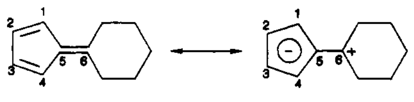


Figure 9. "Absolute" chemical shifts of benzene in solvents **1–17** (external reference: benzene in cyclohexane).

a change in the solvent–solute interaction pattern cannot be quantitifed on the basis of the simple linear model embodied in eq 1.

(2) We have determined both $\delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6}$ and $(\Delta'\delta_f^{int})_{C_i}$ for 6,6-pentamethylene fulvene (F). The experimental results obtained by following the procedure of Grant and his co-workers are given in Table VIII.

An increase in the dielectric constant of the solvent should favor the "aromatic" form FB, relative to FA.



FA FB

From the standpoint of the chemical shifts of the cyclopentadienyl moiety, this should lead to both a deshielding, because of the increased aromaticity and to a shielding because of the increased charge density in the ring. Carbon F6, on the other hand, is subject to two deshielding effects arising from the depletion of negative charge and the increased aromaticity of the cyclopentadienyl cycle. Of course, all these factors should coexist with the "local" effects.

Apparently, there is a substantial cancellation of the "dielectric effects" acting on the cyclopentadienyl moiety, because F1 and F5 would fit reasonably well in Figure 7.

This no longer applies to F6 for which we find simultaneously the largest positive *s* value with a large, negative $(\Delta'\delta_f^{int})$.

III. "Absolute" Shifts (A.S.). A. Benzene. The bulk-corrected chemical shifts of benzene Δ_s, in solvents **1–17**, relative to benzene in cyclohexane solution (external reference) are given in Table III.

We observe that, with the only exception of toluene (**12**), for which $\Delta_s = -0.02$ ppm, all other shifts are downfield and increase with the dipolarity–polarizability of the solvent. This is interesting, for, within solvents **1–9** (and **11–17**) polarizability effects are nearly constant, and, if the observed shifts are essentially of electrostatic origin, we must rationalize why they are downfield. A naive interpretation in terms of an enhanced polarization of the C–**H** bonds would lead to predict the opposite effect. We suggest that polarization of the C–H bonds *and* of the π electronic system have to be considered.

We have plotted in Figure 9, the benzene shifts Δ_s, vs. the π^* parameter.

Considering solvents **1–9**, we find a moderately good ($r = 0.937$) linear relationship with a standard deviation of fit of 0.06 ppm. The distribution of the experimental points around the regression line suggests that the linear model is only an approximation (the observed scatter might well be a consequence of the local anisotropy of the heteroatoms of these solvents). For Me_2SO (**10**), the difference of 0.48 ppm between the experimental and the calculated values can be taken as a measure of enhanced dispersive interactions.

Aromatic solvents **11–14** and **16** fall on a line of roughly the same slope as that for the "select" solvents. We notice, again, the particular behavior of **17** and a general upfield shift of some 0.35 ppm for aromatic relative to "select" solvents.

B. Other Hydrocarbons. 1. "Select" Solvents. The "absolute" shifts, $(\int^{C_i}_{C_6H_{6(ext)}})_S$ are calculated by means of eq 7 by using the pertinent data given in Tables I–III.

$$\left(\int^{C_i}_{C_6H_{6(ext)}}\right)_S = \delta_{S,C_6H_{12}}\int^{C_i}_{C_6H_6} + \Delta_s \tag{7}$$

For compounds A to E, the total range of medium effects on the AS is ca. 2 ppm, and it reaches 6.7 ppm for F6.

Small upfield shifts with increasing solvent dipolarity–polarizability are found for C9, C11, and D11. The largest is that for F5 (0.78 ppm). *All these carbons are quaternary.* For other quaternary carbons we find very small (±0.10 ppm) "random" medium effects. *No appreciable, systematic upfield shifts are found for tertiary carbons.*

We have attributed the behavior of Me_2SO to the existence of strong dispersive interactions.[33] This is supported by the finding that for carbons undergoing upfield shifts, Me_2SO behaves as a much *less* "polar" solvent. Thus, for carbon D13, the AS for solvents 6 to **9** are respectively equal to 9.19, 8.99, 8.76, and 8.88 ppm, while that for **10** is 9.03 ppm. For carbon C1, on the other hand, the following AS are determined (in ppm): 1.27 (**6**), 1.43 (**7**), 1.69 (**8**), 1.55 (**9**) and 2.26 (**10**).

The case of azulene is worth commenting: the AS for carbons B1 and B9 are essentially solvent-independent (excluding DMSO) while they for all the others are downfield.

Plots (not given here) of the AS for carbons B2 and B6, vs. π^* confirm our previous conclusions based an the comparison of medium and TEMPO effects. The results for azulene, naphthalene, and phenanthrene, showing nil or downfield shifts for *all* carbons, do not seem to support the validity of the simple reaction field model. The consideration of differential solvent effects has led to the same conclusion.

We tentatively suggest that the apparent lack of sensitivity of (for example) A9, B1, B9, and D15 may originate in the cancellation of medium-induced diamagnetic and paramagnetic contributions to chemical shifts.[29]

Since Δ_s varies in an approximately linear way with π^*, it follows from eq 1 and 7 that the AS will be linearly related to π^*. This is confirmed for all cases wherein the range of variation is sufficiently large ($|s| > 0.2$) (As expected the correlations involving B2 and B6 are poorer). The generally higher quality of the correlations involving differential shifts is likely to be a consequence of the elimination of local anisotropy effects as well as (a part of) the dispersive interactions in Me_2SO.

2. Aromatic Solvents. The overall range of medium effects is relatively small: 0.6 ppm for compounds A to E and 2.2 ppm for F6, as compared to 2 and 6.7 ppm for the some solutes in "select" solvents.

In general, all the AS are downfield, D11 and F5 show small upfield shifts of 0.29 and 0.45 ppm (maximum range). With these exceptions, and that of F6, the AS's of quaternary carbons are extremely small. Tertiary carbons systematically undergo downfield shifts (relative to benzene or toluene).

Correlation of the AS's with π^* are generally poor (an exception being B5, for which $s = 1.3$ ppm and $r = 0.97$), as can be expected from Figure 9 and the discussion given in I.B.

The general trends are similar to those found for the "select" solvents, although factors such as ASIS, the efficient interaction

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(32) (a) Stewart, J. R.; Poindexter, E. H.; Potenza, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 6017. (b) Potenza, J. A.; Poindexter, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 6309.

(33) Rummens, F. H. A. In *NMR, Basic Principles*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1975; Vol. 10.

of the solutes with the aromatic moiety of the solvents, and, possibly, donor–acceptor interactions preclude a more quantitative dissection of the experimental data.

IV. Conclusion. 1. The ^{13}C NMR spectra of aromatic compounds (benzene as well as nonalternant and alternant hydrocarbons) are sensitive to solvent dipolarity–polarizability effects.

2. These results conclusively show the important role of quadrupoles and higher multipoles in solvent–solute interactions.

3. In the case of "select" solvents, there is a generally good linear relationship between the differential solvent induced shifts (relative to benzene) and the π^* scale of solvent dipolarity–polarizability.

4. Although the differential shifts induced by aromatic solvents sometimes follow the same kind of relationship, ASIS and specific interactions often lead to a more complex pattern.

5. ASIS contributions are very large, compared to the overall size of solvent effects.

6. Relative to other "select solvents", dispersive (van der Waals) diamagnetic shifts in Me_2SO are very important.

7. "Absolute" shifts (relative to an external reference) induced by "select" and aromatic solvents are always downfield for tertiary carbons and upfield for a few quaternary ones.

8. There is no simple relationship between the response to solvent effects and the electronic charge distribution of the solute molecules.

9. These results highlight the limitations of the simple reaction-field model.

10. The analysis of the experimental data for both aromatic hydrocarbons and 6,6-pentamethylene fulvene strongly suggests that these solvent effects involve both a "general dielectric effect" and a more localized noncontinuum action of the peripheral solvent atoms on the peripheral solute atoms.[34]

Experimental Section

1. Compounds. The solvents as well as the aromatic hydrocarbons were materials of the highest commercial purity, dried and/or further purified by standard methods. Cyclohexylidene fulvene was column chromatographed on silica gel and eluted with ACS reagent grade *n*-hexane immediately prior to use. The samples were prepared by weight and volumetrically.

2. Spectra. The results given in Tables I and II, in which benzene is used as an internal reference have been obtained at 20.0 MHz on a Varian FT 80A spectrometer at a nominal temperature of 36 °C.

The samples were contained in 10-mm NMR tubes. For locking purposes, a 5-mm coaxial tube containing ^2H_2O was used. Full proton decoupling was used in all cases. The spectra (2×10^3–4×10^4) were accumulated with 8 K data points and a spectral width of 4000 Hz, yielding a digital resolution of 0.5 Hz. The chemical shifts were reproducible to 0.01–0.02 ppm.

The "absolute" shifts given in Table III have been determined as follows.

1. In a series of experiments performed on the Varian 80A, the shifts of benzene dissolved in compounds **1–17** were measured with respect to an external reference of benzene in $(C^2H_3)_2SO$. The solutions were placed into 10-mm NMR tubes, fitted with an 8-mm coaxial tube containing the reference (also used for locking). These shifts (relative to cyclohexane solvent) are noted $\delta^{\perp}$ (the magnetic field is perpendicular to the axis of the tubes).

2. The same solutions were studied on a Brucker FTNMR spectrometer WM360 at 90 MHz (spectral width 18 000 Hz, 16 K data points. The instrument allowed the determination of the shifts in the absence of an internal lock. We thus obtained a series of shifts, noted δ'' (the magnetic field is parallel to the axis of the tubes) at 36 °C.

3. According to Becconsall[35] the intrinsic (i.e., corrected for bulk susceptibility effects) shift, Δ_s is given by

$$\Delta_s = \tfrac{1}{3}(\delta'' + 2\,\delta^{\perp}) \tag{8}$$

These Δ_s values were checked as follows: (i) $\delta^{\perp}$ were determined by using both 8-mm and 5-mm tubes for the external reference. The results agreed within 0.01 ppm. (ii) δ'' values were measured with and without lock, with the same level of aggreement. (iii) Both δ'' and $\delta^{\perp}$ were measured for benzene in acetone and in methyl iodide. These compounds are endowed with widely different bulk susceptibilities. Also, magnetic susceptibilities χ are available at 20 °C for 12 of the 17 solvents used in this work. Now, Δ_s values can also be determined through eq 9. We

$$\Delta_s = \delta'' - (4\pi/3)(\chi_s - \chi_{C_6H_{12}}) \tag{9}$$

have found that both sets of results agree within 0.03 ppm.

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Registry No. A, 91-20-3; B, 275-51-4; C, 208-96-8; D, 206-44-0; E, 85-01-8; F, 3141-04-6; TEMPO, 2564-83-2.

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(34) This conclusion is strongly supported by the results of a recent theoretical study on the influence of dispersion interactions on NMR shifts (ref 16d).

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