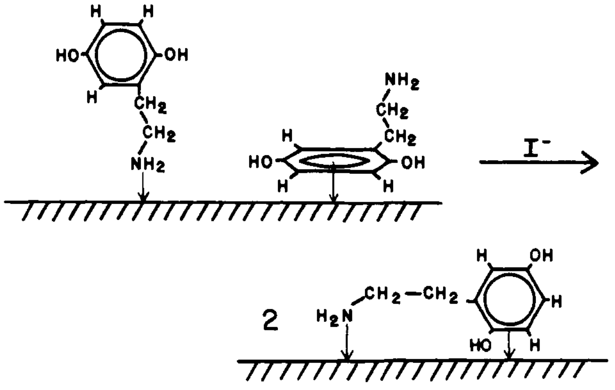
allylhydroquinone, ($\sigma_f = 32.5 \pm 2.1$; $\sigma_{\rm calcd} = 33.6$ Å^2), and 1,6-η^2-4-allylprocatechol, ($\sigma_f = 33.2 \pm 2.1$; $\sigma_{\rm cald} = 31.6$ Å^2). Compound **20** has a longer alkene side chain (hexene). However, the initial coverage ($\sigma_i = 77.0 \pm 2.1$ Å^2) and the absence of reversible electroactivity of the adsorbed layer indicate that it is initially adsorbed exclusively in the η^6 orientation, with the side chain extended away from the surface ($\sigma = 74.2$ Å^2). Under the influence of iodide, this structure reorients most probably to a 4,5-η^2 orientation in which the chain remains extended away from the surface ($\sigma_f = 30.4 \pm 1.4$; $\sigma_{\rm calcd} = 29.6$ Å^2).

Compounds **22** and **23** have amine side chains, and at pH 7, a small fraction of the initial adsorption occurs through the amine nitrogen.[1] For these compounds, unlike all of the other compounds studied, *larger* values of σ_f are obtained at pH 7 than in acid (41.7 vs. 34.6 Å^2 for **22**; 48.8 vs. 40.3 Å^2 for **23**), although σ_f remains smaller than σ_i. This can be understood if attachment of dangling amine groups and aromatic rings accompanies reorientation of η^6-bonded aromatic rings to the more space-efficient η^2 orientations. The final structure is attached to the surface in two places (see eq 9). Further evidence for double attachment in the final state is that the electroactive material initially adsorbed loses its electroactivity as a result of iodide exposure. Since 20% of the initially adsorbed material was found to be reversibly electroactive[1] (and therefore presumably N attached), the observed σ_i can only be accounted for if the remaining 80% adopted a η^6 orientation in which the amine chain was positioned away from the surface. Therefore, double attachment occurs only after exposure to iodide. This situation is not analogous to that of phenylhydroquinone since the latter is always double attached, even in the initial flat orientation.



(9)

Conclusions

The results of the present study reveal that changes in coverage, orientation, and/or mode of attachment occur when a parallel-oriented adsorbed layer of aromatic compounds is exposed to a solution of a strongly surface-active anion such as iodide. Under these conditions (10^{-4} M aromatic and/or 5×10^{-4} M iodide in 1 M perchlorate electrolyte): (i) Displacement of adsorbed aromatic molecules from the platinum surface by iodide solution is greatest in acidic media. (ii) Alkyl substituents stabilize adsorbed aromatic compounds toward displacement by iodide. (iii) Monocyclic aromatic molecules adsorbed in a flat orientation *reorient* to an edgewise orientation unless they are extensively desorbed when exposed to iodide solution. (iv) The more stable η^2 oriented structures are those that occupy minimal electrode surface area and for which the ring edge closest the electrode does not contain bulky substituents. (v) Fused polycyclic aromatic molecules adsorbed parallel to the surface do not reorient under the influence of acidic iodide, although they undergo some desorption. (vi) The biphenyl moiety adsorbed with both rings parallel to the surface undergoes reorientation by iodide such that both rings are edgewise to the surface. (vii) Aromatic molecules attached to the surface by an SH group are not displaced by iodide. (viii) In general, reorientations induced by iodide convert structures making inefficient use of surface area into orientations occupying smaller surface area.

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Registry No. 1, 128-31-9; **2**, 120-80-9; **3**, 95-71-6; **4**, 452-86-8; **5**, 1948-33-0; **6**, 98-29-3; **7**, 615-90-7; **8**, 608-43-5; **9**, 150-78-7; **10**, 527-18-4; **11**, 771-63-1; **12**, 87-87-6; **13**, 533-73-3; **14**, 608-80-0; **15**, 319-89-1; **16**, 16867-04-2; **17**, 123-33-1; **18**, 5721-21-1; **19**, 1126-61-0; **20**, 81255-51-8; **21**, 1079-21-6; **22**, 21581-41-9; **23**, 81255-52-9; **24**, 571-60-8; **25**, 130-15-4; **26**, 117-14-6; **27**, 84-50-4; **28**, 2889-61-4; I⁻, 20461-54-5; Pt, 7440-06-4.

Paramagnetic Carbon-13 Shifts Induced by the Free Radical 2,2,6,6-Tetramethylpiperidinyl-1-oxy. 1. Simple Aromatic and Paraffinic Hydrocarbons

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Abstract: Using the free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as a shift reagent, both apparent and true molar paramagnetic shifts of 22 compounds are reported. Paramagnetic shifts increase monotonically with measures of conjugation and aromaticity. The nonalternant hydrocarbons experience greater effects than the corresponding alternant systems. Steric hindrance effects become important factors in various methyl derivatives. As previously supposed the shifts do not appear to relate primarily with either the frontier spin densities or with π-charge densities. Therefore, the direct charge-transfer or spin delocalization proposals requiring a strong intermolecular interaction of the π-stacking variety is felt not to be attractive. Linear correlation exists between these and Morishima's data and between the data for TEMPO and 4-OH-TEMPO. In each case TEMPO is more effective as a shift reagent than the other two nitroxide free radicals. A shift model involving a pseudocontact interaction during the existence of a transient weak complex is supported by these data.

Chelated lanthanide compounds have been widely used as shift reagents in NMR.[1] Recently Morishima et al.,[2] Sysoeva et al.,[3] and Draney and Kingsbury[4] have obtained similarly interesting results on the paramagnetic shifts and relaxation behavior in a

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(1) Reuben, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1975**, *9*, 1.

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variety of compounds induced by DTBN and other nitroxide free radicals. These initial results suggest the importance of organic free radicals as specialized shift reagents, but the generality as well as the mechanism of these kind of paramagnetic shifts still require further experimental and theoretical work to clarify the full significance of such studies.

Instead of using DTBN (di-*tert*-butyl nitroxide) and other radicals, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), a relatively stable free radical, has been selected for use in this study. The reasons for this selection are as follows. (1) At ambient temperatures it is a solid, stable radical which is not denatured upon storage in the refrigerator for relatively long periods of time. It is readily available commercially and has been used as a spin-probing or spin-labeling reagent in ESR. (2) TEMPO has a relatively high solubility in many organic solvents and is rather chemically inert. Therefore, it is a convenient reagent for inducing large paramagnetic shifts. Although in ^{1}H NMR the lines are seriously broadened when the concentration of TEMPO is high, the corresponding line broadening in the ^{13}C NMR is not very significant. Therefore, in this study we are only concerned with ^{13}C NMR. (3) TEMPO can also be used as a relaxation reagent. When small amounts of TEMPO (e.g., <0.05%) are dissolved in solution, it promptly decreases the nuclear relaxation times, especially those of nonprotonated carbon atoms. On the basis of the above criteria, the superior characteristics of TEMPO are exhibited.

Although many of the mechanistic features of free radical induced paramagnetic shifts are yet to be resolved, there is general agreement that the existence of only a collision or otherwise very weak transient complex between the radical and other compounds in solution is sufficient to give rise to a paramagnetic shift. Paramagnetic shifts may arise from a contact or pseudocontact shift via spin polarization and aid by spin delocalization or charge-transfer mechanisms. Of course, it is simpler to define the process if only one kind of mechanism is dominant, whereas if several mechanisms exist simultaneously it may not be possible to delineate the various factors.

For simplification of the problem as much as possible, simple aromatic compounds were first studied as well as some aliphatic compounds for comparison. The results of 22 compounds are reported in this paper.

Experimental Section

A. Chemicals. TEMPO and aromatic compounds were purchased from Aldrich and Eastman Kodak Co. The purity of these chemicals was sufficient to use them directly without further purification.

B. Preparation of the Sample. Most of the aromatics were dissolved in CCl$_4$; only tripycene and triphenylene were dissolved in CS$_2$ because of their low solubility in CCl$_4$. By weighing the solution in a calibrated 10-mL volumetric flask, an accurate concentration of the compound, including cyclohexane as the internal standard, was obtained. TEMPO was then put into the NMR tube and weighed carefully. Finally the solution was introduced into the NMR tube which was previously standardized by using a microsyringe pipette. With use of this method, the amount of TEMPO was conserved without sacrificing the accuracy of the concentration. For every compound five or six samples were prepared with different free radical concentrations. One of the samples contained no free radical.

C. NMR Measurement. All of the spectra were recorded on a Varian SC-300 superconducting NMR spectrometer operating at 75.511 MHz for the ^{13}C nucleus with the decoupler frequency at 300.248 MHz. The sweep widths were 15 kHz, and 2000 transients were normally taken. For the samples without free radical because of their longer relaxation times, longer acquisition times were required especially if nonprotonated carbon atoms were present. In these samples CDCl$_3$ was added as an internal lock. Samples containing the free radical need not be locked during the relatively short acquisition period because the SC-300 is sufficiently stable over the period of data acquisition that the data were highly reproducible. Some compounds with low solubility required a greater number of transients. An 8K data table produced spectra of adequate quality.

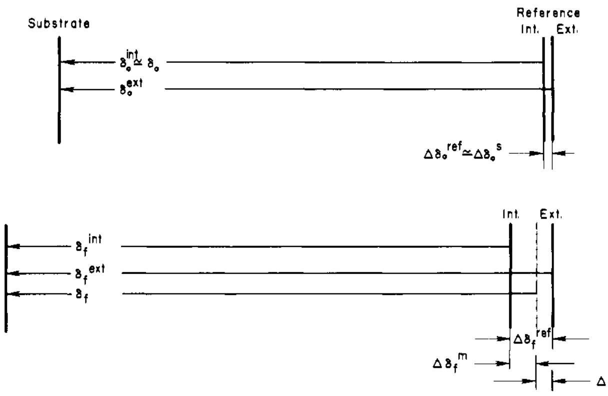

Figure 1. Schematic diagram of the relationship between δ_f^{int}, δ_f^{ext}, $\Delta\delta_f^{m}$, and $\Delta\delta_f^{s}$ and the true paramagnetic shift $\Delta\delta_f = \delta_f - \delta_0$.

D. Referencing of Shifts in the Presence of a Paramagnetic Free Radical. The introduction of a free radical creates a fairly serious problem for referencing chemical shifts. If an internal standard is used, then the chemical shift measures only the differential effect of the free radical upon the analytical and reference compounds, respectively. Draney and Kingsbury[4] identified this problem with the data of Morishima et al.,[2] which was all recorded relative to internal reference compounds. Use of an external reference suffers from the very large changes noted in the bulk magnetic susceptibility arising from the presence of a free radical. Thus, chemical shifts recorded relative to an external sample must be corrected for the susceptibility changes in order to be of any value. Thus, in both cases a correction must be made before the relevant chemical shift difference, $\Delta\delta_f = \delta_f - \delta_0$, due to the free radical can be determined.

Figure 1 portrays graphically the relationships which exist between the internal, δ^{int}, and external, δ^{ext}, chemical shift measurements and indicates the nature of corrections which must be applied to both measurements. The difference between an internal and external chemical shift results from changes in both the bulk magnetic susceptibility, $\Delta\delta^{s}$, and intermolecular interactions, $\Delta\delta^{m}$, between the internal standard and its molecular environment. In samples not containing a free radical, a reference compound is usually selected for which $\Delta\delta_0^{m}$ is relatively small enough to be negligible. Thus, $\delta_0 \simeq \delta_0^{int}$ and $\Delta\delta_0^{ref} \simeq \Delta\delta_0^{s}$. Unfortunately, neither δ_f^{int} nor δ_f^{ext} can be related to δ_f without applying the significant corrections

$$\delta_f = \delta_f^{int} + \Delta\delta_f^{m}$$

or

$$\delta_f = \delta_f^{ext} - \Delta\delta_f^{s}$$

Thus

$$\delta_f^{ext} - \delta_f^{int} = \Delta\delta_f^{m} + \Delta\delta_f^{s} = \Delta\delta_f^{ref}$$

where $\Delta\delta_f^{ref}$ is the separation between the resonance lines of the same reference compound in the external and internal sample compartments (usually a coaxial double-sample tube). As $\Delta\delta_f^{ref}$ is very easily obtained and as a determination of either $\Delta\delta_f^{m}$ or $\Delta\delta_f^{s}$ yield directly the other quantity, then it actually does not matter whether raw data are recorded relative to internal or external standard because the same effort must be expanded to determine the two corrective components in $\Delta\delta^{ref}$. As $\delta_0 \simeq \delta_0^{ext} - \Delta\delta_0^{s}$, then the appropriate expressions for $\Delta\delta_f$ are given by

$$\Delta\delta_f = \delta_f - \delta_0 = \delta_f^{int} - \delta_0^{int} + \Delta\delta_f^{m}$$

or

$$\Delta\delta_f = \delta_f^{ext} - \delta_0^{ext} - \Delta\delta_f^{s} + \Delta\delta_0^{s}$$

Note, in the above equations the δ's and Δδ's are algebraic quantities and must carry the correct sign as indicated by the direction of the arrows in Figure 1. There appears to be some serious confusion in the literature because of sign conventions, and care must be used reading the previous literature. In this study, a downfield shift is a positive quantity.

We selected cyclohexane (also selected by Morishima et al.[2] and Draney and Kingsbury[4] for some of their studies) as a reference in this

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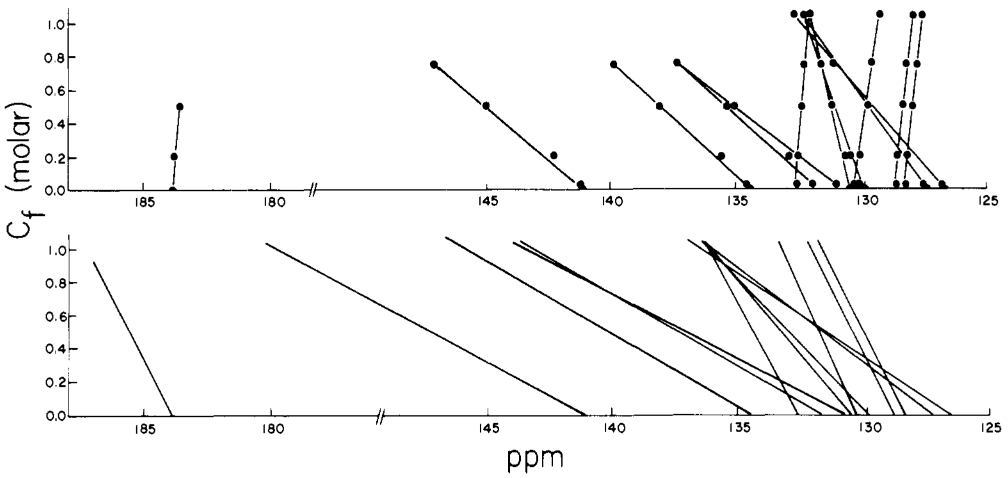

Figure 2. Chemical Shifts of perinaphthenone as a function of free radical concentration: (a) top, δ_f^{int}; (b) bottom, δ_f^{ext}. The abscissa indicates the chemical shift values of the resonance lines with respect to Me_4Si (in ppm). The ordinates indicate the molar concentration of the free radical.

work. The average molar value of $\overline{\Delta\delta^{\text{ref}}}$ ($\Delta\delta^{\text{ref}}/C_{fr}$) was found in this study on TEMPO to be 6.94 (range 6.90–7.04 ppm) for large number of different analytical solutions. This relatively small variation for $\overline{\Delta\delta^{\text{ref}}}$ could easily be explained with minor deviations from ideal solution behavior, and therefore we content ourselves with an explicit error of about 0.1 ppm even though the precision in our measurement is 1–2 orders of magnitude less than this quantity.

E. Bulk Magnetic Susceptibility Measurements. The spinning sideband method[4,5] of Malinowski and Pierpaoli was also used in this work to measure the change in volume magnetic susceptibility induced by the addition of TEMPO. Equations to be used are the same as those in the paper of Draney and Kingsbury[4] and of Malinowski and Pierpaoli.[5]

$$\nu_m/\nu_0 = \frac{2\pi}{kr^2}[a^2\chi_{\text{central}} + (b^2 - a^2)\chi_{\text{glass}} - b^2\chi_{\text{annular}}] \qquad (1)$$

k is the Bessel function argument which can be calculated from the line intensities of the sidebands as

$$J_0^2(k)/J_1^2(k) = I_0/I_1 \qquad (2)$$

The experiment was performed on a Varian XL-100 spectrometer since this method cannot be carried out in a superconducting magnet in which the static magnetic field is parallel to the spinning axis. The cyclohexane reference and acetone-d_6 was placed in the annular part of a 10- and 12-mm coaxial tubes, while benzene in CCl_4 with or without TEMPO was put in central tube. Equation 1, to be valid, requires that the annular part should be as narrow as possible so that the average value of r may be used. Otherwise $k\nu_m$ is not constant with different spinning speeds. Compounds of known magnetic susceptibility were used to calculate χ_{glass}, and eq 1 and 2 were again used to calculate χ_{central} of the free radical containing solution.

Using three different free radical concentrations, the results are $\overline{\Delta\delta_f^{\text{s}}} = 2.88 \pm 0.03$ ppm, which agrees unusually well with the value 2.81 ± 0.02 ppm of Draney and Kingsbury.[4]

A rough estimation of $\overline{\Delta\delta_f^{\text{s}}}$ can be made by using the results of Pople.[6] If the nitroxide radical is considered to be a spin $^1/_2$ system, then the estimated value will be 2.61 ppm in reasonably good agreement with the measured values.

With use of the above value for $\overline{\Delta\delta_f^{\text{s}}}$ and the average value of $\overline{\Delta\delta_f^{\text{ref}}} = 6.94 \pm 0.10$ ppm, a value for $\Delta\delta_f^{\text{m}} = 4.06 \pm 0.10$ ppm is obtained for correcting our shift values measured with an internal reference.

Results and Discussion

A. Presentation of the Spectra. A plot of the concentration of the free radical vs. the resonance frequencies was made for all compounds studied. If the concentration of the free radical did not exceed 1.2 M, the lines connecting these experimental points were found to be linear. Thus, a linear regression analysis was used to calculate the molar free radical shift $\overline{\Delta\delta_f^{\text{int}}}$ relative to internal cyclohexane. These values are given in the Table I for the samples studied in this work. Figure 2a gives a representative plot for perinaphthenone. The data not corrected for the free radical effect upon cyclohexane are treated in the manner of Morishima et al.[2] These kinds of plot were very useful because the lines may sometimes cross with each other and such plots can assist in the proper assignment of the shifted lines. In the more complicated compounds such as perinaphthenone, the lines are very closely spaced. These plots can be used to easily recognize nonprotonated from protonated carbons, as non-protonated carbons generally have similar $\overline{\Delta\delta_f^{\text{int}}}$ values compared to the cyclohexane reference. They appear to move upfield with addition of free radical. Care must be taken not to saturate the nonprotonated carbons by using pulse delay settings which are too short. As two lines may coincide for a given solvent and free radical concentration, data taken for a variety of free radical concentrations can often avoid this accidental degeneracy in line positions.

Upon correcting the values of the apparent paramagnetic shifts with $\overline{\Delta\delta^{\text{m}}} = 4.06$ ppm, one obtains the true value for $\overline{\Delta\delta_f}$. These are given also in the table and are plotted in Figure 2b for perinaphthenone to illustrate the effect of making the required corrections on the internal reference. The table contains δ_0, δ_0^{lit}, $\overline{\Delta\delta_f^{\text{int}}}$, for all compounds contained in this study.

B. Assignment of Lines. For samples without free radical, the assignments of most of the compounds were taken from the literature. Where differences exist in the literature, selective decoupling methods were used to resolve the problem. The types of plots contained in Figure 2 also can provide corroborative assignment data for closely positioned peaks of different spectral type. The assignment of triptycene was carried out in this fashion.

C. Discussion of Systematic Effects. From the representation plot given in Figure 2b and the value of $\overline{\Delta\delta_f}$ in the table, it may be observed that all carbons shift downfield uniquely in marked contrast with the uncorrected results in Figure 2a and with earlier discussions of upfield shifts in the literature. Of course, the line crossing behavior is still preserved since they are merely topological mapping with a constant correction for all carbon lines. From the data on isooctane, a structural trend is observed. First, it may be noted that saturated hydrocarbons relative to aromatics experience less interaction with TEMPO. And second, within the saturated hydrocarbons the strength of interaction is $CH_3 > CH_2 > CH > C$, suggesting the importance of the number of protons in the interaction. If a double bond is present, as in the 2,4,4-

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(12) Jones, A. J.; Grant, D. M.; Kuhlmann, K. F. *J. Am. Chem. Soc.* **1969**, *91*, 5013. The assignments of position 10 and 1 are inverted in P. E. Hansen's review.

Table I. The Apparant and True Paramagnetic Shifts of Simple Aromatic and Paraffinic Hydrocarbons

compd	position	$\delta_0{}^a$	$\delta_0{}^{(\text{lit})}$	$\overline{\Delta\delta}_f{}^{\text{int}}$	$\overline{\Delta\delta}_f$	ref
8% isooctane	1	30.25	30.20	+0.27	4.33	7
4% cyclohexane	2	31.17	31.20	−1.91	2.15	
88% CCl_4	3	53.31	53.40	−0.77	3.29	
	4	24.72	24.90	−1.28	2.78	
	5	25.59	25.50	+0.39	4.45	
90% iooctane	1	30.15	30.20	+0.26	4.32	7
10% cyclohexane	2	31.07	31.20	−2.36	1.70	
	3	53.41	53.40	−0.96	3.10	
	4	24.72	24.90	−1.50	2.56	
	5	25.49	25.50	+0.39	4.45	
2,4,4-trimethyl-1-pentene	1	114.43	113.20	+0.63	4.69	7
	2	143.51	142.50	−1.72	2.34	
	3	51.81	51.00	−0.27	3.79	
	4	31.47	30.40	−1.91	2.15	
	5	30.20	29.20	+0.31	4.37	
	6	25.30	24.20	+1.14	5.20	
squalene	a	15.88	15.7	+1.08	5.14	8
	b	17.53	17.5	+1.33	5.39	
	c	25.59	25.5	+1.45	5.51	
	d	26.71	27.0	−0.23	3.83	
		26.85		−0.23	3.83	
	e	28.21	28.5	−0.35	3.71	
	f	39.72	40.0	−0.17	3.89	
	g	124.57	124.6	−0.58	3.48	
		124.72		−0.58	3.48	
	h	130.94	130.7	−1.93	2.13	
	i	134.77	134.8	−1.94	2.12	
		134.96		−1.94	2.12	
benzene (1.1 molar)	1	128.56	128.7	+1.58	5.64	9
benzene/CCl_4 (1:4)	1	128.52	128.7	+1.58	5.64	
benzene/CCl_4 (1:1)	1	128.33	128.7	+1.72	5.78	
benzene/CCl_4 (4:1)	1	128.28	128.7	+1.50	5.56	
cycloheptatriene	1	120.60	120.40	+0.92	4.98	7
	2	126.92	126.80	+0.75	4.81	
	3	131.20	131.00	+0.81	4.87	
	7	27.98	28.10	+1.27	5.33	
cyclooctatetraene	1	132.34	133.0	+1.03	5.09	9
quadricyclane	1	14.72	14.70	+1.04	5.10	9
	2	22.97	22.90	+0.71	4.77	
	3	32.05	31.90	+0.57	4.63	
1,2,3-trimethylbenzene	1	136.12	136.1	−1.23	2.83	9
	2	134.70	134.8	−1.16	2.90	
	4	127.90	127.9	+0.23	4.29	
	5	125.51	125.5	+0.36	4.42	
	1-Me	20.51	20.4	+1.40	5.46	
	2-Me	15.20	15.0	+1.15	5.21	
1,2,3,4-tetramethylbenzene	1	133.65	133.5	−1.39	2.67	9
	2	134.49	134.4	−1.34	2.72	
	5	127.25	127.3	+0.05	4.11	
	1-Me	20.58	20.6	+1.37	5.43	
	2-Me	15.57	15.5	+1.14	5.20	
1,2,3,5-tetramethylbenzene	1	135.89	136.0	−1.53	2.53	9
	2	131.49	131.6	−1.43	2.63	
	4	128.90	128.9	−0.23	3.83	
	5	134.24	134.3	−1.65	2.41	
	1-Me	20.40	20.3	+1.51	5.57	
	2-Me	14.77	14.6	+1.18	5.24	
	5-Me	20.78	20.9	+1.64	5.70	
biphenyl	1	141.67	141.70	−0.98	3.08	10
	2	127.39	127.57	+1.09	5.15	
	3	128.85	129.16	+1.76	5.82	
	4	127.39	127.68	+1.76	5.82	
naphthalene	1	128.12	128.05	+1.64	5.70	11
	2	125.89	125.95	+1.65	5.71	
	4a	133.90	133.70	−1.04	3.02	
1,4-dimethylnaphthalene	1	132.22	132.1	−1.33	2.73	11
	2	126.39	126.0	+0.70	4.76	
	4a	133.12	132.5	−2.00	2.06	
	5	124.78	124.4	+0.37	4.43	
	6	125.40	125.1	+1.35	5.41	
	Me	19.29		+2.11	6.17	

Table I (*Continued*)

compd	position	$\delta_0{}^a$	$\delta_0{}^{(\mathrm{lit})}$	$\overline{\Delta\delta}_f{}^{\mathrm{int}}$	$\overline{\Delta\delta}_f$	ref
1,3-dimethylnaphthalene	1	133.85	133.6	−1.53	2.53	11
	2	129.05	128.7	+0.38	4.44	
	3	134.68	134.8	−1.55	2.51	
	4	125.65	125.1	+0.60	4.66	
	4a	134.29	133.7	−1.42	2.64	
	5	128.07	127.7	+1.19	5.25	
	6	125.65	125.4	+1.32	5.38	
	7	124.92	124.6	+1.24	5.30	
	8	123.99	123.7	+0.45	4.51	
	8a	131.33	130.8	−1.21	2.85	
	1-Me	19.18		+2.39	6.45	
	3-Me	21.56		+2.46	6.52	
phenanthrene	1	128.80	128.90	+1.82	5.88	11
	1, 3	126.66	126.75	+1.87	5.93	
	4	122.88	123.05	+2.23	6.29	
	9	127.15	127.30	+1.81	5.87	
	11	132.39	132.30	−0.98	3.08	
	12	130.74	130.50	−1.02	3.04	
pyrene	1	125.02	125.23	+3.21	7.27	11
	2	126.84	126.13	+2.70	6.76	
	4	127.54	127.63	+2.97	7.03	
	11	131.47	131.28	−1.23	2.83	
	15			−1.37	2.69	
triptycene	α	125.23		+2.05	6.11	
	β	123.75		+3.46	7.52	
	γ	54.23		+2.76	6.82	
	δ	144.73		−1.38	2.68	
triphenylene	1	123.00	123.2	+3.09	7.15	11
	2	127.00	127.1	+2.32	6.38	
	4a	129.55	129.7	−0.71	3.35	
acenaphthene	1	30.33	30.2	+1.65	5.71	7
	3	119.26	118.9	+0.96	5.02	
	4	127.90	127.5	+0.85	4.91	
	5	122.55	122.0	+0.85	4.91	
	9	145.86	145.6	−1.03	3.03	
	11	139.69	139.0	−1.11	2.95	
	12	132.02	131.4	−1.09	2.97	
acenaphthylene	1	129.54	129.42	+2.48	6.54	11
	3	124.05	124.15	+3.19	7.25	
	4	127.65	127.77	+2.54	6.60	
	5	127.32	127.29	+2.88	6.94	
	9	140.09	139.74	−0.98	3.08	
	11	128.87	128.19	−1.35	2.71	
	12	128.44	128.39	−1.18	2.88	
azulene	1	118.1	119.2	+1.77	5.83	11
	2	136.9	137.9	+1.39	5.45	
	4	136.4	136.9	+3.33	7.39	
	5	122.6	123.2	+3.53	7.59	
	6	136.9	137.4	+3.99	8.05	
	9	140.2	140.8	−0.92	3.14	
fluoranthene	1	121.66	122.90	+2.94	7.00	12
	2	127.97	128.50	+2.91	6.97	
	3	126.71	127.25	+3.04	7.10	
	9	127.64	128.20	+2.29	6.35	
	10	119.96	120.65	+3.79	7.85	
	11	139.87	140.15	−1.45	2.61	
	13	137.49	137.65	−1.46	2.60	
	15	132.88	132.90	−1.33	2.73	
	16	130.35	130.70	−1.18	2.88	
perinaphthenone	1	183.80		−0.69	3.37	11
	2	129.87	128.9	+2.22	6.28	
	3	141.08	141.3	+8.14	12.20	
	3a	128.71	127.5	−0.73	3.33	
	4	130.75	131.0	+8.66	12.72	
	5	126.62	126.4	+5.85	9.91	
	6	131.66	131.6	+7.48	11.54	
	6a	132.61	131.9	−0.57	3.49	
	7	134.43	134.5	+7.36	11.42	
	8	127.35	126.7	+4.53	8.59	
	9	130.45	129.8	+1.50	5.56	
	9a	130.26	129.3	−1.07	2.99	
	9b	128.31	127.3	−0.79	3.27	

[a] Measured relative to cyclohexane and converted to Me_4Si by adding 27.00 ppm. [b] $\overline{\Delta\delta}_f = \overline{\Delta\delta}_f{}^{\mathrm{int}} + 4.06$ ppm.

trimethylpent-1-ene, the shift of the carbon adjacent to the double bond increased slightly, suggesting that a π interaction may be slightly preferable to σ interactions. Thus, $=CH_2 > \;>CH_2$ and $=C< \; > -C-$. From the data on squalene we also find that

=C—H > -C—H. In fact the ability to unravel and systematize the contact or pseudocontact shifts in squalene gives validity to this method for assigning the lines in a complex molecule, indicating the potential use of TEMPO as a shift reagent. Shifts of ring carbons having one hydrogen are found to be larger than singly protonated carbons in chain compounds. As aromaticity and conjugation increase, the paramagnetic shifts also appear to increase in according with the series benzene > cyclooctatetraene > cycloheptatriene. Since cyclooctatetriaene does not exhibit the aromaticity of benzene, it is not unexpected that the shift is smaller than benzene. The conjugation of its four double bonds appears to give rise to slightly larger effects than are found for cycloheptatriene where the cyclic conjugation is interrupted by a CH_2 moiety. A $-CH_2-$ or CH_3- group adjacent to a double bond shows hyperconjugation effects. Thus, $=C-CH_2-C= \; > \; =C-CH_2- \; > \; -CH_2-$. When the number of fused benzene rings increases, the shift also monotonically increases. The maximum molar shifts (ppm/mol of TEMPO) are as follows: benzene (5.64), naphthalene (5.71), biphenyl (5.82), phenanthrene (6.29), pyrene (7.27), triptycene (7.52), triphenylene (7.15). In addition, the nonalternant hydrocarbons experience greater effects than the corresponding alternant systems, viz. acenaphthylene (7.25) azulene (8.05) fluoranthene (7.85) and perinaphthenone (12.72), where the effect is especially high. These data indicate that in aromatic systems, π interactions are apparently very important. The lower stability at nonalternant systems appears to enhance the paramagnetic shift in some manner. However, the exact nature of the mechanism involved in the π interaction still remains to be resolved. Some authors have intuitively suggested a π-stacking model in which direct spin transfer may occur. If this were true, we feel that there would be some indication that the free radical was either an electron donor or acceptor. Furthermore, the shifts should bear some relationship with the frontier spin densities as is observed in ESR. Such correlations do not appear to exist. Two experimental results have been suggested[2] as a proof of the π-stacking model; first for the nonalternants there seems to be a linear relation between π-charge density and the apparent paramagnetic shift. We also obtained a similar result (see Figure 3), but actually this plot is suspect since it cannot correlate the shifts of the nonprotonated carbons of both nonalternants and alternants alike. The second argument is based on the shifts in pyrene. Without making the internal reference correction, it was thought that the absolute value of the shift of internuclear carbon (C_{15}, 0.30) is greater than the shift of the peripheral nonprotonated carbon (C_{11}, 0.275). This led to the conclusion that C_{15} has stronger interaction with the free radical than C_{11}. With the proper correction applied, the resulting paramagnetic shift of C_{15} is actually smaller than C_{11}. Therefore, the direct charge-transfer or spin delocalization proposal requiring a strong interaction of the π-stacking variety is not felt to be attractive.

By inspection of effects among different methyl derivatives, it is interesting to note that the shift of methyl carbons clearly exhibits steric hindrance effects. Furthermore, the outer methyl carbons always exhibit a greater effect than inner methyl carbons. The shift of ring carbons were greatly reduced in the methyl derivatives as compared with their parent molecules. However, the shifts of $C_{6,7}$ of 1,4-dimethylnaphthalene (5.41) and the shifts of C_6, C_7, and C_5 of 1,3-dimethylnaphthalene (5.38, 5.30, 5.25) were only slightly smaller than the corresponding shifts in naphthalene (5.70, 5.71) since these positions were far from the methyl group. Other positions which were closer to the methyl group were greatly reduced. Therefore, for methyl derivatives, it would seem to be reasonable to propose that steric hindrance is an important factor.

D. Comparison of the TEMPO with Other Free Radicals. A plot of our data versus those of Morishima et al. indicates that a two parameter linear fit between these data may be made by using

$$Q = k(M + C)$$

where Q indicates our $\overline{\Delta\delta_f}$ values for TEMPO and M is the corresponding Morishima values using the free radical DTBN.

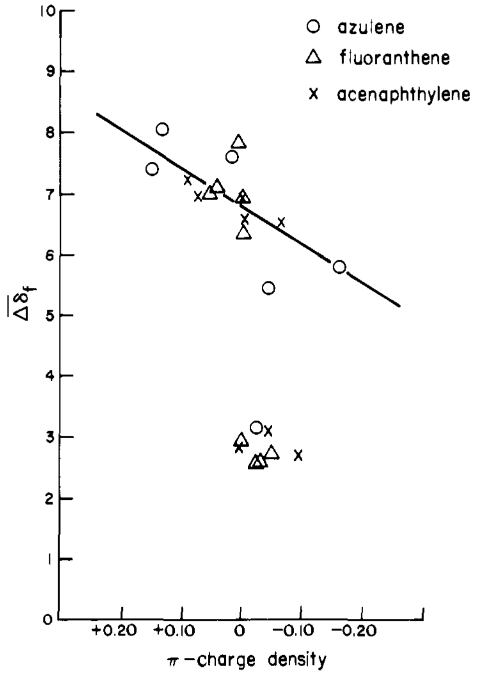

Figure 3. Relationship between $\overline{\Delta\delta_f}$ and the π-charge densities of three nonalternant aromatic hydrocarbons. The upper group of points ($\Delta\delta_f > 4$) belongs to protonated carbons. There seems to be a linear relationship similar to Morishima, although the correlation coefficient is very low (0.7156). Including the nonprotonated carbons in the lower group ($\overline{\Delta\delta_f} < 4$), prevents a linear relationship for both sets of points.

The linear regression parameters for the plot are $k = 2.400$, $C = 1.829$ ppm, and correlation coefficient = 0.9514. Here k reflects the effectiveness that TEMPO, as a shift reagent, has relative to DTBN. The interaction between the selected aromatics and TEMPO is 2.4 times stronger than the DTBN, and C represents the paramagnetic shift which the cyclohexane internal reference would have to experience to put Morishima's data on the same basis as our corrected data. Similarly, the free radical 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy (4-OH-TEMPO) was used as a shift reagent with fluoranthene, and the results were compared with similar TEMPO data. Here the new data for 4-OH-TEMPO is represented by H and

$$Q = k'(H + C')$$

yielding $k' = 1.605$, $C' = 2.642$ ppm, and the correlation coefficient = 0.9989. These results indicate that 4-OH-TEMPO is less effective as a shift reagent than Tempo but is still more effective than DTBN ($k/k' = 1.50$e and ($C'/C = 1.45$). The two ratios are close, indicating that the shift due to molecular interaction is directly proportional to the relative effectiveness of the radical. One possible explanation of this difference is that the molecular diameter of 4-OH-TEMPO is greater than the TEMPO due to the additional OH group. So when a transient molecular complex is formed via the molecular collision in the solution, the average distance between the substrate and free radical is increased and thereafter the strength of the interaction is decreased. DTBN is not a ring compound with three methyl groups on each side of nitroxyl group. The steric hindrance may therefore be greater than the TEMPO, and the strength of the interaction will also be decreased.

E. Nature of Intermolecular Free Radical–Substrate Interactions. All models for explaining paramagnetic shifts require the physical proximity of the free radical, F, and the interacting substrate, S. Thus equilibrium expressions will exist for each molecule in the solution of the type

$$F + S_1 \rightleftarrows FS_1 \quad K_1 = [FS_1]/[F][S_1]$$

$$F + S_2 \rightleftarrows FS \quad K_2 = [FS_2]/[F][S_2]$$

If the intermolecular interactions involve only weak van der Waal

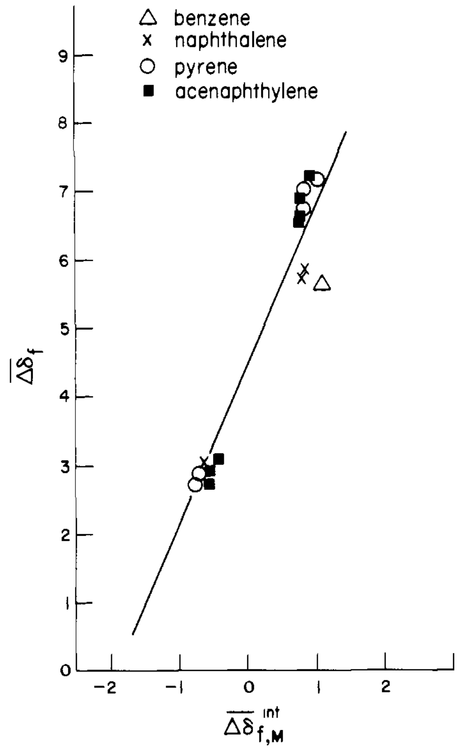

Figure 4. Relationship between these and Morishima's data. The abscissa indicates the $\overline{\Delta\delta_f}^{int}$ of Morishima's data (M) and the ordinate indicates $\overline{\Delta\delta_f}$ of these data (Q).

forces, then to a good approximation, ideal solution behavior will obtain and the various equilibrium constants will be small. Therefore, as pointed out by Draney and Kingsbury[4]

$$\delta_f = \frac{K(F)}{1 + K(F)}\delta_{FS} + \frac{1}{1 + K(F)}\delta_S \simeq K(F)\delta_{FS} + \delta_S$$

$$\Delta\delta_f = \delta_f - \delta_0 \simeq K(F)\delta_{FS}$$

This indicates that the chemical shift appears functionally independent of the substrate concentration (S) and is linearly proportional to the free radical concentration (F) which is coincident with our observation. Since the CCl_4 solvent shows very large shifts, it was suspected at first that most of the TEMPO would be complexed by the CCl_4, leaving a minor portion to complex the compounds. The consequence of this conjecture would be the shift of the compound would ultimately depend upon the concentration of the compound. It is, therefore, important to note that the result of 90% isooctane/10% cyclohexane mixture is exactly the same as the data listed in the table for a 8% isooctane, 4% cyclohexane, and 88% CCl_4. Benzene/CCl_4 samples with different molar ratio (1:4, 1:1, 4:1) were also prepared and only very minor differences were observed. These results have led us to conclude that the ideal solution behavior is obtaining at least for the hydrocarbons studied, the equilibrium constants are small, and the paramagnetic shifts actually are operative only during the momentary contact in a collision and lasts only for the duration of the collision complex. The solvent cage, of course, governs the time and these periods relate to the rate of liquid diffusions. Thus the model of Poindexter et al.,[13] involving pseudocontact interaction via transient complexation would seem to be supported by these data. This conclusion is supported further by high linearity in plots of the type shown in parts a and b of Figure 2. Curvature would be expected for strong interactions which lead to competitive or nonideal solution behavior. Furthermore, the failure to observe differential site effects for different free radicals on the same substrate also corroborate the ideal solution proposal. If strong interactions were present, it is unlikely that they would not be radical or site dependent and the high uniformity of relative shifts between different radicals which is observed in Figure 4 and 5 would seem to be unlikely. Thus, several arguments for the Poindexter model[13] are found in this work.

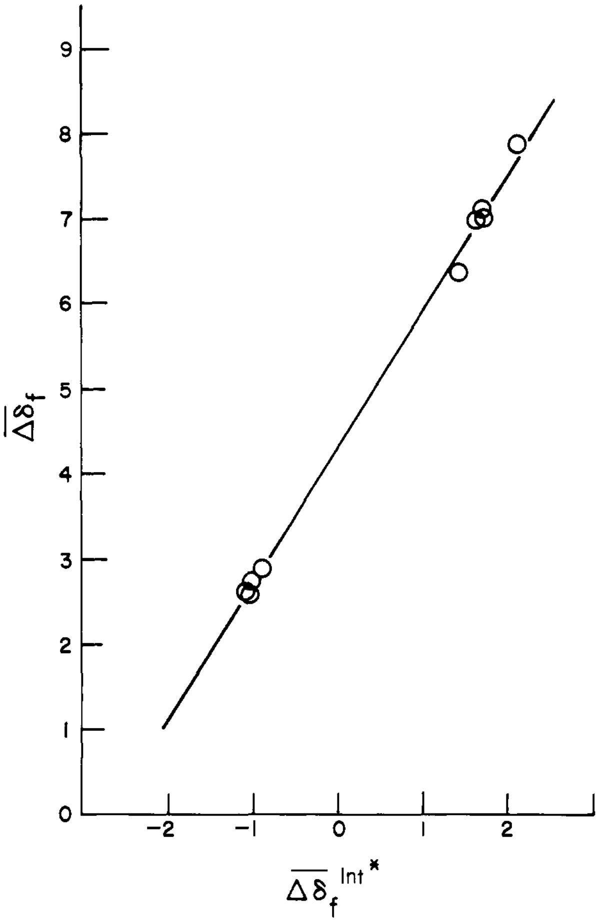

Figure 5. Relationship between fluoranthene/TEMPO system and the fluoroanthene/4-OH-TEMPO system: the abscissa is $\overline{\Delta\delta_f}^{int}$ of fluoranthene/4-OH-TEMPO system (H) and the ordinate is $\overline{\Delta\delta_f}$ of fluoranthene/TEMPO system (Q).

Difference in effectiveness of various free radicals, i.e., different steric and structural environments about the free electron site and differential effective collision distances to the various affected substrate sites, are factors which obviously will affect the strength of pseudocontact shifts. Furthermore, variation in the electronic structure of the substrate can modify the electron–nuclear spin interactions to provide differential amplification or attenuation factors in the interaction. This explains the greater sensitivity of CCl_4 and even the aromatic and unsaturated compounds over that of paraffin hydrocarbons. These effects are sufficient to avoid partitioning in the transient complexes. Further investigation of other systems in which stronger intermolecular associations are present is in progress to further clarify these issues.

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Registry No. 2,4,4-Trimethyl-1-pentene, 107-39-1; squalene, 111-02-4; benzene, 71-43-2; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9; quadricyclane, 278-06-8; 1,2,3-trimethylbenzene, 526-73-8; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,3,5-tetramethylbenzene, 527-53-7; biphenyl, 92-52-4; naphthalene, 91-20-3; 1,4-dimethylnaphthalene, 571-58-4; 1,3-dimethylnaphthalene, 575-41-7; phenanthrene, 85-01-8; pyrene, 129-00-0; triptycene, 477-75-8; triphenylene, 217-59-4; acenaphthene, 83-32-9; acenaphthylene, 208-96-8; azulene, 275-51-4; fluoranthene, 206-44-0; perinaphthenone, 548-39-0; 2,2,6,6-tetramethylpiperidinyl-1-oxy radical, 2564-83-2.

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