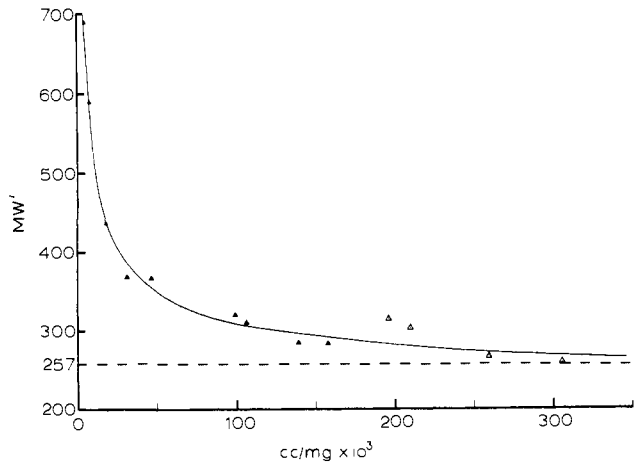
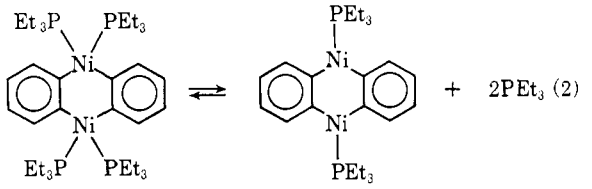


Figure 2. The concentration dependence of the apparent molecular weight (MW') of **2** in *n*-butane at 0°.

Figure 2 shows a plot of the observed molecular weight *vs.* the reciprocal of the concentration. The nine most dilute points were used to calculate a least-squares linear regression equation which is plotted as a solid line and which gives an intercept at infinite dilution of 257 amu (dotted line). The standard deviation of the intercept was ±9 amu, allowing limits of 232–282 to be imposed at a 95% confidence level. These data are not compatible with a monomeric formulation for **2**, since its dissociation should give either a two- or three-particle system at infinite dilution and limiting molecular weights of 185 and 124, respectively. On the other hand, they are in good agreement with the alternative cyclic dimer structure,[6] which would give a limiting molecular weight of 247 as a three-particle system (eq 2).



Evidence for this type of dissociation was found in the pmr spectrum of **2**. The triethylphosphine CH_3 protons do not appear to be coupled to the phosphorus nucleus in an adjacent ligand. The characteristic virtual coupling of CH_3 protons to phosphorus nuclei in nondissociating planar bis(triethylphosphine)–group VIII metal complexes has served as a basis for configurational assignments.[3,7] Addition of triethylphosphine to a solution of **2** in dimethyl ether (excess Et_3P:Ni = 2:1) caused essentially no change in the fine structure or in the chemical shifts of the aromatic proton resonances or of the Et_3P ligand methyl resonances. The P–CH_2 resonance increased in complexity and was shifted *ca.* 13 Hz to high field relative to its position in the spectrum of **2**. The spectrum of triethylphosphine in dimethyl ether is very different from that of the Et_3P ligands in **2**, yet no "free" triethylphosphine could be detected in the mixture. The results suggest that the Et_3P ligands are exchanging rapidly on the pmr time scale.

The near quantitative yield of **2** poses intriguing questions concerning the mechanism by which it is formed. Further studies of this and related organotransition metal systems are in progress.

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(6) Molecular models indicate that the dimer, 9,10-di[bis(triethylphosphine)nickelo]-9,10-dihydroanthracene, should not exist as a planar molecule. If the nickel bonding systems possess cis-planar configurations, the planes of the benzene rings lie substantially outside of the nickel bonding planes and the heterocyclic ring should be frozen in a pseudoboat conformation. The rather severe steric requirements of the Et_3P ligands in the cis-planar configuration could account for the very pronounced tendency of the molecule to dissociate in solution. We were unable to construct an analogous model of the hypothetical cyclic trimer. The steric restrictions are so severe that each nickel atom can accommodate only one Et_3P ligand.

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Application of Solvent Effects to the Study of Diamagnetic and Paramagnetic Ring Currents

Sir:

Because of their diamagnetic ring currents and specific solvent–solute interactions, aromatic solvents induce strong shifts in the proton nmr spectra of dipolar molecules.[1] In the present communication we suggest that specific solvent effects in potentially homoaromatic and antiaromatic solvents can provide valuable information about molecular magnetic anisotropies.

The chemical shift difference between acetonitrile and cyclohexane (internal reference) in a solvent X is $\Delta\sigma_X = \Delta\sigma_{gas} + \Delta\sigma_{medium}$. Referring all $\Delta\sigma_X$ values to $\Delta\sigma_{cyclohexane}$ (the observed chemical shift difference between acetonitrile and cyclohexane in neat cyclohexane), the relative solvent shifts $\Delta\sigma_X - \Delta\sigma_{cyclohexane}$ (for brevity, S) are isolated. For benzenoid hydrocarbons, S values are very large owing to a specific anisotropy effect: the positive end of the acetonitrile dipole is preferentially located above the plane of the ring where π-electron density and diamagnetic shielding are greatest.[2] This specific anisotropy effect is very much larger than the reaction field and van der Waals and nonspecific anisotropy terms, and will outweigh these even in only moderately anisotropic hydrocarbon solvents. S values should therefore be a direct measure of the magnetic anisotropy experienced in the time-averaged complex, if acetonitrile were associated with all hydrocarbons to the same extent. In practice, the association constants differ but are sufficiently similar to make S a valuable qualitative measure for the anisotropy experienced.[3]

The S values of "normal" olefins are close to zero (Figure 1).[4,5] The S value of benzene, on the other

(1) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); (b) P. Laszlo, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 231 (1967); (d) J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, **2**, 83 (1969).

(2) W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).

(3) The determination of association constants and limiting solvent shifts for the quantitative study of some systems of interest is currently in progress.

hand, is +1.00 ppm. We shall discuss the solvents giving rise to S values outside the range from 1,5-cyclooctadiene (S = −0.01) to piperylene (S = +0.12). The numbers in parentheses are S values in parts per million, plus signs denoting upfield shifts.

1,3,5-Cycloheptatriene (Tropilidene) (S = +0.33). It appears reasonable to ascribe the solvent effect to the presence of a homoaromatic ring current, in accord with the diamagnetic exaltation observed by Dauben.[6] As expected, the S value of 1,3,5-cyclooctatriene (S = +0.04) is much smaller than that of tropilidene.

Cyclopentadiene (S = +0.39). A diamagnetic ring current due to hyperconjugation has been considered by Dauben.[6] The susceptibility exaltation method, however, was considered too inaccurate to permit definitive conclusions. The high S value is in accord with Flygare's very recent microwave data[7] which indicate a magnetic anisotropy of almost 60% of the benzene value. Note that the S value of 1,4-cyclohexadiene (S = +0.01) is very small.

Cyclooctatetraene (COT) (S = −0.16). As a [4n]-annulene COT should show a strong paramagnetic ring current if it were planar.[8] Being far from planar, however, it is expected to show only weak ring current effects. Considering 1,3-cyclooctadiene (S = +0.02), 1,5-cyclooctadiene (S = −0.01), and 1,3,5-cyclooctatriene (S = +0.04) as model compounds, it seems likely that the downfield shift is at least partly due to a paramagnetic ring current. Previous workers[6] have concluded that COT has no ring current. However, the exaltation method is limited by the reliability of the Pascal-type increments used and an exaltation of less than 20% of the benzene value might easily go undetected.

Norbornadiene (S = +0.16). The strong shielding experienced in norbornadiene is surprising in view of the low S value of 1,4-cyclohexadiene (S = +0.01). These compounds are of interest because of their potential bishomocyclobutadiene character. However, data on related compounds are needed before any conclusions can be drawn.

Solids may be studied in 1,5-cyclooctadiene (1,5-COD) solution.[9] The S value of a mixture of 1,5-COD and the compound under investigation may then be compared with the S value of a corresponding mixture (same concentrations) of 1,5-COD and some suitable reference compound. Thus we find the ratio of S values (biphenylene-1,5-COD:naphthalene-1,5-COD) to be 1:3,[10] further strong evidence for a considerable antiaromatic contribution to the total anisotropy of biphenylene.[11]

(4) Cyclohexane, 1.4% by volume (1.3 M); acetonitrile, 1.4% by volume (2.67 M); temperature, 33 ± 1.5°. S_X values should be extrapolated to infinite dilution of acetonitrile for the evaluation of subtle differences.

(5) Presumably the small shielding effect of normal double bonds is largely cancelled by a slight deshielding contribution due to association.

(6) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, **91**, 1991 (1969).

(7) R. C. Benson and W. H. Flygare, *ibid.*, in press, quoted in S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *ibid.*, **92**, 5250 (1970).

(8) (a) J. A. Pople and K. G. Untch, *ibid.*, **88**, 4811 (1966); (b) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, **No. 21**, 109 (1967); (c) F. Baer, H. Kuhn, W. Regel, *Z. Naturforsch. A*, **22**, 103 (1967).

(9) 1,5-COD is a better solvent for olefins than cyclohexane, has a low anisotropy, and has no nmr absorptions close to acetonitrile or cyclohexane.

(10) Molar ratio of solute:1,5-COD = 1:12.4.

(11) H. P. Figeys, *Angew. Chem., Int. Ed., Engl.*, 7, 642 (1968).

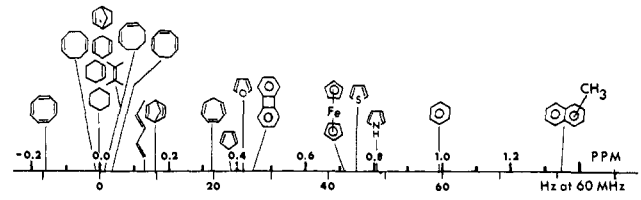

Figure 1. Acetonitrile solvent shifts.

Finally, the method may be extended to compounds other than hydrocarbons, such as heteraromatics and organometallics. For ferrocene, $S \simeq +0.72$ ppm is obtained,[12] in qualitative agreement with the results of Mulay's[13a] and Fox's[13b] single-crystal studies ($\Delta\chi$ = 0.83 and $\Delta\chi$ = 0.94, respectively).[14] For pyrrole S is slightly higher (S = +0.82, $\Delta\chi$ = 0.71),[14,15] and for furan S is lower (S = +0.42, $\Delta\chi$ = 0.65)[14,15] than expected on the basis of Flygare's microwave data, reflecting the high π basicity of pyrrole and the concomitant increase of the association constant, and in furan presumably the involvement of association at the periphery resulting in a deshielding contribution.

Acknowledgments. G. E. Schenck thanks the Unisity of California for a Regents' Graduate Intern Fellowship. This work was supported by National Science Foundation Grant No. GP-10571.

(12) In 1,5-COD, referred to benzene in 1,5-COD.

(13) (a) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963); (b) R. Mathis, M. Sweeney, and M. E. Fox, *ibid.*, **41**, 3652 (1964).

(14) Anisotropies $\Delta\chi$ are expressed as fractions of the benzene anisotropy.

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Cyclic Peroxides. V.[1] An α-Lactone Intermediate *via* Photodecarboxylation of a Monomeric Malonyl Peroxide

Sir:

Among the small ring heterocycles, the α-lactones are experimentally as well as theoretically intriguing and challenging molecules. Their isoelectronic relationship to cyclopropanones at least in part accounts for their elusive nature.[2] The first mention of α-lactone intermediates in the chemical literature was made by Cowdrey, Hughes, and Ingold[3] in their classical work on the hydrolysis of optically active α-bromopropionic acid. Since then α-lactones have been sporadically invoked as reactive intermediates in nucleophilic substitution reactions,[4-6] in free-radical substitution reactions,[7-9] in the thermolysis of cyclic anhydrosulfites[10]

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(2) R. Hoffmann, *ibid.*, **90**, 1475 (1968).

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