and C(4) and their symmetry equivalent atoms (the Mo–C(2) distance of 2.47 A is definitely longer than the Mo–C(3) and Mo–C(4) distances, where the difference of 0.05 A is not significant based on our present analysis), while the Mo–C(1) distance is very much greater. The C(1)–C(1′) link appears to be almost a pure double bond, while C(1)–C(2) has a very high degree of single-bond character; the distances in this portion of the molecule are similar to those found in free cyclooctatetraene in the gas phase.[8] The bond angles, C(2)–C(3)–C(4) and C(3)–C(4)–C(4′), approach the ideal value for a regular octagon (135°). The group of six atoms C(2), C(2′), C(3), C(3′), C(4), and C(4′) is significantly nonplanar with C(3) and C(3′) deviating by 0.16 A from the best plane through the other four atoms. The angle between the plane through C(1), C(1′), C(2), C(2′) and that through C(2), C(2′), C(3), C(3′) is 130°. The wide variation in the C(5)–Mo–C(7) and C(7)–Mo–C(7′) angles was also a feature of the analysis of cycloheptatrienemolybdenum tricarbonyl.[9] We consider that structure IV, as proposed by Winstein and co-workers,[3] is a good representation of the geometry, providing it does not imply that the Mo is equally associated with six carbon atoms.

There is no evidence for crystallographic disorder which could be indicative of valency tautomerism occurring in the crystal at 25°. This structure is an interesting contrast to that of cyclooctatetraeneiron tricarbonyl (III),[5] where the iron atom is bonded to a butadiene-like residue in the cyclooctatetraene ring, and where valency tautomerism has been detected in solution at temperatures as low as −100°; but at −140 to −150° the spectrum corresponding to a frozen complex is observed.[3]

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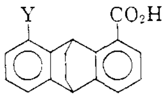
Evidence for the Dipolar Field Effect[1]

Sir:

Attempts to distinguish between inductive and field propagation models for the transmission of polar effects have not been entirely successful. The problem persists because, in most instances, molecular structure requires that the low dielectric cavity of the field effect model[2] be occupied by the chemical bonds important in the inductive effect model.[3] If a small attenuation factor is adopted for through-bond transmission of the polar effect, both models predict similar results.[4] However, these limiting models predict quite different results when the angle between a dipolar substituent and the reaction site is varied.[5] Roberts and Carboni point out that, although *o*-chlorophenylpropiolic acid is somewhat stronger than phenylpropiolic acid, it is weaker than expected on the basis of an inductive model.[5] Wells and Adcock note that the lessened acidities of 7-chloro-1-naphthoic and 8-chloro-2-naphthoic acids, for example, are compatible with the angular dependence implicit in the field effect model.[6] We now report the first example of a reversed substituent effect supporting these interpretations and offering secure evidence for the importance of dipolar field effects.

The ethano-bridged anthracenes I–IV were selected for investigation because simple electrostatic considerations indicated that substituent effects would be reversed. Moreover, resonance contributions are excluded and hydrogen bonding is unlikely.

The acids were prepared by the addition of ethylene to the corresponding anthroic acids which were obtained from benzanthrone or 1,8-dichloroanthraquinone by conventional methods.[7] The dissociation constants were determined in 50% ethanol–water (w/w) at 25°.[8]



I, Y = H; pK_H = 6.04 ± 0.03
II, Y = Cl; pK_{Cl} = 6.25 ± 0.02
III, Y = CO_2CH_3; p$K_{CO_2CH_3}$ = 6.20 ± 0.02
IV, Y = CO_2H; pK_1 = 5.67 ± 0.03; statistical correction = 5.97 ± 0.03
Y = CO_2^-; pK_2 = 7.19 ± 0.02; statistical correction = 6.89 ± 0.02

Two lines of evidence point to the importance of the field effect model. First and most pertinent, pK_{Cl} and p$K_{CO_2CH_3}$ are larger than pK_H. This reversal in normal substituent effects is cogent evidence for the angular dependence of the polar effect. As noted, electrostatic considerations predict log $(K_{Cl}/K_H) = -2.4/D_E$. The effective dielectric constant, D_E, may not be defined with complete confidence for these acids, but a value near 10 is not unreasonable.

Second, log (K_2/K_H) is unusually small, −0.85. This ratio is generally larger (less negative), since, in most compounds, the influence of the charge and the carboxylate dipole act in opposition.[9] For IV, however, the predicted contribution of the carboxylate dipole is near zero. The reduction in log (K_2/K_H) is therefore also predicted by the angular dependence implicit in the field effect model.

The similar values of pK_{Cl} and p$K_{CO_2CH_3}$ and the normal value of log $(K_1/4K_2)$ exclude an interpretation based on hydrogen bonding.[10]

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[7] Satisfactory microanalyses were obtained for all unknown compounds. The substances exhibited spectroscopic properties compatible with the assigned structures.

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[10] For IV, log $(K_1/4K_2)$ = 0.92. This result is comparable to that for glutaric and succinic acids, 0.73 and 1.30, respectively, in 52.3%

Other derivatives of this series are under investigation to substantiate these findings.

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ethanol-water (w/w) at 20° (G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933)). The distances between the removable protons in these acids are similar: 4.6 ± 0.2 A in IV, 5.15 A in glutaric acid, and 4.66 A in succinic acid.

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Kinetics of Ligand Exchange in Tetrahedral Complexes. Triphenylphosphine Exchange with Dihalobis(triphenylphosphine)cobalt(II) and -nickel(II) by Proton Magnetic Resonance[1]

Sir:

Relatively little is known of the kinetics of ligand substitution in tetrahedral coordination compounds. There have been no reports of such studies on divalent first-row transition metal complexes of this stereochemistry where the importance of ligand-field effects may be assessed. We report here a proton magnetic resonance (pmr) study of the kinetics of triphenylphosphine (TPP) exchange with the dihalobis(triphenylphosphine)cobalt(II) and -nickel(II) compounds of known pseudo-tetrahedral structure.[2-6] The pmr spectra of compounds of this type have been reported previously;[7-9] however, quantitative kinetic data were not obtained and an erroneous conclusion was reached[9] regarding the relative lability of the cobalt and nickel complexes.

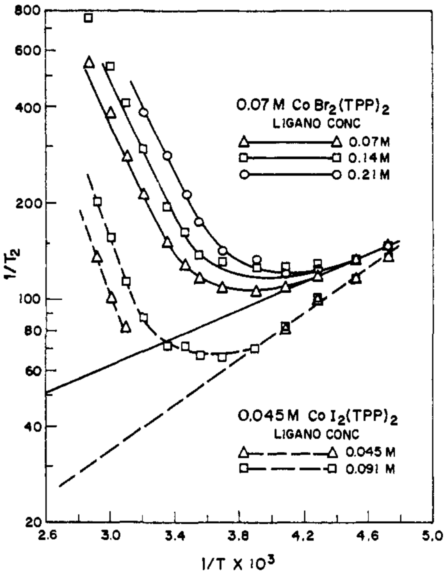

Figure 1. Plot of log $(1/T_2)$ *vs.* $1/T$ for deuteriochloroform solutions of $CoBr_2(TTP)_2$ and $CoI_2(TPP)_2$ with various concentrations of excess triphenylphosphine (TPP) as indicated. The points for $CoI_2(TPP)_2$ at a TPP concentration of 0.045 *M* between $1/T$ = 3.2 and 4.0 were omitted because of precipitate formation in this range.

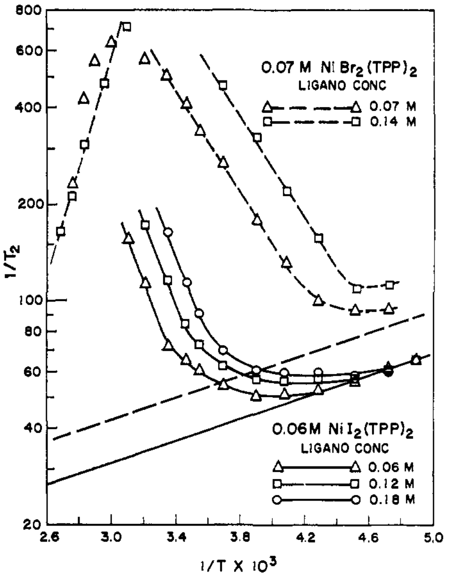

Figure 2. Plot of log $(1/T_2)$ *vs.* $1/T$ for deuteriochloroform solutions of $NiBr_2(TPP)_2$ and $NiI_2(TPP)_2$ with various concentrations of excess triphenylphosphine(TPP) as indicated.

The present experiments were carried out on deuteriochloroform solutions of the complexes $MX_2(TPP)_2$, (M = Co, Ni; X = Br, I) containing known concentrations of excess TPP, using a Varian A-60A spectrometer equipped with a variable-temperature probe. In these solutions (except for $NiBr_2(TPP)_2$ above about 40°) separate resonances are observable for free TPP and for the isotropically shifted[7,8] coordinated ligand protons. Kinetic parameters were obtained from the measured line widths at half-height, $\Delta\nu_{1/2}$ (cps), of the downfield shifted phenyl *meta* proton resonance of coordinated TPP. In such a system the effective transverse relaxation time of a ligand proton, T_2, is given by $(1/T_2) = \pi\Delta\nu_{1/2}$. This is related to T_{2M}, the transverse relaxation time in the absence of exchange, and τ_M, the average residence time of a ligand in the complex, by eq 1.[10,11]

$$\frac{1}{T_2} = \frac{1}{T_{2M}} + \frac{1}{\tau_M} \qquad (1)$$

Figures 1 and 2 show plots of log $(1/T_2)$ *vs.* $1/T$ for the cobalt and nickel compounds, respectively, in the presence of various concentrations of excess TPP. $CoI_2(TPP)_2$ is the least labile of the complexes studied and at low temperatures shows the expected[9,10] decrease in $1/T_{2M}$ as the temperature increases. At higher temperatures $1/T_2$ increases as the exchange term, $1/\tau_M$, becomes important. Values of $1/T_{2M}$ in this region were obtained by extrapolation of the low-temperature behavior; however, for $NiBr_2(TPP)_2$ the

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[1] This research was supported by the National Science Foundation through Grant GP3397.

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