with water, and vacuum dried. BDCC was obtained as 240.2 g (91%) of off-white powder, mp 198–206 °C. For characterization purposes, a small sample was recrystallized from acetonitrile with 78% recovery to afford pure **2**, mp 215-217 °C (lit.[1] mp 216–217 °C).

7,7,8,8-Tetracyanoquinodimethane. A 500-mL, round-bottomed, four-necked flask (or three-necked flask with a Y adapter) was fitted with a mechanical stirrer, thermometer, 5-mm-i.d. gas introduction tube extending to near the bottom of the flask, and a 50-mL buret positioned for liquid addition into an open neck. The flask was charged with 25.0 g (0.120 mol) of crude BDCC from the above preparation and 300 mL of acetonitrile, and the buret was filled with 39.0 mL (0.483 mol) of pyridine. The gas tube was connected to a chlorine cylinder by PVC tubing that included an in-line rotameter (glass ball) calibrated to supply chlorine at a rate of 620 mL/min. The gas tube was temporarily removed from the flask during the initial phase of the procedure. The stirrer was started, and the contents of the flask were warmed to 40–50 °C. The heating mantle was removed, and the gas flow was started at the precalibrated rate. (On a reaction of this scale, this flow rate has been found experimentally to supply 0.24 mol of chlorine in almost exactly 10 min and corresponds to an "effective" flow rate of ca. 550 mL/min.) When the gas flow had stabilized, the tube was reinserted into the reaction flask, and a stopwatch was started at the same instant. After 15 s, the pyridine addition was started at a flow rate of exactly 4 mL/min (1 mL/15 s). Throughout the reaction, the chlorine and pyridine additions were continuously regulated to maintain precisely constant rates, and the temperature was held between 40 and 50 °C by occasional application of a cooling bath. Initial precipitation of the product occurred at 4–5 min. At a reaction time of 8 min (when 31 mL of pyridine had been added) the pyridine addition rate was increased to 8 mL/min for 1 min. The addition of the entire 39 mL of pyridine was thus completed at the 9-min point. The chlorine addition was continued for 30 s, when a rapid color change from dark brown to orange was observed.[15] This color change serves as a visual endpoint for the reaction; as soon as it occurs the chlorine tube must be removed from the solution immediately. The reaction mixture was allowed to stir for an additional 5 min, and the color slowly reverted from orange to brown. The end-point color was then restored by reintroduction of the chlorine tube for 15 s. The reaction mixture was cooled to 0 °C, and the precipitated product was collected by suction filtration, washed with 150 mL of cold acetonitrile, and vacuum dried. TCNQ was obtained as 21.6 g (88%)[16] of orange-bronze crystals: mp 287–289 °C (lit.[1] mp 289–291 °C); estimated purity 99%.[17]

Note: This procedure is best conducted with two operators. One operator normally regulates the chlorine flow and temperature while the other controls the pyridine addition. Mastery of the technique may require one or two practice runs. The 25-g run described here is a convenient scale for demonstration purposes. We normally carry out the reaction on 10 times this scale with no change in procedure or results. The average yield for ten consecutive 250-g runs was 87 ± 1%.

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Registry No. BDCC, 1518-15-6; TCNQ, 1518-16-7; hydroquinone, 123-31-9; malononitrile, 4341-85-9.

(15) Optimum yields of TCNQ are obtained when chlorine is in *very* slight excess during the simultaneous addition. This is why the pyridine addition is started after a 15-s delay. However, the end-point color change can only be observed when pyridine is in excess. The increase in the pyridine addition rate near the end of the reaction serves to "set" the color for the end-point change. The slight excess of pyridine late in the reaction is not detrimental.

(16) The yield in this reaction is 95% if recrystallized BDCC is used. However, this results in a lower overall yield with no difference in TCNQ purity.

(17) This purity value was obtained by two independent methods: (1) measurement of the percent residue after sublimation and (2) comparison of the UV extinction coefficient with that of a purified standard.

Correlation Analysis: Hammett Substituent Constants and Hydroxyl Proton NMR Chemical Shifts of Triarylcarbinols

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Correlation analysis, the study of the relationships between the parameters known as substituent constants that appear in linear free energy expressions (e.g., the Hammett equation) and various directly measurable quantities, has been a subject of intense interest among chemists. Extensive reviews of the many aspects of this field have appeared in two recently published volumes.[1,2] In particular, many efforts have been made to establish a linear correlation (eq 1) between Hammett σ constants and NMR chemical shifts (δ).

$$\delta = a + b\sigma \quad (1)$$

In a recent review,[3] Tribble and Traynham list 182 published relationships purporting to be linear correlations of Hammett σ constants and proton NMR chemical shifts. However, the significance of most of these correlations is questionable. One reviewer[4] has stated, "To support any serious claim that there is a *precise* parallel between δ and σ, the linear correlation must be extremely good,...and should summarize the data so as to give r [the linear correlation coefficient] >0.95". In fact, only 40% of the relationships cited by Tribble and Traynham satisfy this criterion.

In addition, most of the aforesaid correlations may be faulted for yet another reason: the observed variation of the chemical shift with change in the σ constant is so small that any apparent trend may be more fortuitous than real. Thus, in the aforementioned listing, the magnitude of this variation (b in eq 1) exceeds 0.40 in only 27, and 1.00 in only 9 of the 182 relationships.

The investigation herein reported was undertaken in the hope of discovering a relationship between Hammett σ constants and proton NMR chemical shifts, which, in contrast to most of those that have been published would be significant by conforming to eq 1 with a correlation coefficient >0.95 and a variation factor (b) > 1.00.

In this study, the measurable quantity chosen for correlation with the Hammett σ constant was the chemical shift of the hydroxyl proton of the triarylcarbinol (**1**) (Chart I) dissolved in deuterated dimethyl sulfoxide. The selection of this particular chemical shift was prompted by the paper of Ouellette, Marks, and Miller[5] upon the conformational and substituent dependence of the hydroxyl proton chemical shift of arylcarbinols. Ouelette and his co-workers reported that the chemical shifts of the hydroxyl protons in each of five series of dimethyl sulfoxide solutions of arylcarbinols (**2**) were linearly correlated with

(1) Chapman, N. B., Shorter, J., Eds. "Advances in Linear Free Energy Relationships"; Plenum Press: New York, 1972.

(2) Chapman, N. B., Shorter, J., Eds. "Correlation Analysis in Chemistry"; Plenum Press: New York, 1978.

(3) Tribble, M. T.; Traynham, J. G. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; 165–172.

(4) Ewing, D. F. In "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; 363.

(5) Ouellette, R. J.; Marks, D. L.; Miller, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 913.

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Hammett σ constants. Even more significant (for our purpose) was their observation that the variation of δ with σ (as measured by the Hammett ρ constant) increased from 0.41 to 0.68 as the size of the groups, R_1 and R_2, increased. Ouelette and his co-workers accounted for this change in ρ by presuming that the transmission of the effect of the substituent X was conformationally dependent. More precisely, they reasoned, "As the steric size of the groups R_1 and R_2 increases, the population of rotamer [3] is expected to increase relative to rotamer [4]. The increased response due to ring substituents [i.e., the value of ρ]... indicates that the transmission of magnetic information is more effective in rotamer [3]".[5]

Subsequently, it occurred to the senior author (E.B.) of this paper, that if this explanation was valid, the transmission of magnetic information from the substituent X would be expected to be especially effective in the triarylcarbinol (1). In contrast to the two distinct conformations possible for each of the compounds studied by Ouelette et al., only one staggered conformation (5) is possible for the triarylcarbinol. Hence, the entire population of the molecules of the triarylcarbinol (1) would exist in the conformation supposedly required for the most effective transmission of the substituent effect. Furthermore, the fact that the proton is favorably oriented with respect to two substituted phenyl groups rather than only one as in the compounds studied by Ouelette implies an additional enhancement of the substituent effect.

Experimental Section

The NMR spectra of seven triarylcarbinols have been examined. Four of these compounds were prepared from a substituted phenylmagnesium bromide and ethyl carbonate. One, triphenylcarbinol was purchased (Aldrich), another, tris(*p*-methoxyphenyl)carbinol was prepared from methyl *p*-anisate and (*p*-methoxyphenyl)magnesium bromide, and another, tri-*p*-nitrophenylcarbinol was prepared by the method of Hawthorne and Hammond.[6]

The sample used to obtain an NMR spectrum was 0.50 mL of a solution prepared by dissolving 0.050 g of the carbinol in 1.0 mL of deuterated dimethyl sulfoxide (containing 1 drop of Me_4Si). The spectrometer was a Varian Model T-60.

The NMR absorption band of the hydroxyl proton (with one exception) appeared as a sharp singlet just upfield of the bands due to the aromatic protons in the carbinol. In the spectrum of the solution of tris(*p*-nitrophenyl)carbinol, this absorption band coincided with the most upfield member of the pair of doublets comprising the aromatic proton absorption. That this was so was established by a comparison of the band intensities. Whereas the two inner bands were of equal intensity, the intensity of the most upfield band exceeded that of the most downfield band. The sharpness and the invariability (with concentration) of the chemical shift of this band are considered to be consequences of strong complete hydrogen bonding between the carbinol and dimethyl sulfoxide.[3,5]

Results

The results of our measurements are presented in Table I. The chemical shifts are those for the hydroxyl protons and were obtained by taking the average of the results of two scans, one upfield, the other downfield. These two results never differed by more than 0.03 ppm and usually agreed to within 0.02 ppm.

Chart I

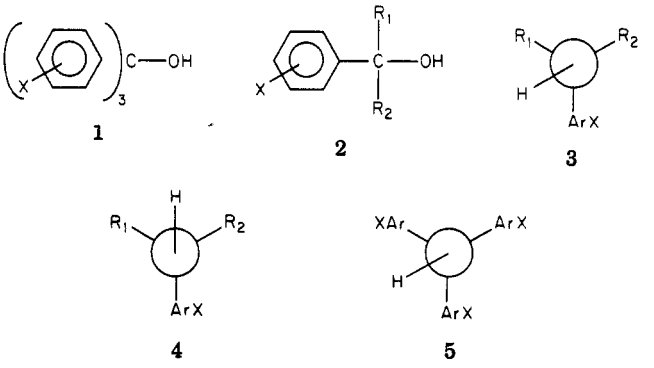

Table I. Correlation of Hammett σ and NMR δ of the Hydroxyl Proton of Triarylcarbinols (1)

X	mp (lit.), °C	σ	δ
p-CH_3O	80-2 (81-2)[7]	−0.27	6.01
p-H_3C	92-4 (93-4)[8]	−0.17	6.10
m-H_3C	oil (oil)[9]	−0.07	6.22
H	158 60 (161-2)[7]	0	6.33
p-Cl	91-3 (93-4)[10]	0.23	6.70
m-F	116-8 (118-9)[11]	0.34	6.83
p-O_2N	188-91 (190-1)[6]	0.78	7.45

With the method of least squares, the data were found to best fit the equation

$$\delta = 6.35 + 1.41\sigma_X \quad (2)$$

The standard deviation of the observed data from this equation is 0.0275. The standard deviations of the intercept and slope are 0.0111 and 0.0311, respectively. The linear correlation coefficient equals 0.999.

Conclusions

This correlation of the Hammett σ constant and a proton NMR chemical shift is notable for several reasons. It certainly satisfies Ewing's criterion for a meaningful linear relationship. Given the magnitude of the slope and of the linear correlation coefficient, eq 2 certainly represents what we had been looking for. This relationship could be used to evaluate or reevaluate reliably Hammett substituent constants (provided, of course, that the appropriate triarylcarbinol is available).

The value (1.41) of the slope of the linear correlation established by this study is not to be equated to a conventional Hammett ρ constant. Inasmuch as three identical substituents influence the result of our measurements, the effective substituent constant for the system used in this study equals $3\sigma_X$. Therefore, the value of the corresponding Hammett ρ constant is one-third of the slope of eq 2. Hence, according to our measurements, the value of ρ in a Hammett relationship correlating for the chemical shifts of triarylcarbinols equals 0.47. This result was unexpected. It is contrary to our initial expectation that ρ should exceed the largest (0.68) of the ρ values reported by Ouellette. Consequently, the results of our work do not support Ouelette's contention regarding the effect of conformation on the transmission of a substituent effect.

Registry No. 1 (X = *p*-CH_3O), 3010-81-9; 1 (X = *p*-CH_3), 3247-00-5; 1 (X = *m*-CH_3), 51226-48-3; 1 (X = H), 76-84-6; 1 (X = *p*-Cl), 3010-80-8; 1 (X = *m*-F), 379-44-2; 1 (X = *p*-O_2N), 596-48-5.

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