Experimental Section

Melting points were determined on a Kofler hot stage and are uncorrected. ^{1}H NMR spectra were determined on a Perkin-Elmer R12A (60-MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7 mass spectrometer at 70 eV. Microanalyses were performed by this department.

Standard Procedure Used for All Examples. A solution of NBS (1 mmol) in dry DMF (5 mL) was added to a solution of substrate (1 mmol) in dry DMF (5 mL) and stirred at room temperature for 24 h. The mixture was poured into water (50 mL) and extracted with pentane or dichloromethane (50 mL). The extract was washed well with water, dried ($MgSO_4$), and evaporated under reduced pressure to yield crude monobromide. For larger scale reactions, concentrations may be increased to 0.1 mol in 50 mL of solvent.

2-Bromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (2). From 1 as described above, direct recrystallization from aqueous methanol yielded green crystals of 2: mp 111–112 °C; ^{1}H NMR, see Table I; mass spectrum, *m/e* (rel intensity) 312, 310 (10, M^+), 297, 295 (5, $M - CH_3$), 282, 280 (10, $M - 2CH_3$), 231 (24, M - Br), 216 (65), 215 (86), 201 (100). Anal. Calcd for $C_{18}H_{15}Br$: C, 69.47; H, 4.86. Found: C, 69.30; H, 4.92.

Acknowledgment. We thank the National Sciences and Engineering Research Council of Canada and the University of Victoria for financial support.

Registry No. 1, 956-84-3; 2, 71807-14-2; 4, 83-32-9; 5, 2051-98-1; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3-trimethylbenzene, 526-73-8; 1,2,3,5-tetramethylbenzene, 527-53-7; 1,2,3,4-tetramethylbenzene, 488-23-3; 2,3-dimethylnaphthalene, 581-40-8; anthracene, 120-12-7; pyrene, 129-00-0; phenol, 108-95-2; 3-methylphenol, 108-39-4; 4-methylphenol, 106-44-5; 1,3-benzenediol, 108-46-3; hydroquinone, 123-31-9; benzenamine, 62-53-3; 4-methylbenzenamine, 106-49-0; 2-bromo-1,3,5-trimethylbenzene, 576-83-0; 1-bromo-2,3,4-trimethylbenzene, 40101-33-5; 1-bromo-2,3,4,6-tetramethylbenzene, 3349-15-3; 1-bromo-2,3,4,5-tetramethylbenzene, 40101-36-8; 1-bromo-2,3-dimethylnaphthalene, 5334-79-2; 9-bromoanthracene, 1564-64-3; 1-bromopyrene, 1714-29-0; 4-bromophenol, 106-41-2; 4-bromo-3-methylphenol, 14472-14-1; 2-bromo-4-methylphenol, 6627-55-0; 4-bromo-1,3-benzenediol, 6626-15-9; quinone, 106-51-4; 4-bromobenzenamine, 106-40-1; 2-bromo-4-methylbenzenamine, 583-68-6; NBS, 128-08-5.

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(14) J. W. Williams and J. M. Fogelberg, *J. Am. Chem. Soc.*, **52**, 1356 (1930).

(15) R. C. Huston and J. A. Hutchinson, *J. Am. Chem. Soc.*, **54**, 1504 (1932).

(16) R. B. Sandin, A. Gillies, and S. C. Lynn, *J. Am. Chem. Soc.*, **61**, 2919 (1939).

(17) Aldrich sample.

Evidence for a Violation of the Reactivity-Selectivity Principle from a Study of Substituent Effect Transmission in α-Activated Arylmethyl Carbanions

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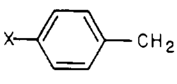
Received July 31, 1979

The response of side chain magnetic monitors[1] to aryl substituents is a sensitive probe of factors[2] and mechanisms[3] governing the transmission of effects. To take advantage of this we investigated in the pair of conjugated substrates 1 and 2 the influence of Y on the sensitivity of the benzylic proton(s) to effects exerted by para substituents X.[4] Evidence is provided that the sensitivity of the benzylic proton in carbanions 2 depends upon the stereochemistry of the anion and responds to the effectiveness of the Y group in removing the negative charge from the carbanide carbon. High sensitivities are thus found for those Y groups such as Y = CN and SO_2R for which we anticipated[5] poor capacities in stabilizing adjacent carbanions by delocalizative mechanisms.



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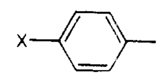

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Table I. Relative Sensitivities of Methylene Protons in α-Substituted Arylmethanes (Equation 1)[a]

entry no.	Y	$\lambda_{CH_2} \pm s^b$	r^c	n^d
1	H	0.68 ± 0.07	0.969	9
2	SPh	0.55 ± 0.03	0.991	9
3	Ph	0.68 ± 0.04	0.990	8
4	CN	0.89 ± 0.08	0.978	8
5	$CONMe_2$	0.83 ± 0.06	0.989	7
6	CO_2Me	0.90 ± 0.04	0.995	7
7	COMe	1.03 ± 0.02	0.998	7
8	COPh	1.03 ± 0.02	0.999	7
9	SOPh[e]	0.73 ± 0.04	0.992	8
9	SOPh[f]	0.95 ± 0.04	0.996	8
10	SOMe[e]	0.62 ± 0.05	0.975	9
10	SOMe[f]	0.80 ± 0.04	0.990	9
11	SO_2Me	1.17 ± 0.11	0.969	9
12	NOH[g]	0.72 ± 0.04	0.991	9
13	NOH[h]	1.01 ± 0.04	0.995	7

[a] Chemical shifts for Me_2SO solutions (0.2 M in substrate). [b] Standard deviation of the slope. [c] Correlation coefficient. [d] Number of points. [e] High-field proton. [f] Low-field proton. [g] Synoximes. [h] Antioximes.

Table II. Relative Sensitivities of Methine Protons in α-Substituted Arylmethyl Carbanions (Equation 2)[a]

entry no.	Y	$\lambda_{CH^-} \pm s^b$	r^b	n^b
3	Ph	0.72 ± 0.05	0.992	5
4	CN[c]	0.95 ± 0.07	0.994	4
5	$CONMe_2$	0.49 ± 0.01	0.998	6
6	CO_2Me	0.53 ± 0.02	0.995	8
7	COMe	0.45 ± 0.01	0.998	7
8	COPh	0.36 ± 0.02	0.993	7
9	SOPh	0.78 ± 0.05	0.994	5
11	SO_2Me	1.06 ± 0.07	0.987	8

[a] Carbanions in Me_2SO solution (0.2 M) are prepared in situ from sodium dimsyl, 0.3 M in Me_2SO. [b] See Table I for explanation. [c] Only a limited number of points are available, since Me_2SO obscures resonances of methine proton in many $ArCH^-CN$.

^{1}H chemical shifts of the methylene protons of a family of compounds (e.g., 1, Y = SO_2Ph) are plotted vs. shifts of another family (e.g. Y = COMe): an analogous treatment

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(1) (a) Review: M. T. Tribble and J. G. Traynham in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, Chapter 4. For additional representative references see: (b) S. H. Marcus, W. F. Reynolds, and S. I. Muller, *J. Org. Chem.*, **31**, 1872 (1966); (c) B. M. Linch, *Org. Magn. Reson.*, **6**, 190 (1974); (d) G. R. Wiley and S. I. Miller, *J. Org. Chem*, **37**, 767 (1972); (e) H. J. Kroth, H. Schumann, H. G. Knivila, C. D. Schoeffer, Jr., and J. J. Zuckerman, *J. Am. Chem. Soc.*, **97**, 1754 (1975); (f) G. A. Caplin, *Org. Magn. Reson.*, **6**, 99 (1974).

(2) (a) J. Niwa, *Bull. Chem. Soc. Jpn.*, **48**, 118 (1975); (b) H. Yamada, Y. Tsuno, and Y. Yukawa, *ibid.*, **43**, 1459 (1970).

(3) (a) T. A. Wittstruck and E. N. Trachenberg, *J. Am. Chem. Soc.*, **89**, 3803 (1967); (b) G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Can. J. Chem.*, **51**, 915 (1973); (c) G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **97**, 3137 (1975).

(4) Although in families 1 and 2 there are available several meta substituents, we have restricted the correlation analysis to para substituents only since meta substituents frequently show anomalies, in part because the effects exerted are more complex than a combination of polar and resonance contributions.[2]

(5) S. Bradamante, F. Gianni, and G. Pagani, *J. Chem. Soc. Chem. Commun.*, 479 (1976);

0022-3263/79/1944-4735$01.00/0

Table III. Sensitivities (ρ's) of Acidities of $ArCH_2Y$

Y	$Me_2SO-H_2O^a$	Me_2SO^b
NO_2		2.70
COMe		3.9
$CONMe_2$	4.82	
CO_2-*t*-Bu	5.15	
CN	5.85	5.46
SO_2Ph		5.07

^{a} Reference 19. ^{b} Reference 20.

is done for benzylic carbanions **2**. Analyses are expressed in terms of eq 1 and 2, where Δ_X is the Leffler–Grunwald

$$\Delta_X\delta_{ArCH_2Y} = \lambda_{CH_2}\Delta_X\delta_{ArCH_2SO_2Ph} + \text{constant} \qquad (1)$$

$$\Delta_X\delta_{ArCH^-Y} = \lambda_{CH^-}\Delta_X\delta_{ArCH^-SO_2Ph} + \text{constant} \qquad (2)$$

operator[6] acting on methylene or methine chemical shifts of $ArCH_2Y$ and $ArCH^-Y$, respectively.[7] The effects are arbitrarily referred to the $ArCH_2SO_2Ph$ and $ArCH^-SO_2Ph$ series because for these the largest number of substituents is presently available to us. Values of the sensitivities λ_{CH_2} and λ_{CH^-} are reported in Tables I and II, respectively. It is observed that in general the Y groups do not induce dramatic changes in sensitivities λ_{CH_2}: for the carbonyl (Y = COMe, COPh, CO_2Me, and $CONMe_2$) and sulfone (Y = SO_2Ph and SO_2Me) families the sensitivities are approximately identical, but higher than those for Y = H, Ph, and SPh. Therefore, polar electron withdrawing groups enhance sensitivities, although their electron demands as expressed by any set of σ constants are not linearly related to the sensitivities of their relative families. Transmission of substituent effects is stereochemically dependent, as evidenced by entries 9, 10, 12, and 13 in Table I. The two diastereotopic protons of sulfoxides have different sensitivities:[11] the low-field resonating proton has a sensitivity comparable to that of sulfones, while the high-field one tends to be similar to that of sulfides.[12] Also in oximes the methine sensitivity of the anti series is sizably higher than that of the syn series.[14] The order of the Y groups in inducing high sensitivities in neutral systems **1** is therefore $SO_2R \approx COR \approx CN$, SOR > Ph > H > SPh. This order is no longer followed in the corresponding anions **2**, where the Ph group ranks high in the scale, together with the SO_2R and CN groups. Carbonyl functions are considerably weaker than before in allowing transmission of effects: furthermore the two enolate anion series where Y = COMe and COPh show considerably different sensitivities. The order of Y groups in enhancing sensitivities of methine protons in benzyl carbanions is therefore $SO_2Me \approx SO_2Ph \approx CN$ > SOPh ≈ Ph > $CO_2Me \approx CONMe_2 \approx$ COMe > COPh.

Table III collects the sensitivities (ρ's) of acidities of a number of carbon acids **1** either in Me_2SO-H_2O or in pure Me_2SO. It can be appreciated that the order of methine sensitivities of the carbanions **2** parallels closely that of acidities of the substituted carbon acids **1**. It is also evident that, despite the fact that benzyl cyanide is more acidic than *N*,*N*-dimethylphenylacetamide and *tert*-butyl arylacetic ester, its acidity and the benzylic proton of its conjugate carbanion are more sensitive to the effect of substituents present on the aryl ring. This clearly constitutes a violation of the reactivity–selectivity principle, according to which more reactive substrates should be less sensitive to the effect of substituents. This result further stresses that the response of extrathermodynamic NMR monitors (SCS) parallels that of thermodynamic monitors (pK_a's). The response of the extrathermodynamic NMR monitor allows deeper insight in the transmission of substituent effects.

The order of methine proton sensitivity appears dominated by the mesomeric electron demand exerted by groups Y and by the stereochemistry of the anion. The first item is suggested by the fact that low sensitivities are associated with carbonyl functionalities, expected to be very effective in withdrawing the negative charge from the carbanionic carbon: conversely high sensitivities of the sulfonyl- and cyano-stabilized carbanions are associated with the high negative charge density that these groups leave on the benzylic carbon[15] and on the phenyl ring attached thereto.[5] To further support this view, the direct quantitative comparison of methine sensitivities of arylaldoximate anions, regarded as limiting forms of α-nitrosobenzyl carbanions in which the nitroso group almost exclusively withdraws the negative charge,[16] and arylmethyl phenylsulfonyl carbanions would have been very informative, but it was unfortunately prevented by insolubility of sodium arylaldoximates in Me_2SO. An indirect comparison can serve as well, however, if one considers that in MeOH the methine proton in *syn*-arylaldoximates is ca. 0.8 time *less* sensitive than that in *syn*-arylaldoximes while the methine proton of arylmethyl phenylsulfonyl carbanions is 1.2–1.5[18] *more* sensitive than the methylene protons of arylmethyl phenylsulfones. It is highly indicative thus that aldoximates, as representative systems which carry negligible negative charge density on the benzylic carbon and on the phenyl ring attached thereto, behave analogously to enolate anions **2** (Y = COR).

The different sensitivities of the two enolates **2** (Y = COMe and COPh) would instead be associated with the different populations of the *E* and *Z* isomers: in the arylacetophenone anions (R = Ph) the *E* isomers are

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(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 20.

(7) In evaluating methylene (methine) sensitivities, intersystem correlations,[8] otherwise called proportionality relationships,[9] have been preferred to comparisons of values derived from Hammett type correlations of methylene (methine) protons vs. substituent constants: as a norm in fact intersystem correlations are considerably more precise since inadequacies of σ constants are bypassed (see, e.g., the NMR deviances of halogens as substitutents.[10])

(8) S. Bradamante and G. Pagani, *J.Org. Chem.*, in press.

(9) B. M. Lynch, *Can. J. Chem.*, **55**, 541 (1977).

(10) (a) R. R. Fraser, Gurudata, R. N. Renand, C. Reyes-Zamora, and R. B. Swingle, *Can. J. Chem.*, **47**, 2767 (1969); (b) K. L. Williamson, N. C. Jacobus, and K. T. Soncy, *J. Am. Chem. Soc.*, **86**, 4021 (1964); (c) A. Pines and M. Rabinowitz, *J. Chem. Soc. B*, 385 (1971); (d) C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962); (e) H. Yamada, Y. Tsuno, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **43**, 1459 (1970).

(11) Our sensitivities differ dramatically from those previously reported in $CDCl_3$ solution.[10a]

(12) Nishio[13] in a study of arylmethyl aryl sulfoxides has proposed that the most sensitive of the two diastereotopic protons is that gauche to the S=O bond and anti to the electron pair.

(13) M. Nishio, *Chem. Pharm. Bull.*, **15**, 1669 (1967)

(14) An analogous result has been found in THF solution: I. Pejkovic-Tadic, M. Hranisavljevic-Jakovljevic, S. Nesic, C. Pascual, and W. Simon, *Helv. Chim. Acta*, 48, 1157 (1965).

(15) S. Bradamante and G. Pagani, unpublished results.

(16) Evidence for this is offered by the following two results: (a) the methine resonance in sodium *syn*-arylaldoximates in MeOH is high-field shifted relative to the neutral precursors by ca. 0.1 ppm only; (b) usual σ and not enhanced σ^- constants are required to account for acidities of *syn*-arylaldoximes in H_2O.[17]

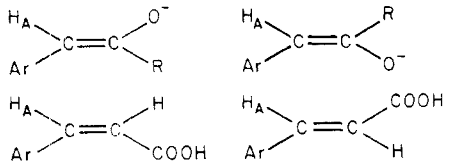
(17) H. H. Jaffe', *Chem. Rev.*, **53**, 191 (1953), quoting data reported by O. L. Brady and N. M. Chokshi, *J. Chem. Soc.*, 946 (1929); O. L. Brady and R. F. Goldstein, *ibid.*, 1918 (1926).

(18) The approximation is due to the fact that only a limited number of substituents X can be used in the intersystem correlation $ArCH^-SO_2Ph$ vs. $ArCH_2SO_2Ph$: the 1.2–1.5 range is obtained also from the indirect comparison of ρ's derived from $ArCH_2SO_2Ph$ vs. σ and $ArCH^-SO_2Ph$ vs. σ,σ^-.[15]

(19) K. Zaharieva, J. N. Stefanovsky, and I. G. Pojarlieff, *Tetrahedron Lett.*, 1663 (1971).

(20) (a) F. G. Bordwell, *Pure Appl. Chem.*, **49**, 963 (1977); (b) D. Algrim, J. E. Bares, J. C. Branca, and F. G. Bordwell, *J. Org. Chem.*, **43**, 5026 (1978).

certainly predominant, while for aryl acetone anions (R = Me) the two isomers would be copresent as a rapidly equilibrating mixture.



That the *E* isomers show lower sensitivity is in line with results obtained for proton H_A in *Z* and *E* cinnamic acids.[3a]

Registry No. 1 (X = Y = H), 108-88-3; 1 (X = H; Y = SPh), 831-91-4; 1 (X = H; Y = Ph), 101-81-5; 1 (X = H; Y = CN), 140-29-4; 1 (X = H; Y = $CONMe_2$), 18925-69-4; 1 (X = H; Y = CO_2Me), 101-41-7; 1 (X = H; Y = COMe), 103-79-7; 1 (X = H; Y = COPh), 451-40-1; 1 (X = H; Y = SOPh), 833-82-9; 1 (X = H; Y = SOMe), 824-86-2; 1 (X = H; Y = SO_2Me), 3112-90-1; (*Z*)-1 (X = H; Y = NOH), 622-32-2; (*E*)-1 (X = H; Y = NOH), 622-31-1; **2** (X = H; Y = Ph), 18802-87-4; **2** (X = H; Y = CN), 18802-89-6; **2** (X = H; Y = $CONMe_2$), 61057-01-0; **2** (X = H; Y = CO_2Me), 61057-02-1; **2** (X = H; Y = COMe), 34438-76-1; **2** (X = H; Y = COPh), 54282-53-0; **2** (X = H; Y = SOPh), 71566-13-7; **2** (X = H; Y = SO_2Me), 32116-29-3.

Response to Polar-Inductive and Mesomeric Effects of Contiguous Substituents in Parent Oxygen Acids XOH and Nitroactivated Parent Carbon Acids XCH_2NO_2. The Phenylogy Principle[1]

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Received July 31, 1979

The universality of substituent constants derived from the benzenoid series is tested here for predicting properties of simple parent substrates XGMon, in which both the substituent functionality X and the monitor Mon are contiguous to the involved (reacting) functionality G. The approach considers the case of Mon = H in XGMon and

XGMon

1a, Mon = H; G = -O-

1b, Mon = H; G = NO_2CH<

uses acidities of the parent molecules XGH **1** for evaluating the effects of substituent X. Groups G = -O- and NO_2CH< have been considered, and Table I reports acidities of parent oxygen acids XOH **1a**, of nitroactivated parent carbon acids XCH_2NO_2 **1b**, and of para-substituted phenols **2** together with our recently proposed set[2] of adjusted σ^-, σ_I, and σ_{R^-} constants. Polar-inductive σ_I constants are used when X exerts polar-inductive effects only (e.g., Me, Br, and OH), while enhanced σ^- constants are used when X is capable of conjugative delocalization with GH or G^-. The plots of Figure 1 show that acidities of at least 14 oxygen acids [from methanol (X = Me) to nitric acid (X = NO_2)] and of 8 nitroactivated carbon acids are linearly accounted for by such treatment: despite some scatter, the precision of the fit is impressive. The point for 4-hydroxypyridine (X = 4-py) is slightly deviant: it is dubious, however, whether it is the σ^- constant which is incorrect or whether it is the pK_a of 4-hydroxypyridine which is uncertain.[3] We noted previously[2a] that, in analogy with para-substituted anilines and phenols,[5] a number of substituents X presented a duality of σ^- constants depending on whether X were adjacent to nitrogen or oxygen functionalities. While the cyano group in XOH correctly requires the enhanced constant,[6] the goodness of the fit is not sensitive enough for preferring one of the two values of the benzoyl substituent. None of the available σ^- values accounts for acidities of parent oxygen acids XOH in which X is a functionality composed of second row atoms ($PhSO_2$, PhSO, $(EtO)_2P{=}O$), although at least for one of the functionalities ($PhSO_2$) no deviance is found for the line of XCH_2NO_2 vs. σ^-. The DSP treatment of oxygen and nitroactivated carbon acid acidities affords the excellent fitting parameters reported in Table II. The success of both treatments in accounting for the substituent effects finds its explanation in the way we have chosen the set of σ_I, σ^-, and σ_{R^-} constants: relative to the literature values, the present parameters were adjusted in consideration of systems in which the substituents were directly bonded to the reacting center and then tested. It is remarkable that sensitivities of oxygen acids in water and of nitroactivated carbon acids in Me_2SO are not so dissimilar as one would anticipate from the widely different stabilizing capacities of the two solvents toward negatively charged species and from the different abilities of Me_2SO and H_2O to hydrogen bond un-ionized oxygen acids. One is left to admit with Bordwell[10] that the electrostatic and mesomeric effects of substituents are submerged in a large sea of solvent effects (no matter how) operating at the reaction site. Inclusion in the DSP treatment (entry 2) of substituents (X = Me, OH, and Br) nonmesomerically interacting with the adjacent group -O- ($\sigma_R \rightarrow 0$) does not cause any statistically significant variation in the ρ_I and ρ_R values of entry 1. The simultaneous use of "mixed" substituents with different interacting properties (polar-inductive or polar-inductive mesomeric) is thus legitimated.

It is accepted that nonmesomeric interactions of substituents with adjacent groups respond linearly with σ^* constants of the substituents (see, e.g., the ionization constants of substituted alcohols[11] and of substituted

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[1] Part 3 in Substituent Effect Treatment of Interactions between Contiguous Functionalities G-X.

[2] (a) S. Bradamante and G. A. Pagani, *J. Org. Chem.*, in press as Part 2; (b) *ibid.*, in press.

[3] The experimental pK_a values for 2- and 4-hydroxypyridine are 11.62 and 11.09, respectively:[4] these values are corrected into 9.09 and 7.74 to take into account the pyridone-hydroxypyridine tautomerism.[4] [$pK_{hydroxy} = pK_{exp} - \log (R + 1)$ where R = the ratio of pyridone-hydroxypyridine.] However, while in the case of the 2 isomer the ratio of tautomers can be accurately determined (2-pyridone:2-hydroxypyridine = 340), in the case of the 4 isomer the ratio is much higher (4-pyridone:4-hydroxypyridine = 2200): we believe that for this reason the above value might be considerably more approximate and thus constitute a source of imprecision.

[4] A. Albert, "Heterocyclic Chemistry", 2nd ed., The Athlone Press, London, 1968, pp 89-93.

[5] S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 50 (1973).

[6] The figure of 3.46 for the pK_a of cyanic acid in water may be approximate: Hine expects[7] a lower value to take into account for the anticipated cyanic-isocyanic acid equilibrium in water. The fact that a single tautomer (isocyanic acid) is present in the solid evidenced in old crystallographic[8] and spectroscopic studies[9] is of little significance for the position of the equilibrium in water. Because of all this, the point for X = CN is subject to some uncertainty: the pK_a value for the cyanic acid, interpolated from line A of Figure 1, is ca. 3.0, thus it is qualitatively in accord with Hine's prediction.

[7] J. Hine, "Structural Effects on Equilibria in Organic Chemistry", Wiley-Interscience, New York, 1975, p 185.

[8] W. C. v. Dohlen and G. B. Carpenter, *Acta Crystallogr.*, **8**, 646 (1955).

[9] C. Reid, *J. Chem. Phys.*, **18**, 1544 (1950).

[10] F. G. Bordwell, *Pure Appl. Chem.*, **49**, 963 (1977).

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