(see below, also) in the measurements for $C_2H_2D_2$, which enter into both $d_0/d_2$ and $d_{2'}/d_4$, thereby tend to cancel. However, the latter ratio is larger than the first by an amount which seems greater than the rather considerable experimental error.

Further detailed discussion is not of value, since apart from the analytical inaccuracy, interpretation of the data for this acetylene formation reaction in terms of isotope effects is further restricted in the following way. Some of the data previously discussed[6] referred of necessity to high pressures: In the absence of relative or absolute quantum yields $\phi$, relative rates of decomposition $(D)$ by $H_2$ split-off for the various ethylenes could be inferred only at high pressures where the stabilization $(S)$ of the excited species became effectively constant as $\phi \rightarrow 0$. An apparent rate constant $k_a$ for ethylene decomposition by $H_2$ or $D_2$ split-off was defined as $k_a = \omega D/S$, where $\omega$ is the collision number. For constant $\omega$, then $k_{aH_2}/k_{aD_2} = D_{H_2}/D_{D_2}$ at high pressures, if the assertion of linearity between $k_a$ and $D$ were to hold. However, we noted that since the reported[4] rate expression, i.e., $1/R^{1/2} = A(1 + BP)$, fits the data on acetylene production rather well, that a *simple* linear relation between the relative apparent rate constant $k_a$ for formation of acetylene and the elementary rate constant $k_d$ of eq. 5 did not apply (i.e., $k_a \neq \omega \cdot D/S$). The justification for using this phenomenon was that the rate $k_a$ *did* involve $k_d$ in an important way and is worthy of consideration. This is indeed so, but in view of eq. g above it is clear that

these observed ratios are not measurements of pure isotope effects well suited for theoretical interpretation (nor indeed are the primary isotope effects). In addition, it has been noted by Ausloos and Gorden[9] that not all the isotope effects involved are understood. For example, they found a ratio of $C_2H_2:C_2HD:C_2D_2$ formation from $asym$-$C_2H_2D_2$ of $1.09:4.65:2.0$ different from that from $sym$-$C_2H_2D_2$ $(0.99:5.85:2)$. Our average rate ratio for *trans* split-off of $H_2:HD:D_2$ is $2.0:4.8:1.11$ over the range 1–16 cm.; for $cis$-ethylene-$d_2$ Callear and Cvetanović have an average of $2.0:5.94:1.01$ from $H_2$ analysis (and $2.0:4.75:0.98$ from isotopic acetylene analyses which are presumably less reliable). Ausloos and Gorden suggested that other mechanisms of decomposition of mercury-photosensitized ethylene should be considered beside that of ref. 4. It may be noted, however, that whereas H migration to form ethylidene precedes $H_2$ split-off from $sym$-$C_2H_4D_2$

$$\text{HDC=CHD} \longrightarrow \text{DC—CH}_2\text{D} \longrightarrow \text{H}_2 + \text{C}_2\text{D}_2$$
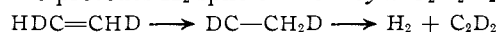
that, by contrast, D migration precedes $H_2$ split-off from $asym$-$C_2H_2D_2$

$$\text{D}_2\text{C=CH}_2 \longrightarrow \text{DC—CH}_2\text{D} \longrightarrow \text{H}_2 + \text{C}_2\text{D}_2$$
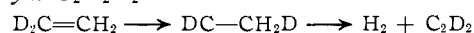
Thus a small isotope effect for the migration step could possibly reconcile the data of Ausloos and Gorden for *asym*.

More recently, Cvetanović, Falconer and Rabinovitch cited secondary intermolecular isotope effects on $Hg(^3P_1)$ photosensitization of butene-1 and butene-1-$d_8$ of magnitude 2.6–2.9.[5]

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# Nitriles and Isonitriles as Proton Acceptors in Hydrogen Bonding: Correlation of $\Delta\nu_{OH}$ with Acceptor Structure[1]

BY ADAM ALLERHAND[2] AND PAUL VON RAGUÉ SCHLEYER[3]

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Infrared spectral shifts due to hydrogen bonding between proton donors and nitriles with widely differing substituents correlated very well with Taft's $\sigma^*$-constants. The range of $\sigma^*$-constants for the compounds studied extended from +2.65 (for $CCl_3CN$) to −0.48 (for cyclopropyl cyanide). The spectral shifts for these extremes were, respectively, 62 to 173 cm.$^{-1}$ with phenol as proton donor. Isonitriles have also been examined as hydrogen bonding bases. Molecular structure evidence indicates the preferred form of these compounds to be $R—\overset{+}{N}\equiv\overset{-}{C}$; the strong hydrogen bond observed to this group is most probably to carbon and not to nitrogen. A Taft correlation was also obtained with isonitriles. The compounds studied ranged from *tert*-butylisonitrile ($\sigma^* = -0.30$) to phenylisonitrile ($\sigma^* = +0.60$). The spectral shifts, from 245 to 203 cm.$^{-1}$, respectively, with phenol as proton donor, were larger than those with nitriles. The Hammett equation correlated the spectral shifts of aromatic nitriles and aromatic isonitriles over a limited range of compounds studied. Because of geometrical limitations, intramolecular hydrogen bonding (found only in $\alpha$- and $\beta$-hydroxynitriles) was weak and involved the $\pi$-electrons of the $C\equiv N$ triple bond and not the nitrogen atom.

Intermolecular hydrogen bonding between hydroxylic proton donors Y–OH and proton acceptors B–R has been studied extensively by infrared spectroscopic methods.[4] The spectral shift, $\Delta\nu_{OH}$, is defined as the difference in OH stretching frequency of free Y–OH and hydrogen bonded Y–OH...B–R. The magnitude of $\Delta\nu_{OH}$ will be influenced by variations in B, the proton acceptor group, in Y[5] and in R.[6] There has been no systematic study of the effect of variations of R on

$\Delta\nu_{OH}$. Caldow and Thompson investigated the systems R–X...HCN (and DCN) where X = Cl, Br, I and $NO_2$; $C_6H_5C\equiv CH$...$O=C(CH_3)R$; and $C_6H_5$-$C\equiv CH$...$N\equiv CR$.[7] An approximately linear relationship was found between $\nu_{CH \cdot B}$, the position of the bonded C–H (or C–D) peak, and the Taft inductive factors, $\sigma^*$,[8] for the groups R. However this study suffers from some deficiencies. Weak proton donors were used resulting in small ranges of frequency shifts— only about 40 cm.$^{-1}$—with changes in R. The measurements were carried out in pure liquid proton acceptors, i.e., not in a constant environment.[9] In some cases the CH bands studied overlapped partially with bands

(1) Paper IX of a series on hydrogen bonding; paper VIII, *J. Am. Chem. Soc.*, **85**, in press (1963). This work was taken from the Ph.D. Thesis of Adam Allerhand, Princeton University, 1962; preliminary communication, *J. Am. Chem. Soc.*, **84**, 1322 (1962).

(2) Merck Foundation Fellow, 1960–1961; Esso Foundation Fellow, 1961–1962.

(3) Alfred P. Sloan Research Fellow.

(4) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(5) An extensive study of the effect of variation in Y upon $\Delta\nu_{OH}$ has been carried out; J. Greer, unpublished.

(6) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940); **9**, 204 (1941).

(7) G. L. Caldow and H. W. Thompson, *Proc. Roy. Soc.* (London), **A254**, 1 (1960).

(8) R. W. Taft, Jr., in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(9) Spectral shifts have frequently been measured by the undesirable technique of using the proton acceptor as solvent; instead, such studies should be carried out in an inert solvent with as low a concentration of proton acceptor as possible.[10,11]
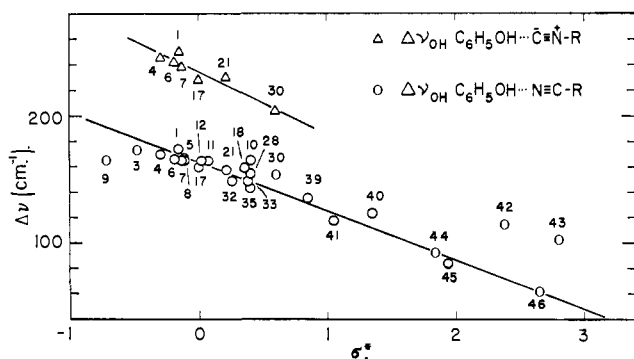
Fig. 1.—$\Delta\nu_{OH}$–$\sigma^*$ correlation of phenol with nitriles and iso-nitriles in CCl₄ solution. Substituent numbers correspond to those used in Tables I and II.



Fig. 2.—$\Delta\nu_{OH}$–$\sigma^*$ correlation of methanol with nitriles and iso-. nitriles in CCl₄ solution. Substituent numbers correspond to those used in Tables I and II.

of the proton acceptor, thus reducing the accuracy of the reported values.[7]

We undertook to carry out a systematic study of the effect of variations of R on $\Delta\nu_{OH}$ for Y–OH. . .B–R systems. If a correlation between the inductive effect of R ($\sigma^*$) and $\Delta\nu$ exists, prediction of $\Delta\nu$ would be possible. Likewise, $\sigma^*$-values could be calculated from hydrogen bonding data.[7] Nitriles were chosen for this study because of practical and theoretical considerations. Many nitriles are commercially available; others can be synthesized easily. Nitriles are linear groups so that possible steric complications would be avoided. Nitriles form moderately strong hydrogen bonds to standard proton donors such as phenol ($\Delta H = -4$ kcal./mole)[10–12] and methanol ($\Delta H = -2$ kcal./mole);[10] spectral shifts are relatively large and are easily and accurately measurable.[13]

Although infrared spectroscopic studies of the proton accepting power of nitriles are numerous[6,7,10–15] and other evidence for X–H. . .nitrile hydrogen bonding exists,[16,17] there is still a residual, erroneous belief that nitriles are very weak proton acceptors.[18] This incorrect impression probably stemmed from a few reported examples of *intramolecular* OH. . .nitrile hydrogen bonding: o-cyanophenol,[19–21] β-hydroxypropinonitrile[19] and some cyanohydrins.[19] Due to adverse geometry no O–H. . .N hydrogen bonding but only the much weaker OH. . .π-electron type[22] was observed. There is no evidence that *intermolecular* OH. . .nitrile hydrogen bonding is weak. A number of additional

intramolecular examples are included in the present study.

Recently it has been shown that isonitriles are strong proton acceptors in hydrogen bonding.[13,23] With isonitriles, carbon and not nitrogen is the likely proton acceptor atom; a comparison of isonitriles with nitriles as proton acceptors is presented in the present paper.

## Experimental

The infrared spectroscopic measurements were carried out as described in a previous paper.[11] Reagent grade carbon tetrachloride was dried over P₂O₅, decanted and used without further purification. Reagent grade methanol and phenol were used without further purification; capillary gas chromatography confirmed the purity of these compounds. Commercially available nitriles were purified carefully by fractional distillation or recrystallization and their boiling or melting points compared with literature values. In many cases infrared and n.m.r. spectra also were recorded. The following nitriles were prepared by known methods: cyclohexyl cyanide, trimethylcyanosilane, triphenylacetonitrile, iodoacetonitrile, phenylpropiolonitrile, dibromoacetonitrile, γ-hydroxybutyronitrile, δ-hydroxyvaleronitrile, β-(9-hydroxy,9-fluorenyl)-propionitrile and α-(2-cyanoethyl)-β-naphthol. Most of the isonitriles were prepared by the technique of Ugi and Meyr.[24] Methyl and phenyl isocyanide were prepared by other methods.

The n.m.r. spectrum of trimethylcyanosilane was recorded on a Varian A-60 spectrometer.

## Results and Discussion

**Intermolecular Hydrogen Bonding.**—Table I summarizes the results of hydrogen bonding of phenol and methanol to more than forty nitriles in CCl₄ solution. Results for isonitriles are given in Table II. Spectral shifts are considerably larger for isonitriles than for corresponding nitriles. In isonitriles, the lone pair of electrons on carbon is the most likely hydrogen bonding site[13,23]; hence, here are unusual examples of OH hydrogen bonding spectral shifts to carbon atoms which are larger than to similarly constituted nitrogen atoms. It is tempting to ascribe this behavior to the greater electron availability provided by negatively charged carbon in the structure, $R—\overset{+}{N}\equiv\overset{-}{C}$. It should be emphasized that the greater OH spectral shifts to isonitriles do not necessarily indicate *stronger* hydrogen bonds[1,25]; thermodynamic measurements of these systems are planned.[26]

Plots of $\Delta\nu$'s against Taft inductive factors $\sigma^*$[8] of the R groups in R–CN and R–NC are linear (Fig. 1 and 2). The degree of linearity is particularly gratifying because of the very large range of $\sigma^*$-constants of the substituents studied. For substituted benzonitriles as proton acceptors, plots of $\Delta\nu$'s against Hammett $\sigma$-constants[27] are also linear (Fig. 3).

(10) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962).

(11) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963).

(12) M. St. C. Flett, *J. Soc. Dyers Colourists*, **68**, 59 (1952).

(13) P. von R. Schleyer and A. Allerhand, *J. Am. Chem. Soc.*, **84**, 1322 (1962).

(14) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

(15) W. Gordy, *Phys. Rev.*, **51**, 564 (1937); M. Freymann and R. Freymann, *Bull. soc. chim. France*, **4**, 944 (1937); H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955); Y. Sato, *Sci. of Light* (Tokyo), **4**, 120 (1955); Y. Sato and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **76**, 1007 (1955); *Chem. Abstr.*, **50**, 5406 (1956); L. J. Bellamy, H. E. Hallam and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958); L. J. Bellamy and H. E. Hallam, *ibid.*, **55**, 220 (1959); C. L. Bell and G. M. Barrow, *J. Chem. Phys.*, **31**, 300 (1959); L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.* (London), **A254**, 119 (1960); P. V. Huong, J. Lascombe and M. L. Josien, *J. chim. phys.*, **58**, 694 (1961); S. Wada, *Bull. Chem. Soc. Japan*, **35**, 707 (1962).

(16) E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

(17) W. G. Schneider in D. Hadži, ed., "Hydrogen Bonding," Pergamon Press, London, 1959, p. 55.

(18) Table 6-I, p. 196 in ref. 4, lists "well recognized hydrogen bonding compounds" but nitriles are not included among the H bonding bases. It has been incorrectly asserted that –CN groups do not readily form hydrogen bonds.[19]

(19) M. St. C. Flett, *Spectrochim. Acta*, **10**, 21 (1957); see ref. 11, footnote 34.

(20) S. B. Hendricks, O. R. Wulf, G. E. Hilbert and U. Liddel, *J. Am. Chem. Soc.*, **58**, 1991 (1936).

(21) V. Prey and H. Berbalk *Monatsh. Chem.*, **82**, 990 (1951).

(22) M. Tichý, *Chem. Listy*, **54**, 506 (1960), and references therein cited.
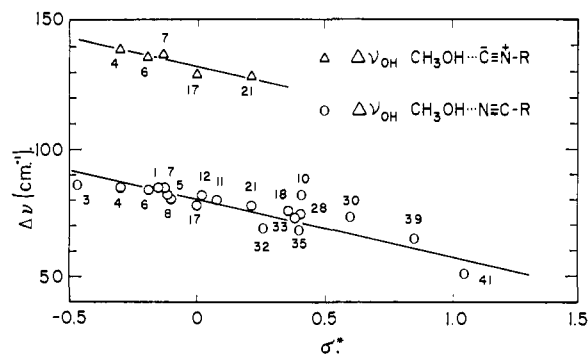
(23) L. Ferstandig, *J. Am. Chem. Soc.*, **84**, 1323, 3553 (1962).

(24) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

(25) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(26) R. West, University of Wisconsin, personal communication.

(27) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

TABLE I

HYDROGEN BONDING OF PHENOL AND METHANOL TO NITRILES[a]

| No.[b] | Substituent | Δν phenol[c] | Δν methanol[d] | σ* calcd.[e] | σ* literature[e] | Ref. |
|---|---|---|---|---|---|---|
| 1 | Cyclohexyl | 174 | 85 | −0.29 | −0.15 | 8 |
| 2 | p-CH₃OC₆H₄– | 174 | .. | − .29 | (− .268)[f] | 8 |
| 3 | Cyclopropyl | 173 | 86 | − .27 | − .475 | 31 |
| 4 | (CH₃)₃C– | 169 | 85 | − .16 | − .300 | 8 |
| 5 | CH₃(CH₂)₂– | 167(164)[g] | 82 | − .11 | − .115 | 8 |
| 6 | (CH₃)₂CH– | 166 | 84 | − .09 | − .190 | 8 |
| 7 | CH₃(CH₂)₃– | 165 | 85 | − .06 | − .130 | 8 |
| 8 | CH₃CH₂– | 165 | 81 | − .06 | − .100 | 8 |
| 9 | (CH₃)₃Si– | 165 | .. | − .06 | − .72 | 37 |
| 10 | trans-C₆H₅CH=CH– | 165 | 82 | − .06 | + .410 | 8 |
| 11 | C₆H₅(CH₂)₂– | 165 | 80 | − .06 | + .080 | 8 |
| 12 | C₆H₅(CH₂)₃– | 165 | 82 | − .06 | + .020 | 8 |
| 13 | Cl(CH₂)₄– | 165 | 80 | − .06 | | |
| 14 | Br(CH₂)₄– | 165 | 79 | − .06 | | |
| 15 | p-CH₃C₆H₄– | 161 | 79 | + .04 | (− .170)[f] | 8 |
| 16 | p-CH₃OC₆H₄CH₂– | 161 | 77 | + .04 | | |
| 17 | CH₃– | 159(160)[g] | 78(81)[g] | + .10 | .000 | 8 |
| 18 | cis-CH₃CH=CH–[h] | 159 | 76 | + .10 | .360 | 8 |
| 19 | β-Naphthyl | 159 | 76 | + .10 | | |
| 20 | p-C₆H₅C₆H₄– | 159 | 76 | + .10 | (− .01)[f,i] | 8 |
| 21 | C₆H₅CH₂ | 158 | 78 | + .12 | .215 | 8 |
| 22 | Cl(CH₂)₃– | 158 | 76 | + .12 | | |
| 23 | Br(CH₂)₃– | 158 | 77 | + .12 | | |
| 24 | m-CH₃C₆H₄– | 157 | 74 | + .15 | (− .069)[f] | 8 |
| 25 | α-Naphthyl | 156 | 73 | + .17 | | |
| 26 | CH₂=CHCH₂– | 155(150)[g] | 74 | + .20 | | |
| 27 | (C₆H₅)₃C– | 155 | .. | + .20 | | |
| 28 | (C₂H₅)₂CH– | 154 | 74 | + .23 | + .405 | 8 |
| 29 | o-CH₃C₆H₄ | 154 | 77 | + .23 | | |
| 30 | C₆H₅– | 153 | 73 | + .25 | .60(0.000)[f] | 8 |
| 31 | p-ClC₆H₄CH₂– | 153 | 73 | + .25 | | |
| 32 | Br(CH₂)₂– | 149 | 69 | + .36 | .26 | 7 |
| 33 | Cl(CH₂)₂– | 148 | 73 | + .38 | .385 | 8 |
| 34 | p-ClC₆H₄– | 144 | 67 | + .48 | ( .22)[f] | 8 |
| 35 | CH₂=CH– | 143(145)[g] | 68 | + .51 | .40 | 30 |
| 36 | o-ClC₆H₄– | 140 | 65 | + .59 | | |
| 37 | m-BrC₆H₄– | 140 | 64 | + .59 | ( .391)[f] | 8 |
| 38 | m-ClC₆H₄– | 139 | 62 | + .61 | ( .373)[f] | 8 |
| 39 | ICH₂– | 135 | 65 | + .72 | .85 | 8 |
| 40 | C₆H₅C≡C– | 123 | .. | +1.03 | 1.35 | 8 |
| 41 | ClCH₂– | 117 | 51 | +1.19 | 1.05 | 8 |
| 42 | I– | 114 | .. | +1.26 | 2.38 | 8 |
| 43 | Br– | 102(102)[g] | .. | +1.57 | 2.80 | 8 |
| 44 | Br₂CH– | 92 | .. | +1.83 | 1.84 | 8 |
| 45 | Cl₂CH– | 84 | [j] | +2.04 | 1.94 | 8 |
| 46 | Cl₃C– | 62 | [j] | +2.61 | 2.65 | 8 |

[a] Solvent, CCl₄; approximate concentrations: nitrile 0.4 $M$, phenol 0.005 $M$, methanol 0.01 to 0.02 $M$; cell thicknesses, 10 mm. [b] These substituent numbers correspond to those in Table II and Fig. 1–3. [c] Measured from the "free" OH band of phenol at 3611 cm.⁻¹. [d] Measured from the "free" band of methanol at 3643 cm.⁻¹. [e] Least squares calculations gave: $\Delta\nu_{OH}$ (phenol–nitriles) = 162.7 − 38.56σ* (1), $\Delta\nu_{OH}$ (methanol-nitriles) = 80.3 − 22.98σ* (2). Cyanogen halides and unsaturated nitriles were omitted from the calculations. σ* calcd. was obtained from eq. 1. It is believed to be accurate to ±0.1. [f] Hammett σ-constant of the substituent on the benzene ring. [g] Ref. 10. [h] When a 1:1 mixture of cis and trans isomers was used the same Δν was obtained. [i] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [j] Shoulder.

Several points deviate significantly from a simple σ*-Δν relationship. The largest deviations are exhibited by BrCN and ICN; the spectral shifts exhibited by these molecules are much larger than expected (Fig. 1). X—CN molecules show evidence of significant contributions from resonance structures X—C≡N ↔ X⁺=C=N⁻[28]; such resonance would explain the enhanced proton accepting ability of the nitrogen atom, the most probable hydrogen bonding site. The Taft substituent constant σ* is a measure only of the inductive effect of a group; substituents which resonate with CN groups should not correlate with σ*. Such resonance might be expected in unsaturated nitriles. Deviations in spectral shifts from the values predicted

on the basis of σ*-constants, possibly due to resonance, were observed with C₆H₅CH=CH—CN (+12 cm.⁻¹), C₆H₅—CN (+11 cm.⁻¹), C₆H₅—C≡C—CN (+10 cm.⁻¹), CH₃—CH=CH—CN (+8 cm.⁻¹); on the other hand, the deviation with CH₂=CH—CN (−7 cm.⁻¹)[29] was in the opposite direction of the observed scatter (Fig. 1 and 2). No definite conclusion can be drawn, but the effect of resonance, if present, on unsaturated nitrile hydrogen bonding must be small.

There are two divergent proposals for the σ*-constant of the cyclopropyl group: +0.11 ± 0.03 based on a correlation of O–H absorption intensities[30] and −0.475 based on ultraviolet and visible spectral changes between 2,4-dinitrophenylhydrazones and their conjugate

(28) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); S. Geller and A. L. Schawlow, *ibid.*, **23**, 779 (1955).

(29) Using the value of σ* (vinyl) = +0.40.[30]

(30) T. L. Brown, *J. Am. Chem. Soc.*, **80**, 6489 (1958).

bases.[31] Our experimental result (Table I, Fig. 1 and 2) is in better agreement with the latter value, but in another instance we have come to the opposite conclusion.[32] The apparent duality of character of the cyclopropyl group has been discussed by Jones and Hancock.[31]

### TABLE II

HYDROGEN BONDING OF PHENOL AND METHANOL TO ISONITRILES[a]

| No.[b] | Substituent | $\Delta\nu$ phenol, cm.$^{-1c}$ | $\Delta\nu$ methanol, cm.$^{-1d}$ |
|---|---|---|---|
| 1 | Cyclohexyl | 250 | . . |
| 4 | tert-Butyl | 245 | 139 |
| 6 | Isopropyl | 241 | 136 |
| 7 | n-Butyl | 238 | 137 |
| 21 | Benzyl | 230 | 128 |
| 17 | Methyl | 228 | 129 |
| 2 | p-Methoxyphenyl | 219 | 121 |
| 30 | Phenyl | 203 | . . |
| 34 | p-Chlorophenyl | 191 | . . |

[a] Solvent, CCl$_4$; conditions of measurement and concentrations similar to those used for nitriles (footnote a in Table I). [b] These substituent numbers correspond to those in Table I and Fig. 1–3. [c] Spectral shift measured from the free peak of phenol at 3611 cm.$^{-1}$. [d] Spectral shift measured from the free peak of methanol at 3643 cm.$^{-1}$.

The influence of inductive effects on $\Delta\nu$ is also illustrated in Table III. The replacement of a CH$_3$ group ($\sigma^* = 0.00$) by a chlorine ($\sigma^* = 2.94$)[8] has little effect on $\Delta\nu$ of phenol–nitrile if the CH$_3$ group is separated by four methylenes from the CN group. As the replacement occurs closer and closer to the proton accepting site, the effect on $\Delta\nu$ becomes large.

### TABLE III

THE MAGNITUDE OF INDUCTIVE EFFECTS OF $\Delta\nu$ OF PHENOL HYDROGEN BONDED TO NITRILES

| Substituent R in R–CN | $\Delta\nu$,[a] cm.$^{-1}$ | Substituent R in R–CN | $\Delta\nu$,[a] cm.$^{-1}$ | $\Delta\nu_{CH_3(CH_2)_nCN}$ − $\Delta\nu_{Cl(CH_2)_nCN}$ |
|---|---|---|---|---|
| CH$_3$(CH$_2$)$_4$– | (165)[b] | Cl(CH$_2$)$_4$– | 165 | 0 |
| CH$_3$(CH$_2$)$_3$– | 165 | Cl(CH$_2$)$_3$– | 158 | 7 |
| CH$_3$(CH$_2$)$_2$– | 167 | Cl(CH$_2$)$_2$– | 148 | 19 |
| CH$_3$–CH$_2$– | 165 | ClCH$_2$– | 117 | 48 |
| CH$_3$– | 159 | Br– | 102 | >57[c] |

[a] In dilute CCl$_4$ solutions. [b] Assumed to be identical with $\Delta\nu$ for phenol–butyronitrile. [c] $\Delta\nu$ for phenol–cyanogen chloride should be smaller than for the bromide; see Table I.

The proton-accepting ability of trimethyl(iso)cyanosilane is of considerable interest in view of the controversy in the literature concerning the structure of this compound. Support for the isocyanide structure (CH$_3$)$_3$Si–NC,[33,34] for the cyanide structure (CH$_3$)$_3$Si–CN,[35] and for an equilibrium mixture of both structures predominating in the latter,[36] have been reported. The infrared and microwave spectroscopic evidence for the cyanide structure[35] is more convincing than the chemical evidence for the isocyanide structure.[33,34] A band at 1592 cm.$^{-1}$ in the infrared spectrum of trimethyl(iso)cyanosilane, but absent from the spectrum of tert-butyl cyanide, was originally cited as evidence for the isocyanide structure.[33] We here confirm the

(31) L. A. Jones and C. K. Hancock, J. Org. Chem., 25, 226 (1960).

(32) J. Greer, unpublished observations, has found that the proton-donating ability of cyclopropanol is much greater than other cyclanols. This indicates that the cyclopropane ring is electron withdrawing and has a positive σ-constant.

(33) J. J. McBride and H. C. Beachell, J. Am. Chem. Soc., 74, 5247 (1952); H. C. Beachell, J. Chem. Phys., 28, 991 (1958).

(34) D. Seyferth and N. Kahlen, J. Am. Chem. Soc., 82, 1080 (1960).

(35) H. R. Linton and E. R. Nixon, J. Chem. Phys., 28, 990 (1958); Spectrochim. Acta, 10, 299 (1958); J. Sheridan and A. C. Turner, Proc. Chem. Soc., 21 (1960).

(36) T. A. Bither, W. H. Knoth, R. V. Lindsey, Jr., and W. H. Sharkey, J. Am. Chem. Soc., 80, 4151 (1958).

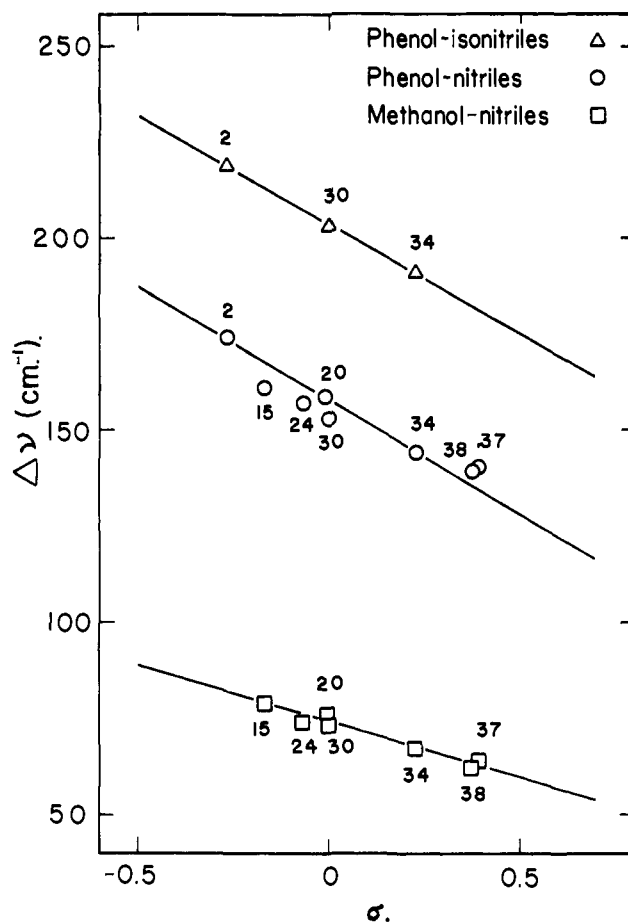Fig. 3.—$\Delta\nu_{OH}$–$\sigma$ correlation of phenol and methanol with substituted benzonitriles and benzoisonitriles in CCl$_4$ solution. Substituent numbers correspond to those used in Tables I and II.

later report[36] that the 1592 cm.$^{-1}$ band is absent in pure trimethyl(iso)cyanosilane. The proton acceptor ability of this compound supports the cyanide structure. From the $\sigma^*$-value of −0.72 for the (CH$_3$)$_3$Si– group,[37] a $\Delta\nu_{PhOH}$ value of about 280 cm.$^{-1}$ for the isocyanide structure and 190 cm.$^{-1}$ for the cyanide structure can be estimated from Fig. 1. The observed value, 165 cm.$^{-1}$, is even lower than the latter estimate. Additional evidence for the nitrile structure was obtained from the n.m.r. spectrum of the compound; only a single sharp peak at $\delta = 0.33$ p.p.m. relative to tetramethylsilane was observed in CCl$_4$ solution. tert-Butyl isocyanide showed a triplet of approximately 1:1:1 intensity due to long range N$^{14}$–H$^1$ coupling, a characteristic of all isonitriles examined so far, but one absent in nitriles.[38] Although this long range coupling is distance dependent and Si is a larger atom than C, it would be expected in trimethyl(iso)cyanosilane if this compound had an isocyanide structure.

Some deviation from linearity in the $\Delta\nu$ vs. $\sigma^*$ plots (Fig. 1–3) may be due to environmental effects.[11] The magnitude of spectral shifts is strongly dependent on nitrile concentration (Table IV).[10,11,23] Ideally, intermolecular $\Delta\nu$ measurements should be made by extrapolation to infinite dilution.[10,11] The values quoted in Tables I and II correspond to a nitrile concentration of 0.4 mole./l. in CCl$_4$; these values may differ significantly in some cases from those at infinite dilution.[10,11] For example, compare the behavior of tert-butyl cyanide ($\sigma^*$ tert-butyl = −0.30) and cyclohexyl cyanide ($\sigma^*$

(37) R. W. Taft, Jr., J. Chem. Phys., 26, 93 (1957).

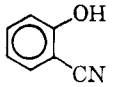(38) I. D. Kuntz, Jr., P. von R. Schleyer and A. Allerhand, ibid., 35, 1533 (1961).

TABLE IV
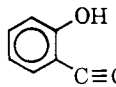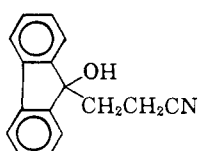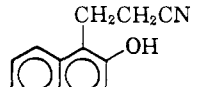
EFFECT OF THE ENVIRONMENT ON THE OH STRETCHING FREQUENCIES OF PHENOL–NITRILE COMPLEXES

| | | $\nu_{OH}$ Phenol–nitrile, cm.$^{-1}$ | |
| Nitrile | Inf. dil.[a] | 0.4 $M$ nitrile in CCl$_4$ | Pure liq. nitrile |
|---|---|---|---|
| Cyclohexyl cyanide | 3449 | 3437 | 3406 |
| *tert*-Butyl cyanide | 3449 | 3442 | 3419 |
| Butyronitrile | .. | 3444 | 3408 (3404)[b] |
| Propionitrile | .. | 3446 | 3402[b] |
| Acetonitrile | 3461 (3456)[b] | 3452 | 3405 (3396)[b] |
| Benzyl cyanide | .. | 3453 | 3412 |
| 3-Chloropropionitrile | .. | 3463 | 3418 |
| 3-Butenenitrile | .. | 3456 | 3414[b] |
| Acrylonitrile | .. | 3468 | 3425[b] |
| Chloroacetonitrile | .. | 3494 | 3451 |

[a] Value obtained by extrapolating to infinite dilution of nitrile in CCl$_4$. [b] Ref. 10.

between the proton-donating and proton-accepting groups is increased, the spectral shift, $\Delta\nu$, becomes larger but the percentage of molecules participating in intramolecular hydrogen bonding is decreased due to unfavorable enthalpy and entropy effects operating against ring formation.[22,39] In the case of diols HO–(CH$_2$)$_n$–OH, the bonded hydroxyl band becomes less and less intense as $n$ increases and finally disappears when $n = 6$.[39,40] In hydroxyacetylenes HO·—(CH$_2$)$_n$—C≡CH, where the energy of the intramolecular hydrogen bond is less, the bonded OH peak already is very weak when $n = 3$ and disappears when $n = 4$.[41] In hydroxynitriles HO–(CH$_2$)$_n$–CN, hydrogen bonding to the triple bond $\pi$-electron is even weaker than in acetylenes due to unfavorable polarization; no intramolecular hydrogen bonding can be detected even when $n = 3$. Bonding to the lone pair of electrons on nitrogen does not occur because of adverse geometry.

TABLE V

THE OH STRETCHING FREQUENCIES OF HYDROXYNITRILES AND THEIR ACETYLENIC ANALOGS IN VERY DILUTE CCl$_4$ SOLUTION[a,b]

| Compound | $\nu_{OH}$ "free" | $\nu_{OH}$ bonded | $\Delta\nu$ | Compound | $\nu_{OH}$ "free" | $\nu_{OH}$ bonded | $\Delta\nu$ |
|---|---|---|---|---|---|---|---|
| HOCH(CH$_3$)CN | None | 3607[c] | .. | HO—CH$_2$—C≡CH | None | 3620[d] | .. |
| (ortho-hydroxyphenyl)–CN | 3597w (3600w)[e] | 3559 (3559)[e] | 38 (41)[e] | (ortho-hydroxyphenyl)–C≡CH | 3623[f] | 3509[f] | 114 |
| HO(CH$_2$)$_2$CN[g] | 3632 | 3617sh | 15 | HO(CH$_2$)$_2$C≡CH | 3640[d] | 3598[d] | 42 |
| HO(CH$_2$)$_3$CN | 3640 | None | .. | HO(CH$_2$)$_3$C≡CH | 3638[d] | 3588w[d] | 50 |
| HO(CH$_2$)$_4$CN | 3639 | None | .. | | | | |
| (dicyclic)–OH, –CH$_2$CH$_2$CN | 3601[h] | | | | | | |
| (naphthyl)–CH$_2$CH$_2$CN, –OH | 3609[i] | None | .. | | | | |

[a] All values are in cm.$^{-1}$. The concentrations of hydroxynitriles were 0.01 mole/l. and lower to avoid intermolecular association; 10- and 20-mm. cells of a quartz tranparent in the near-infrared were used. [b] Abbreviations: sh = shoulder, w = weak. [c] Reported[19] 3604 cm.$^{-1}$. [d] Ref. 41. [e] Ref. 19. [f] Ref. 21; these values are probably accurate to within ±20 cm.$^{-1}$. [g] Reported[19] OH bands: 3625 and 3610 cm.$^{-1}$; $\Delta\nu = 15$ cm.$^{-1}$. [h] Very sharp band; intramolecular hydrogen bonding to an aromatic ring presumably occurs. 9-Methyl-9-fluorenol shows a very sharp band at 3602 cm.$^{-1}$. [i] Compare with $\nu_{OH}$ of phenol at 3611 cm.$^{-1}$.

cyclohexyl = $-0.15$) at different concentrations (Table IV).[11]

**Intramolecular Hydrogen Bonding.**—The OH stretching frequencies of hydroxynitriles are listed in Table V. If the hydroxyl group is in an alpha or beta position to the nitrile, weak intramolecular hydrogen bonding occurs. The small spectral shifts indicate that the bonding is not to the nitrogen atom but to the $\pi$-electrons of the C≡N bond (compare the acetylene data, Table V). If the hydrogen is in the $\gamma$-position with respect to the cyano group or further removed, intramolecular hydrogen bonding of neither type can be detected. In a molecule HO–(CH$_2$)$_n$–B, as the number of methylene groups and hence the distance

The O—H...N≡C hydrogen bond would have to be linear or nearly so; it is difficult to conceive of a simple organic molecule in which this interaction would occur. If $n$ is very large, such bonding would be possible in principle, but very improbable in practice due to the adverse thermodynamics of large ring formation.

(39) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).
(40) P. von R. Schleyer and W. Baitinger, Jr., unpublished results.
(41) P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).