the infrared exhibited a band with a maximum at 745 cm.$^{-1}$ and a shoulder at about 726 cm.$^{-1}$ which presumably encompasses the two bending motions. The N–Ga frequency is estimated to fall in the range 300–450 cm.$^{-1}$. A sharp and moderately intense line at 370 cm.$^{-1}$ in the Raman spectrum of the deuteriated compound may possibly be due to this motion. Unfortunately, halation from the exciting line was too intense to permit satisfactory observation of this region in the spectrum of the hydrogen compound.

It is of interest to note that the Ga–H stretching frequencies observed in the present work clearly fall at higher values than those given in the literature for the Al–H stretching motions in the AlH_3 complex with trimethylamine.[6] The positions of the latter frequencies have not been determined precisely since the bands in the infrared spectra of solutions are rather broad with maxima which appear appreciably solvent sensitive. However, the range reported, from about 1725 to 1800 cm.$^{-1}$, is sufficiently below the Ga–H frequencies that there is no doubt as to their relative position. The significance of this observation and the implied greater strength of the Ga–H bond is not immediately clear. It does appear consistent with the greater sensitivity toward water and the more reactive nature reported for the alane complex and provides another example of the alternation of physical and chemical properties observed in the main groups III through VII.[7]

(6) R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960); G. Schomburg and E. G. Hoffmann, *ibid.*, **61**, 1110 (1957).

(7) R. T. Sanderson, *J. Am. Chem. Soc.*, **74**, 4792 (1952); A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.* **5**, 269 (1958); A. L. Allred and A. L. Hensley, Jr., *ibid.*, **17**, 43 (1961).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
DUWARD F. SHRIVER
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
ROBERT L. AMSTER
ROBERT C. TAYLOR

RECEIVED JANUARY 15, 1962

STRONG HYDROGEN BONDS TO CARBON IN ISOCYANIDES[1]

Sir:

In continuation of studies on the scope of hydrogen bonding,[2] we have considered the possibility of observing strong hydrogen bonds to carbon. Interaction of proton donors with carbon π-electron systems is now well established,[2,3] but these hydrogen bonds invariably are relatively weak. We wish to report that isocyanides can function as strong proton acceptor groups in hydrogen bonding. The site for such bonding appears most certainly to be to carbon and not to nitrogen.

Table I lists spectral shifts in the 3 μ region of the infrared caused by hydrogen bonding between alcoholic proton donors and isocyanides. Data for similar cyanides taken from a much more extensive study[4] are included for comparison; the spectral shifts are significantly larger for isocyanides than for cyanides. With carbon π-electron systems, the interactions are much weaker. Spectral shifts of phenol in the presence of olefins and acetylenes range up to about 100 cm.$^{-1}$.[3] The Hammett equation[5] is moderately successful in correlating the observed spectral shifts with both the aromatic isocyanides and the aromatic cyanides[4]; the Taft equation[6] correlates the results with the aliphatic compounds.[4,7] The high $\Delta\nu$ for *p*-methoxyphenyl cyanide indicates considerable resonance interaction between the two functional groups, but no such resonance interaction is detectable in *p*-methoxyphenyl isocyanide. Dipole moment studies have given the same conclusion.[8]

TABLE I

HYDROGEN BONDING OF PHENOL AND METHANOL TO ISOCYANIDES AND CYANIDES[a]

Substituent	$\Delta\nu$ Phenol, cm.$^{-1b}$		$\Delta\nu$ Methanol, cm.$^{-1c}$	
	Isocyanides	Cyanides	Isocyanides	Cyanides
Cyclohexyl	250	174	...	85
tert-Butyl	245	169	139	85.5
Isopropyl	241	166	136	83
n-Butyl	238	165.5	137	85.5
Benzyl	230	158	128	78
Methyl	228	159	129	78
p-Methoxyphenyl	219	174.5	121	...
Phenyl	203	153.5	...	73
p-Chlorophenyl	191	144	...	67

[a] Solvent, CCl_4; approximate concentrations: isocyanide or cyanide 0.4 *M*, phenol 0.005 *M*, methanol 0.01 to 0.02 *M*; cell thicknesses, 1 cm.; instrument, Perkin–Elmer Model 21 Spectrophotometer with LiF prism. At the concentrations used, proton donor dimer peaks were absent. [b] Spectral shifts measured from the free peak of phenol at 3611 cm.$^{-1}$. [c] Spectral shifts measured from the free peak of methanol at 3643 cm.$^{-1}$. The reproducibility of these measurements is within ±2 cm.$^{-1}$ provided the same concentrations were employed.[4] After standing, the solutions gave identical spectroscopic results, indicating stability under the conditions of measurement.

Abundant physical evidence on the molecular structure of isocyanides is available. Analysis of infrared and Raman spectra,[9] parachor measurements,[10] dipole moment studies,[8,10] microwave[11] and nuclear magnetic resonance[12] spectroscopic results and electron diffraction studies[13] all indicate that isocyanides are best represented by the polar

---

(1) Dr. L. L. Ferstandig of the California Research Corporation has discovered this phenomenon independently. We wish to express our appreciation to Dr. Ferstandig for permitting delay in the appearance of his paper to allow simultaneous publication of our observations.

(2) P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); P. von R. Schleyer and R. West, *ibid.*, **81**, 3164 (1959).

(3) R. West, *ibid.*, **81**, 1614 (1959), and refs. cited therein.

(4) Observations to be published in full subsequently.

(5) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

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

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

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 249, 283f, 317f, 321f.

(9) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1959, pp. 332–334; H. W. Thompson and R. L. Williams, *Trans. Far. Soc.*, **48**, 502 (1952); R. L. Williams, *J. Chem. Phys.*, **25**, 656 (1956); M. G. K. Pillai and F. F. Cleveland, *J. Molec. Spect.*, **5**, 212 (1960).

(10) N. V. Sidgwick, *Chem. Revs.*, **9**, 77 (1931).

(11) M. Dessler, H. Ring, R. Trambarulo and W. Gordy, *Phys. Rev.*, **79**, 54 (1950); R. Trambarulo and W. Gordy, *ibid.*, **79**, 224 (1950); B. Bak, L. Hansen-Nygaard and J. Rastrup-Andersen, *J. Molec. Spect.*, **2**, 54 (1958).

(12) I. D. Kuntz, Jr., P. von R. Schleyer and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961).

(13) W. Gordy and L. Pauling *J. Am. Chem. Soc.*, **64**, 2952 (1942).

structure, $R{-}^{+}N{\equiv}C^{-}$. Isocyanides are linear; the NC triple bond has almost the same length in isocyanides as in cyanides and both groups have almost identical infrared stretching vibrational frequencies; the electron density at the nitrogen atom in isocyanides is axially symmetrical.[12]

The electropositive nitrogen atom in isocyanides would not function as a proton acceptor while the π-electrons would be comparatively weak sites.[3,14] The lone pair of electrons on carbon in an sp orbital is the most likely hydrogen bonding site. Inorganic complexes of isocyanides are well established.[15]

This work was generously supported by a grant from the National Science Foundation.

---

[14] *Cf.* the intramolecular hydrogen bonding in *o*-cyanophenol, in which molecular geometry restricts the type of bonding possible (V. Prey and H. Berbalk, *Monat. Chem.*, **82**, 990 (1951)). We have not yet been successful in attempts to prepare either *o*-isocyanophenol or 2-isocyanoethanol.

[15] L. Malatesta, *Prog. Inorg. Chem.*, **1**, 283 (1959); D. Seyferth and N. Kahlen, *J. Am. Chem. Soc.*, **82**, 1080 (1960); F. A. Cotton and F. Zingales, *ibid.*, **83**, 351 (1961).

[16] Merck Foundation Fellow, 1960–1961; Esso Foundation Fellow, 1961–1962.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
PAUL VON R. SCHLEYER
ADAM ALLERHAND[16]

RECEIVED DECEMBER 14, 1961

TRANS-CIS-TRANS-PHOTOTROPISM OF 2-STYRYLPYRIDINE METHIODIDE

Sir:

Earlier publications[1,2] described the photodimerization and photoisomerization of *trans*-2-styrylpyridine, its hydrochloride, and methiodide. Irradiation of solutions of *trans*-2-styrylpyridine methiodide in water by sunlight produced mixtures of the corresponding dimer and *cis*-2-styrylpyridine methiodide. Sequential irradiation with short exposures of ultraviolet light of *trans*-2-styrylpyridine methiodide solutions has revealed that conversion of the *trans* form to the *cis* is very fast compared to the rate of dimerization.

Irradiation of a solution containing 2.5×10^{-5} mole per liter of *trans*-2-styrylpyridine methiodide in water was carried out in 1-cm. quartz cells at a distance of 15 cm. from a Hanovia 550-watt water-cooled medium-pressure mercury source. Exposure of the solution of *trans*-2-styrylpyridine methiodide for 25 sec., with a Kodak Wratten Filter 18A (pass-band 330–400 mμ) inserted between the source and the sample, produced a shift of wavelength of $\lambda_{\max}$ 334 mμ (ϵ 27,600) to $\lambda_{\max}$ 319 mμ (ϵ 10,800). Two subsequent exposures using the Wratten Filter 18A produced no further change. The sample was then exposed for 5 sec. without the insertion of the Wratten Filter 18A. A shift of wavelength of $\lambda_{\max}$ to 325 mμ (ϵ 13,600) occurred. This process of alternating between exposures with and without the Wratten Filter 18A was repeated eight times. The wave length of $\lambda_{\max}$ alternated between 325 and 319 mμ, while the extinction coefficients simultaneously alternated between 13,600 and 10,800. In an analogous manner, a sample of *cis*-2-styrylpyridine methiodide, $\lambda_{\max}$ 317 mμ (ϵ 10,000), prepared by the synthetic route described earlier,[2] was irradiated in water solution. Direct exposure of the solution of the *cis* form to the Hanovia 550-watt source caused a shift of the wavelength of $\lambda_{\max}$ from 317 mμ (ϵ 10,000) to 325 mμ (ϵ 13,600). A subsequent 25-sec. exposure, using the Wratten Filter 18A, of this solution caused the wave length of $\lambda_{\max}$ to shift from 325 mμ (ϵ 13,600) to 319 mμ (ϵ 10,800). The sample was then exposed for 5 sec. directly to the Hanovia source, causing a shift of wavelength of $\lambda_{\max}$ from 319 mμ (ϵ 10,800) to 325 mμ (ϵ 13,600). This solution was then cycled ten times in the manner just described for the equilibrium mixture solution obtained from *trans*-2-styrylpyridine methiodide.

Further experiments were carried out using a Bausch and Lomb grating monochromator in conjunction with a General Electric BH-6 high-pressure mercury arc. The output of light from this system was lower, requiring longer exposure times. Irradiation of a solution of *trans*-2-styrylpyridine methiodide by light of 365 mμ wavelength from the monochromator produced a shift of the *trans* form ($\lambda_{\max}$ 334 mμ, ϵ 27,600) to *cis* ($\lambda_{\max}$ 319 mμ, ϵ 10,800). Exposure of this solution of the *cis* form to light of wavelength 313 mμ from the monochromator caused a shift of the wavelength of $\lambda_{\max}$ from 319 to 325 mμ.

Thus, when water solutions of either *cis*- or *trans*-2-styrylpyridine methiodide are irradiated, a new equilibrium is established involving the two isomers. The position of the equilibrium depends on the wavelength distribution of the light used. The study of this phototropic phenomenon is being extended to include other styrylpyridine derivatives. A future publication will deal more fully with the subject.

RESEARCH LABORATORIES
EASTMAN KODAK COMPANY
ROCHESTER 4, NEW YORK
J. L. R. WILLIAMS

RECEIVED FEBRUARY 22, 1962

---

[1] J. L. R. Williams, *J. Org. Chem.*, **25**, 1839 (1960).

[2] J. L. R. Williams, *ibid.*, **26**, 4893 (1961).

CARBON AS A HYDROGEN BONDING BASE: A HYDROGEN BOND BETWEEN TWO CARBON NUCLEI

Sir:

Among the surprising species which form weak hydrogen bonds are olefins, acetylenes, aromatic compounds, cyclopropyl systems,[1] and even the metal in metallocenes.[2] However, there are no reports of a substituted carbon behaving at the base in a hydrogen bond.[3] I wish to report such a species which forms strong hydrogen bonds, and to report a bond between this species and a hydrogen already attached to another carbon.

Benzyl isocyanide forms a strong hydrogen bond with *n*-amyl alcohol in carbon tetrachloride solution.[4] The infrared spectrum of this solution

---

[1] P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

[2] D. S. Trifan and R. Bacskai, *ibid.*, **82**, 5010 (1960).

[3] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco, California, 1960.

[4] The measurements were made with a Perkin-Elmer Model 21 Spectrophotometer with LiF optics using 0.1 mm. and 1.0 mm. cells. The concentrations in volume per cent. varied from 0.5 to 10 for the hydrogen donor and from 20 to 90 for the benzyl isocyanide, the remainder being carbon tetrachloride.