structure, $R\text{—}^{+}N{\equiv}C^{-}$. 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.

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(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.

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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 λ_{max} 334 mμ (ϵ 27,600) to λ_{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 λ_{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 λ_{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, λ_{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 λ_{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 λ_{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 λ_{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 (λ_{max} 334 mμ, ϵ 27,600) to *cis* (λ_{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 λ_{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.

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RECEIVED FEBRUARY 22, 1962

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(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

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(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.