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.

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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.

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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.

shows the ν_s for free OH at 3630 cm.$^{-1}$ and a new band at 3483 cm.$^{-1}$ but no band at 3330 cm.$^{-1}$. This is in contrast with a solution of alcohol alone in carbon tetrachloride: free OH band at 3634 cm.$^{-1}$ and alcohol–alcohol bonded OH band at 3330 cm.$^{-1}$. The 3483 cm.$^{-1}$ band is not present in the absence of benzyl isocyanide nor is it present in the benzyl isocyanide spectrum in the absence of alcohol. The intensity of this new band grows with increasing benzyl isocyanide concentration, at constant alcohol concentration, at the expense of the free OH band. Furthermore, in dilute solutions of alcohol in benzyl isocyanide as solvent, the intensity of the 3483 cm.$^{-1}$ band is proportional to alcohol concentration and the free OH band is very small if not absent. The position of the new band and its direct relationship to isocyanide and alcohol concentrations constitute proof of a hydrogen bond between these two molecules.

The hydrogen bond is, almost without a doubt, to the carbon in the isocyanide group. The most compelling evidence for this is that this carbon is the most negative site in the molecule. According to Pauling, the canonical form $CH_3\overset{+}{N}\equiv\overset{-}{C}:$ contributes 74% to the resonance hybrid of methyl isocyanide.[5] In benzyl isocyanide, this sort of polarized form should contribute even more to the hybrid. Therefore, the electron seeking hydrogen should bond to carbon rather than electron deficient nitrogen. Other possible sites for the hydrogen bond are with the π electrons in the ring or in the N to C bond. The ring π electrons, which form only weak hydrogen bonds at best,[1] would be no better and perhaps even poorer as a site for hydrogen bonds in benzyl isocyanide than in alkylaromatic compounds. Furthermore, the shift in ν_s for hydrogen bonds to aromatic systems is never as large[1] as shown in this case. The π electrons of the N to C bond probably are even weaker hydrogen bonding sites than either the aromatic π electrons or acetylene π electrons which are also very weak.[1]

The strongly basic carbon in isocyanides will form a *carbon–hydrogen–carbon bond* with certain compounds. Phenylacetylene has been reported to be a hydrogen donor with several conventional bases.[6] In this work, infrared evidence for a hydrogen bond between benzyl isocyanide and phenylacetylene was found to be similar to that for phenylacetylene and benzonitrile, a conventional base. The acetylenic C–H stretching band shifts about 30 cm.$^{-1}$ to lower wave numbers in benzyl isocyanides as solvent. While it is a small shift, it is almost identical with the shift in benzonitrile as base. More impressive evidence for the acetylenic hydrogen bond is found in dilute solutions of the acetylene and benzyl isocyanide in carbon tetrachloride. Under these conditions, the original C–H band at 3314 cm.$^{-1}$ is present as well as a shoulder about 30 cm.$^{-1}$ lower. This phenomenon is best explained by a mixture of bonded C–H and free C–H. A single but shifted band would be expected by a mere change in the dielectric constant of the medium.

Thus, isocyanides form hydrogen bonds with typical hydrogen donors. These bonds are strong; it appears that the benzyl isocyanide–alcohol bond is even stronger than the benzonitrile–alcohol bond. Details of the above data and a comparison of the strength of these bonds and other hydrogen bonds will be published soon.

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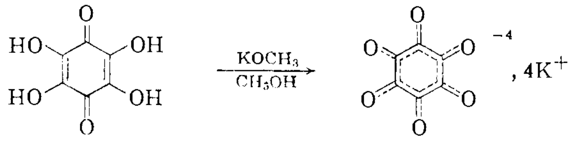
RECEIVED NOVEMBER 9, 1961

SYMMETRICAL RESONANCE STABILIZED ANIONS, $C_nO_n^{-m}$. II. $K_4C_6O_6$ AND EVIDENCE FOR $C_6O_6^{-3}$

Sir:

In an earlier communication[1] it was pointed out that anions of the type $C_nO_n^{-2}$ represent a previously unrecognized series of symmetrical aromatic anions. It now appears that this series can be generalized to include anions of other charge types. In particular, we now wish to report isolation of the tetrapotassium salt of the anion $C_6O_6^{-4}$, and evidence for the possible existence of the radical-ion $C_6O_6^{-3}$.

The anion $C_6O_6^{-4}$ is obtained directly from tetrahydroxyquinone (THQ) by removal of four protons:



However, special technique is necessary to avoid the precipitation of the insoluble dipotassium salt of THQ, and scrupulous care must be taken to prevent oxidation of the anion. All of the operations must be carried out in an inert atmosphere. In a typical run a solution of 30 mg. of THQ in 10 ml. of dry oxygen-free methanol was slowly injected into a solution of 5 g. of potassium metal in similarly pure methanol, at room temperature. $K_4C_6O_6$ precipitated immediately as a black powder. The methanol solution was drawn off and replaced successively with deoxygenated samples of tetrahydrofuran and ether. After removal of most of the ether, the product was dried *in vacuo*. *Anal.* Calcd. for $K_4C_6O_6$: K, 48.2; C, 22.30; H, nil. Found: K, 47.0; C, 22.82; H, nil.

The infrared spectrum of $K_4C_6O_6$ contains five bands in the 350–4000 cm.$^{-1}$ region. The anion must therefore have a highly symmetric structure, since models with low symmetry would be expected to give many more infrared bands. However, the totally symmetric planar structure (D_{6h}) should give rise to only three infrared-active fundamentals in this region. The observed spectrum is compatible with a structure in which the C–C and C–O distances are all equal with the ring slightly puckered into a chair form (D_{3d} symmetry).[2] In the visible region, solid $K_4C_6O_6$

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(5) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, Third Edition, 1960, p. 270.

(6) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961).

(1) R. West, H.-Y. Niu, D. L. Powell and M. V. Evans, *J. Am. Chem. Soc.*, **82**, 6204 (1960), which should be regarded as paper I of this series.

(2) Calculations indicate that the anion could adopt this non-planar puckered form with only a small loss in aromatic resonance energy.[3]