The Electronic Character of Vinyl Isocyanide[1a,b]

Donald S. Matteson[1c] **and Rodney A. Bailey**[1d]

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163.

Received January 10, 1968

Abstract: The synthesis of vinyl isocyanide provides a new, relatively small molecule useful for testing theories of bonding and conjugation. N-Formylethanolamine treated with benzenesulfonyl chloride in pyridine yielded 2-isocyanoethyl benzenesulfonate, which was converted to vinyl isocyanide by alcoholic potassium hydroxide. The 60-MHz nmr spectrum of vinyl isocyanide has been fully interpreted, and the vinyl protons show considerably more diamagnetic shielding than those in acrylonitrile, in accord with predicted conjugative effects and in opposition to inductive effects. Vinyl isocyanide undergoes 1,3-dipolar addition of diphenyldiazomethane to the vinyl group but at only $^1/_{150}$ the rate that acrylonitrile does at 25°. Other reactions of vinyl isocyanide include the formation of complexes with transition metals and the condensation with benzaldehyde and piperidine to yield N-vinyl-α-(1-piperidino)phenylacetamide.

We undertook the synthesis of vinyl isocyanide ($CH_2{=}CHN\underset{\rightarrow}{=}C$, **1**) because its close structural relationship to acrylonitrile ($CH_2{=}CHC{\equiv}N$, **2**) is of theoretical interest. These isoelectronic isomers differ only in the location of one nuclear charge, but grossly different π-electron distributions in the vinyl groups are expected as a result of conjugation. The cyano group, but not the isocyano group, withdraws π-electron density from the terminal vinyl carbon.

However, if inductive effects dominate the electron distribution, the vinyl group in vinyl isocyanide will be the more electron deficient. This outcome seems implicitly predicted by the theoretical viewpoint expressed by Dewar[2] and refined by Dewar and Gleicher,[3] who have pointed out that the ground-state properties of classical conjugated hydrocarbons are additive functions of bond properties, and therefore there is no evidence that "resonance" in the chemical sense is important in such systems. This view has been challenged on the basis of recent advanced quantum mechanical calculations.[4,5] It is difficult to find a system in which Dewar's views actually predict different experimental results from conventional theory. Most types of experiments do not measure ground-state properties, and changes in hybridization or other nonconjugative effects can be invoked to explain those which do.[2] However, vinyl isocyanide and acrylonitrile use exactly the same set of bonding orbitals. We therefore hoped that some useful comparisons could be made without intrusion of the usual ambiguities.

Results

Synthesis. The synthesis of vinyl isocyanide from ethanolamine is based on the general isonitrile synthesis of Hertler and Corey[6] and is straightforward and convenient. Treatment of N-formylethanolamine in pyridine with benzenesulfonyl chloride yielded 2-isocyanoethyl benzenesulfonate (**3**), which eliminated benzenesulfonic acid on treatment with ethanolic potassium hydroxide to form vinyl isocyanide (**1**).

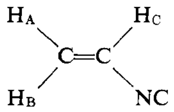
$$HOCH_2CH_2NH_2 \xrightarrow{EtOCHO} HOCH_2CH_2NHCHO \xrightarrow[\text{pyridine}]{C_6H_5SO_2Cl}$$

$$\underset{\mathbf{3}}{C_6H_5SO_2OCH_2CH_2NC} \xrightarrow{KOH} \underset{\mathbf{1}}{CH_2{=}CHNC}$$

The oily benzenesulfonate **3** can be crystallized from ether below room temperature, but becomes unstable when freed of pyridine, as if traces of benzenesulfonic acid can be eliminated and catalyze the polymerization of the isonitrile. An attempt to distil all the pyridine from a 300-g sample of the benzenesulfonate **3** by warming under vacuum ended in a moderately forceful detonation to a black cloud of sticky tar. The toluenesulfonate ester analogous to **3** was a reasonably stable solid and provided a fully characterized isocyanide of this class, though it was less convenient as a synthetic intermediate.

The gross physical properties of vinyl isocyanide resemble those of ethyl isocyanide. The atrocious odor is followed by a bitter aftertaste. The compound can be stored several months at −15° with little loss, though it turns dark brown. Ground-glass surfaces catalyze polymerization to a brown amorphous solid so rapidly that syringes sometimes freeze before the liquid can be transferred.

Nmr Spectrum. The 60-MHz proton nmr spectrum of vinyl isocyanide is shown in Figure 1. The sets of triplets resulting from ^{14}N splitting are characteristic of isonitriles.[7] The proton *trans* to the nitrogen has a coupling constant, J_{NA}, of about 6.1 Hz, the *cis* proton shows $J_{NB} \cong 3.1$, and the *gem* proton has $J_{NC} \cong 2.3$ Hz. An analysis of the proton ABC pattern[8] is summarized in Table I.



---

[1] (a) Preliminary communication: D. S. Matteson and R. A. Bailey, *Chem. Ind.* (London), 191 (1967). (b) Supported in part by National Science Foundation Grants GP-2953 and GP-6069. (c) Alfred P. Sloan Foundation Fellow. (d) National Foundation Science Cooperative Fellow, 1965–1967. Abstracted in part from the Ph.D. thesis of R. A. B.

[2] M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

[3] M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 692 (1965).

[4] J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967).

[5] M. D. Newton and W. N. Lipscomb, *ibid.*, **89**, 4261 (1967).

[6] W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **23**, 2221 (1958).

[7] J. Casanova, N. D. Werner, and R. E. Schuster, *ibid.*, **31**, 3473 (1966).

[8] J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 61–88.

Table I. Observed and Calculated Frequencies and Intensities of the Proton ABC Pattern of Vinyl Isocyanide

ν_{obsd}[a]	Intensity,[b] obsd	ν_{calcd}[c]	Transition[c]	Intensity,[c] calcd	ν_{calcd}[d]	Transition[d]	Intensity,[d] calcd
315.8	1.4	315.6	8 → 5	0.84	315.7	6 → 2	0.49
316.3		316.3	6 → 2	0.59	316.3	8 → 5	0.90
323.6	2.7	323.5	7 → 3	1.14	323.5	4 → 1	1.18
324.2		324.2	4 → 1	1.29	324.2	7 → 3	1.19
324.7?	Weak	324.5	8 → 6	0.11	324.7	5 → 2	0.83
325.2	0.9	325.1	5 → 2	0.74	325.3	8 → 6	0.06
339.8	3.0	339.6	7 → 4	1.91	339.7	3 → 1	1.52
340.3		340.3	3 → 1	1.38	340.3	7 → 4	1.81
344.7	0.2	344.9	6 → 3	0.15	344.8	6 → 3	0.21
345.8	1.9	345.8	8 → 7	2.05	345.8	8 → 7	2.05
353.7	1.1	353.7	5 → 3	1.10	353.8	5 → 3	1.05
361.0	0.4	360.9	6 → 4	0.37	360.8	6 → 4	0.36
368.8	0.4	368.9	2 → 1	0.33	368.8	2 → 1	0.33

[a] Center line of ^{14}N triplet, hertz downfield from tetramethylsilane. [b] Given as sum where doublet is not fully resolved. Normalized to total 12 to match calculated probabilities. [c] Calculated with $J_{AB} = -0.5$, $J_{BC} = 15.6$, $J_{AC} = 8.6$, $\nu_A = 320.6$, $\nu_B = 335.0$, and $\nu_C = 354.0$ Hz. [d] Calculated with $J_{AB} = -1.8$, $J_{BC} = 15.8$, $J_{AC} = 8.4$, $\nu_A = 320.8$, $\nu_B = 335.1$, $\nu_C = 353.9$ Hz.

The splitting constants which yield the correct calculated spectrum are $J_{AB} = -0.5$, $J_{BC} = 15.6$, and $J_{AC} = 8.6$ Hz. These are typical values for vinyl groups[9,10] and permit unequivocal assignments of the spectral lines to the protons indicated. The chemical shift of proton A is τ 4.66, of B is τ 4.42, and of C is τ 4.10. The evidence points to the set of parameters with J_{AB} near -0.5 and not that with J_{AB} at -1.8 Hz for the following reasons. The triplet centered at 325.2 Hz is observed and that calculated to be near 324.7 is missing, which agrees with the intensity pattern only if J_{AB} is -0.5 Hz. In addition, the slightly resolved pairs of lines due to the A and B protons are more closely spaced at the outer side of each ^{14}N triplet, that is, increasing $\Delta\nu/J$. If J_{AB} is -0.5 Hz, these lines must exchange relative positions when $\Delta\nu$ is increased enough, but should merely separate with increasing $\Delta\nu$ if J_{AB} were -1.8 Hz. The relative intensities within the slightly resolved pairs cannot be determined, and sweeping the spectrum in the opposite direction reverses their apparent ratios.

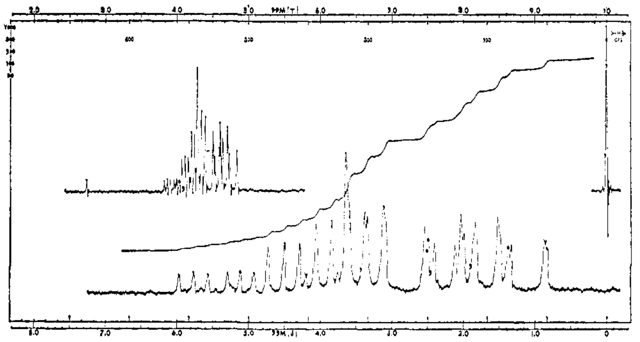
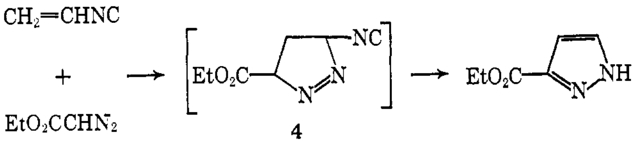


Figure 1. The 60-MHz nmr spectrum of vinyl isocyanide (~10%) in deuteriochloroform (with 1% tetramethylsilane). Upper trace: 500-Hz sweep width. Lower trace: 300-Hz offset, 100-Hz sweep width.

Reactions. We wished to find a typical vinyl group reaction that could be carried out with both vinyl isocyanide and acrylonitrile. Such reactions are rare. The nucleophilic character of the isocyanide group is too great to permit any of the usual electrophilic additions to the double bond. Anionic additions, characteristic of acrylonitrile, are not expected with vinyl isocyanide. Indeed, the synthesis of vinyl isocyanide in the presence of alcoholic potassium hydroxide indicates that it is much less susceptible to base attack than acrylonitrile, which is destroyed under these conditions.[11]

Radical additions to the vinyl groups would provide a comparison of the two compounds, but these are frustrated by the radical-inhibiting character of the isonitrile group. About 5 mol % of vinyl or *t*-butyl isocyanide in acrylonitrile prevents formation of polyacrylonitrile in *t*-butyl alcohol with azobisisobutyronitrile as the initiator at 80°. Either vinyl or *t*-butyl isocyanide inhibits the light-initiated addition of bromotrichloromethane to 1-hexene. Since darkening of the vinyl isocyanide occurs on irradiation, the result is ambiguous, but the *t*-butyl compound inhibits the reaction without darkening.

Vinyl isocyanide does react with diazo compounds in a manner characteristic of vinyl compounds which have a moderately electron-withdrawing substituent. Allowing equimolar quantities of vinyl isocyanide and ethyl diazoacetate to stand several days at 20–25° yielded about 20% of crystalline 3(5)-carbethoxypyrazole, verified by infrared comparison with an authentic sample.[12] The initially formed isocyanocarbethoxypyrazoline (**4**) must tautomerize and eliminate hydrogen cyanide.



4

Diphenyldiazomethane gave a rapid enough rate of reaction with vinyl isocyanide to permit kinetic measurements, though we were unable to isolate the postulated product, 3,3-diphenyl-5-isocyano-1-pyrazoline (**5**), or any derivative of it. Following the reaction by nmr in deuteriochloroform indicated the disappearance of the vinyl isocyanide protons in the τ 4–5 region and the ap-

---

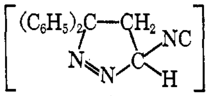
(9) "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., New York, N. Y., 1967: (a) J. A. Elvidge, pp 29–33, 187; (b) E. O. Bishop, pp 74–76; (c) R. J. Abraham, pp 136–140.

(10) T. Schaefer, *Can. J. Chem.*, **49**, 1 (1962).

(11) H. A. Bruson, *Org. Reactions*, **5**, 89 (1949).

(12) D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

pearance of four peaks at τ 6.55–6.80 and a multiplet at τ 8.0–9.0, integral ratio 1:2, a reasonable ABX pattern for the $-CHCH_2-$ group of the postulated product **5**. An attempt to prepare the adduct without the use of any solvent ended in an explosion after the mixture had stood about 1–2 hr.



5

The 530-mμ absorption of diphenyldiazomethane was used to follow the rate of reaction with excess vinyl isocyanide. The accuracy of the measurements was impaired by the tendency of the vinyl isocyanide to discolor on standing. A freshly distilled sample was used for each kinetic run, vinyl isocyanide was included in the reference solution, and the rates were based on the first 50–75% of the reaction to minimize this problem. The discoloration was more serious at 38° than at 20°, as shown by a greater scatter in the data. The observed rate constants and standard deviations are summarized in Table II.

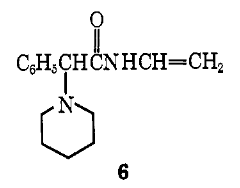
Table II. Second-Order Rate Constants for the Reaction of Diphenyldiazomethane with Vinyl Isocyanide

Solvent	Temp, °C	10^5k, l./mol sec
Ethanol (abs)	20.2	1.37 ± 0.02
Ethanol	30.2	3.08 ± 0.06
Ethanol	38.1	4.60 ± 0.16
Acetonitrile	30.2	1.74 ± 0.08
o-Xylene	30.2	2.16 ± 0.13

We also measured the rate constants for reaction of diphenyldiazomethane with acrylonitrile in absolute ethanol. The values found were 1.82×10^{-3} at 17.4°, 3.57×10^{-3} at 29.4°, and 6.55×10^{-3} at 40.0°. Interpolating to 25°, the rate constant for acrylonitrile is about 150 times that for vinyl isocyanide.

From a least-squares treatment of Arrhenius plots, the reaction of diphenyldiazomethane with vinyl isocyanide in ethanol has $\Delta H^* = 11.4$ kcal/mol and $\Delta S^* = -41$ eu. With acrylonitrile, ΔH^* is 9.2 kcal/mol and ΔS^* is -39 eu.

We have also examined a few typical reactions of the isocyanide group, which behaves similarly in vinyl and aryl isocyanides. For example, vinyl isocyanide may serve as a useful source of N-vinylamides. Condensation with benzaldehyde and piperidinium acetate[13] yields N-vinyl-α-(1-piperidino)phenylacetamide (**6**). The structure is confirmed by the 60-MHz nmr spectrum (in deuteriochloroform). The piperidino protons appear as unresolved multiplets near τ 7.5 and 8.6, the benzyl proton as a singlet at τ 6.11, the phenyl protons as a peak at τ 2.73, and the amide proton as a 30-Hz-wide band at τ 1.1, each with the expected integral. The vinyl protons appear as an AB(X + X′) pattern with the X and X′ parts roughly equal in intensity. Restricted rotation of the amide nitrogen is the probable cause. The proton *trans* to the nitrogen, A, is centered at τ 5.59, the *cis* proton B is at τ 5.32, and the *gem* proton appears as two quartets, X at τ 3.16 and X′ at τ 2.97 (with one peak hidden by the phenyl absorption). The apparent coupling constants are $J_{AB} = 0$, $J_{AX} = J_{AX} = 8.5$ Hz, and $J_{BX} = J_{BX'} = 16$ Hz. The positions of the A and B protons have been verified by spin decoupling, and although it was not possible to decouple all the X and X′ lines at once, it was clear that all these lines are coupled to A and B.



6

The isocyanide group of vinyl isocyanide also complexes with transition metals such as cobalt in the usual manner.[14] With aqueous cobalt(II) nitrate and cobalt metal from borohydride reduction of cobalt(II), the yellow-brown complex penta(vinyl isocyanide)cobalt(I) nitrate, $(CH_2{=}CHNC)_5Co^+NO_3^-$ (**7**), is formed. Although it contains five vinyl groups, this cation shows no tendency to polymerize. It reacts rapidly with bromotrichloromethane at room temperature, evidently forming a cobalt(II) complex. The infrared bands of the isocyano group are shifted from the original 4.55–4.7 μ to a set at 4.34, 4.43, and 4.57 μ, and the nmr lines are broadened. However, no crystalline product could be isolated.

The 60-MHz nmr spectrum of the diamagnetic complex **7** in deuteriochloroform is a distorted ABX pattern. Simple inspection of the spectrum places the terminal *trans* proton A at τ 4.56, $J_{AX} = 8$ Hz, the *cis* proton B at τ 4.40, $J_{BX} = 15$ Hz, $J_{AB} = 0$, and the *gem* proton X at τ 3.69. If the chemical shift differences were as small as in vinyl isocyanide itself, τ_A would be lowered 0.01, τ_B lowered 0.04, and τ_X raised 0.05. The actual corrections needed must be somewhat smaller than these. In view of the 2–3 Hz line widths and the possibility of errors due to paramagnetic contaminants, a detailed analysis of the spectrum of this complex would not be justified.

We have also prepared the manganese(I) complex of vinyl isocyanide, to be reported in detail in a sequel to the preliminary communication.[15] The nmr spectrum of this complex (free from Mn(II)) shows the A and B protons at the same positions, ±2 Hz, as those of the cobalt(I) complex, and the X proton shifted downfield 3–5 Hz from that of the cobalt complex.

Attempts to prepare a chromium(0) complex[16] from vinyl isocyanide and chromous acetate yielded an unstable orange solid. The infrared spectrum was consistent with that expected for $(CH_2{=}CHNC)_6Cr$, but elemental analyses invariably indicated that the complex had undergone some oxidation. One nmr spectrum was obtained, but its appearance strongly suggests what we subsequently found to be shifts due to exchange with a paramagnetic species in the case of manganese complexes.[15]

---

[13] J. W. McFarland, *J. Org. Chem.*, **28**, 2179 (1963).

[14] L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

[15] D. S. Matteson and R. A. Bailey, *J. Am. Chem. Soc.*, **89**, 6389 (1967).

[16] L. Malatesta, A. Sacco, and S. Ghielmi, *Gazz. Chim. Ital.*, **82**, 516 (1962).

Discussion

Vinyl isocyanide is a small enough molecule to permit advanced quantum mechanical calculations[17] and precise structural measurements.[18,19] Our major reason for synthesizing it was its apparent utility for such purposes. In the following paragraphs, we present the conclusions which can be drawn from measurements and simple calculations of the types accessible to organic chemists.

All our experimental results agree qualitatively with conventional theories of π bonding and conjugation. We do not believe these results can be reconciled completely with Dewar's suggestion that conjugation may be "unimportant" in butadiene-like molecules.[2,3] However, we can go no farther than the conclusion that it is "not unimportant."

It turns out that the electron distribution is the only structural feature for which the theories give different predictions. Simple Hückel-type molecular orbital calculations[20] yield delocalization energies which favor acrylonitrile over vinyl isocyanide only by an insignificant 0.02β. The π-electron densities and bond orders for the conjugated p orbitals are shown in the molecular diagrams below.

$$\begin{array}{ccccccc} 1.02 & & 0.98 & & 1.20 & & 0.80 \\ C & — & C & — & N & — & C \\ & 0.89 & & 0.40 & & 0.91 & \end{array} \qquad \begin{array}{ccccccc} 0.89 & & 1.02 & & 0.80 & & 1.29 \\ C & — & C & — & C & — & N \\ & 0.87 & & 0.42 & & 0.90 & \end{array}$$

The parameters used were $\alpha_N = \alpha_C + 0.5\beta$, the terminal bond integrals both β, and the central bond integral 0.9β. Better parameters[20] would not change the qualitative result at the terminal vinyl carbon, and complete self-consistent field calculations[17] also indicate a lower electron density in acrylonitrile than in vinyl isocyanide at this atom. The resonance structures $^+CH_2CH{=}C{=}N^-$ for acrylonitrile and $^-CH_2CH{=}N^+{=}C$ for vinyl isocyanide suggest the same order of electron densities. In contrast, if conjugation is truly negligible, the terminal vinyl carbon of vinyl isocyanide must have a lower electron density than that of acrylonitrile, due to the inductive effect of the nitrogen atom.

The chemical shifts in the proton nmr spectra indicate that the electron distributions are strongly influenced by conjugation. For acrylonitrile in deuteriochloroform, the α proton is at τ 4.37, the β proton *cis* to the cyano group is at τ 3.81, and the *trans* proton is at τ 3.93 (each ± 0.03), estimated from inspection of our own 60-MHz spectra and the parameters found for the neat liquid by Castellano and Waugh.[21] For vinyl isocyanide, the α proton is relatively deshielded at τ 4.10 and the *cis* and *trans* β protons are more highly shielded at τ 4.42 and 4.66 (see Results). Complexing the isocyanide group with cobalt(I) shifts the α proton 0.4 τ unit in the expected downfield direction due to electron withdrawal, and the β protons τ 0.02 to 0.1 downfield, the back π bonding evidently not being strong enough to overcome the inductive effect. No self-consistent explanation of these data is possible on the basis of inductive effects alone.

This interpretation assumes that increasing electron density on a carbon atom shifts an adjacent proton upfield provided anisotropic influences[9a] are kept fairly constant. This assumption is supported by numerous empirical correlations, for example, in substituted benzenes[22] and azulene,[23] and seems to be generally accepted.[24] It holds qualitatively for saturated nitriles and isonitriles. The α protons of propionitrile and ethyl isocyanide appear at τ 7.60 and 6.55, respectively, and the β protons at τ 8.69 and 8.59, the inductive order.

A weakness in the foregoing arguments lies in the complexity of the factors contributing to the chemical shift and the consequent possibility of failure of semiempirical correlations.[25] For example, the relationships between the chemical shifts of the vinyl and ethyl cyanides and isocyanides are not quantitatively self-consistent in the present treatment. The dipole moment[18] will provide a more valid basis for verifying the electron distribution. However, the 60° angle between the contributing vectors will tend to make the differences between one calculated model and another rather small, and it will be necessary to compare a series of compounds very carefully in order to reach any conclusion.

The relative reactivities of acrylonitrile and vinyl isocyanide toward diphenyldiazomethane are in qualitative accord with the molecular orbital calculations. The mechanism of the reaction is well understood, and electron-deficient double bonds react much faster than those that are not.[26] In view of the probable π-complex nature of the transition state, it has been suggested that the lower the energy of the first empty orbital of the vinyl compound, the faster the reaction will be.[12] The calculated level for acrylonitrile is 0.49β, for vinyl isocyanide 0.57β, again consistent with the much faster rate shown by the former. Although correlation of reaction rates with electron densities or other ground-state properties cannot provide critical evidence for conjugation,[2] we made this kinetic study to be sure that this system contains no hidden surprises.

In accord with the calculated π-bond orders, the infrared C=C stretching frequency is 10 (± 3) cm^{-1} higher in vinyl isocyanide than in acrylonitrile. However, comparisons of this sort based on simple Hückel calculations cannot be expected to be accurate. In addition to the usual gross approximations,[20] the nitrogen atoms in the two compounds are in different environments and there is no valid way to estimate what Coulomb and bond integral values should be used.

In summary, comparison with the properties of vinyl isocyanide indicates that the terminal vinyl carbon of acrylonitrile is relatively electron deficient. This is contrary to the relative inductive effects of the cyano and isocyano groups. Therefore, either "π-electron" delocalization or an experimentally indistinguishable

---

(17) E. Clementi and D. W. Klint have carried out complete self-consistent field calculations on vinyl isocyanide and acrylonitrile (to be published); personal communication from D. W. Klint.

(18) J. Sheridan has measured the microwave spectrum.

(19) E. L. Wagner and F. Baglin have carried out a partial analysis of the infrared spectra of acrylonitrile and vinyl isocyanide.

(20) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(21) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, 34, 295 (1961).

(22) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956).

(23) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *ibid.*, **80**, 3497 (1958).

(24) M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *ibid.*, **86**, 5698 (1964).

(25) J. I. Musher in "Advances in Magnetic Resonance," Vol. 2, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1966, p 177.

(26) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, 73, 170 (1961).

analogous effect appears to be an important structural factor in the ground state of simple conjugated systems. The delocalization energy must be at least enough to overcome the opposing simple inductive effects. There is much previous work in the organic chemical literature which points to this same qualitative conclusion. The uniqueness of our comparison lies in the close structural similarity of the two isomers, which are isoelectronic and differ only in the location of one nuclear charge. We hope that vinyl isocyanide will prove useful to physical chemists interested in molecular structure and bonding on an advanced level.

Experimental Section[27]

Vinyl Isocyanide. N-Formylethanolamine[28] was prepared by dropwise addition of ethyl formate to ethanolamine. The reaction is exothermic and does not require the suggested[28] subsequent reflux. The product was distilled at 125–140° (0.2 mm), yield 97%. A solution of 133.5 g of N-formylethanolamine in 1500 ml of pyridine was stirred at 10 ± 2° while 540 ml of benzenesulfonyl chloride was added dropwise in 1 hr under nitrogen, then kept at 5° for 2 hr. The solution was poured onto 2 l. of ice. The product was extracted with three 500-ml portions of methylene chloride and concentrated rapidly under vacuum, first at 15 and finally at 1 mm, to a final volume of ~700 ml. *Caution:* Heating must be avoided at end of distillation; the product may explode if all the pyridine is removed. This crude 2-isocyanoethyl benzenesulfonate (**3**) was mixed with 400 ml of 95% ethanol and stirred below 10° during the dropwise addition of 85 g of potassium hydroxide in 400 ml of ethanol in 45 min under nitrogen. After 3 hr at 5°, about 250 ml of vinyl isocyanide–ethanol mixture was distilled from the slurry at 15 mm into a receiver cooled with Dry Ice in acetone. Vinyl isocyanide (**1**) was isolated by distillation through a 30-cm column packed with Podbielniak nichrome helices. The yield was 39 g (49%), bp 45–47° (700 mm). The infrared spectrum of the neat liquid showed a weak C–H peak at 3.24 μ, a strong $N\equiv C$ peak at 4.69 μ, the medium $C=C$ peak at 6.19 μ, other medium peaks at 9.00, 10.52, 10.78, and 11.40 μ, and broad weak bands at 7.2, 7.7, and 14.3 μ. *Caution:* We have estimated from bond energies that the heat of formation of vinyl isocyanide is +55–60 kcal/mol, comparable to vinylacetylene. We have seen no evidence of explosive character, but heat-initiated explosions of methyl and ethyl isocyanide have been recorded[29] and due caution is advised.

Anal. Calcd for C_3H_3N: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.60; H, 5.51; N, 26.10.

2-Isocyanoethyl *p*-Toluenesulfonate. A solution of 380 g of *p*-toluenesulfonyl chloride in 400 ml of pyridine was added to 90 g of N-formylethanolamine in 150 ml of pyridine in 6 hr with stirring at −10°. Ice (300 g) was added, and the mixture was extracted repeatedly with 5:1 ether–pentane solution. The organic phase was washed with water, dried over sodium sulfate, and concentrated under vacuum. The residue was dissolved in 200 ml of 4:1 ether–pentane at 25° and chilled to −15° to crystallize. After recrystallization from ether–pentane, the yield was 70 g (31%), mp 57–57.5°, infrared NC band at 4.65 μ.

Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.31; H, 4.93; N, 6.22; S, 14.23. Found: C, 53.13; H, 4.75; N, 6.46; S, 14.02.

Penta(vinyl isocyanide)cobalt(I) Nitrate. Finely divided cobalt was prepared from 12 g of cobalt nitrate hexahydrate in 120 ml of water and 2.4 g of sodium borohydride in 120 ml of water, which was added in several portions. The precipitate was stirred with 12 g of cobalt nitrate in 100 ml of water at 5° under nitrogen while 6.7 g of vinyl isocyanide was distilled in. The solution was filtered and concentrated to dryness under vacuum, always below 25°. The residue was recrystallized from the minimum amount of water (10 ml, 30°) by freezing to a loose mush, yield 6.1 g (66%), after recrystallization from water (2 ml/g), mp 114–117° dec. The infrared spectrum (in $CHCl_3$) showed two very strong isocyanide complex bands at 4.55–4.7 μ with satellites at 4.50 and 4.94 μ, and a strong $C=C$ band at 6.23 μ.

Anal. Calcd for $C_{15}H_{15}CoN_6O_3$: C, 46.65; H, 3.92; Co, 15.26; N, 21.76. Found: C, 46.44; H, 3.86; Co, 15.42; N, 21.95.

Hexa(vinyl isocyanide)chromium(0). Under nitrogen, 2.2 ml of vinyl isocyanide in 10 ml of methanol was added in 30 min to a stirred suspension of 2.0 g of chromous acetate[30] in 25 ml of methanol in a modified Schlenk tube. A dark red solution and precipitate resulted. The mixture was cooled to −78° and filtered. The solid was recrystallized from chloroform–ethanol in a nitrogen-filled glovebox, yield 0.4 g (35%) of orange-red crystals, mp 105° dec. The infrared spectrum (in CH_2Cl_2) showed weak absorption at 3.3–3.4 μ, a very strong band at 5.1 μ with a satellite at 4.88 μ, a strong sharp band at 6.23 μ, and moderately weak peaks at 7.18, 7.73, 10.6, 10.93, and 11.3 (broad) μ. Analyses always yielded low carbon values.

Anal. Calcd for $C_{18}H_{18}N_6Cr$: C, 58.4; H, 4.9; N, 22.7; Cr, 14.0. Found: C, 51.7; H, 4.6; N, 21.6; Cr, 14.0.

N-Vinyl-α-(1-piperidino)phenylacetamide (6). A solution of 1 ml of vinyl isocyanide, 1.59 g of benzaldehyde, 2.55 g of piperidine, and 1.80 g of acetic acid in 15 ml of methanol was allowed to stand 2 days at 20–25°. The crystalline product which separated, 1.9 g, was recrystallized from 20 ml of methanol, mp 167–169°.

Anal. Calcd for $C_{15}H_{20}N_2O$: C, 73.74; H, 8.25; N, 11.46. Found: C, 73.52; H, 8.25; N, 11.22.

Kinetics. Redistilled acrylonitrile was used. Vinyl isocyanide was distilled under vacuum just prior to each run. A weighed quantity of vinyl compound was diluted to 10.0 ml with the selected solvent, and the 3-ml sample and reference cells were filled with the solution. The cells had tight-fitting Teflon stoppers and were kept in a thermostated water bath (±0.05°) protected from light, but moved to a thermostated cell compartment for each reading. To the reaction cell was added ~12 mg of diphenyldiazomethane[31] and the 410–650-mμ region was scanned with a Cary Model 14 spectrophotometer at appropriate intervals, 7–9 points in 12–24 hr for the vinyl isocyanide runs. The 530-mμ maximum was used for the points, together with an assumed infinity value of zero. For vinyl isocyanide, the pseudo-first-order rate constants were calculated by a least-squares computer program. The data with acrylonitrile showed little scatter. After ten half-lives, the vinyl isocyanide reaction mixtures were generally a little darker than the corresponding reference solution. The possible systematic error could have been 4% in the worst case, though it is likely that most of this darkening occurred after the first two half-lives, on which the results were based.

---

[27] Nmr spectra were obtained with a Varian A-60, infrared spectra with a Beckman IR-8. Microanalyses by Galbraith Laboratories.

[28] G. F. D'Alelio and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 111 (1937).

[29] (a) T. M. Lowry and S. T. Henderson, *Proc. Roy. Soc.* (London), **A136**, 471 (1932); (b) P. Lemoult, *Compt. Rend.*, **143**, 902 (1906).

[30] H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1948, p 161.

[31] L. I. Smith and K. L. Howard, *Org. Syn.*, **3**, 351 (1955).