[Contribution from the Chemistry Research Laboratory, Aeronautical Research Laboratories, Air Force Research Division, Air Research and Development Command]

Infrared and Ultraviolet Absorption Spectra of Enaminonitriles[1a]

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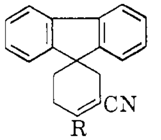
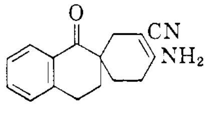
Infrared, ultraviolet, and NMR spectral data are presented to show that the structure of enaminonitriles (β-amino-α,β-unsaturated nitriles) is best represented by the tautomeric form III. Pertinent correlations and observations with other closely related systems are made.

In the previous paper,[1b] the synthesis of 4-aminospiro[Δ^3 - cyclohexene - 1,9′ - fluorene] - 3 - carbonitrile (I) is described. We have also prepared 4 - amino - 1′ - oxo - 3′,4′ - dihydrospiro[Δ^3 - cyclohexene - 1,2′(1′*H*) - naphthalene] - 3 - carbonitrile (II) by the same general procedure. In this system there is the possibility of tautomerism among forms III, IV, and V. It will be shown in this paper that the infrared, ultraviolet, and NMR spectral data support form III as the true structure for this type of compound.

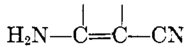


I. R = NH_2
VII. R = OH



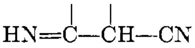
II

Infrared absorption spectra. The infrared data for the spiro compounds I and II are compiled in Table I together with the published data for acyclic as well as other similar five-, six-, and seven-membered ring compounds. The enaminonitrile structure III rather than the tautomeric iminonitrile structure IV[2] has previously been assigned to the acyclic compounds[3] and to the five-membered ring compounds[4] on the basis of their infrared spectra.[5] The infrared data for the six-membered ring compounds I and II from the present work agree so closely with that for the foregoing compounds that the enaminonitrile structure III is likewise assigned to them. The data for the six-membered ring pentacyano compound 9[6] are not clear-cut and will be discussed later in the paper. The data for the seven-membered ring compounds 11–13,[7] although incomplete, still favor their formulation as enaminonitriles rather than iminonitriles.



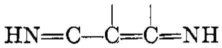
$H_2N-\overset{|}{C}=\overset{|}{C}-CN$

III



$HN=\overset{|}{C}-\overset{|}{C}H-CN$

IV



$HN=C-\overset{|}{C}=\overset{|}{C}=NH$

V

The infrared spectral data for some enaminonitriles wherein tautomerism is precluded by the substitution of alkyl groups for hydrogen atoms on the amino group[3c,8] are presented at the bottom of Table I. It can be seen that the spectral data for these *N*-disubstituted enaminonitriles correlate well with those for the *N*-unsubstituted compounds. It is therefore concluded that III is the most likely structure for the *N*-unsubstituted compounds.

From Brown's useful generalization regarding the behavior of five- and six-membered ring compounds[9] one would predict that the enaminonitrile structure for the six-membered ring should be favored over the same structure for the five-membered ring. Alternatively, more of the five-membered ring should assume the iminonitrile structure than the six-membered ring. The infrared data in Table I cited above, however, demonstrate that this is not the case, and also that both the five- and six-membered ring compounds are almost exclusively in the enaminonitrile form.[10] Thus, this system apparently does not behave according to Brown's generalization.

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[1] (a) Presented in part before the Division of Organic Chemistry at the 137th meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, Abstr. p. 29-O. (b) S. Baldwin, *J. Org. Chem.*, **26**, 3280 (1961).

[2] The alternative tautomeric form V is considered unlikely for reasons which will be discussed later in the paper.

[3] (a) W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958); (b) R. A. Carboni, D. D. Coffman, and E. G. Howard, *J. Am. Chem. Soc.*, **80**, 2838 (1958); (c) P. Kurtz, H. Gold, and H. Disselnkötter, *Ann.*, **624**, 1 (1959).

[4] (a) C. F. Hammer and R. A. Hines, *J. Am. Chem. Soc.*, **77**, 3649 (1955); (b) Q. E. Thompson, *J. Am. Chem. Soc.*, **80**, 5483 (1958).

[5] The enaminonitrile structure, 1-amino-1-methyl-2-cyanoethylene (β-aminocrotononitrile), was first assigned to the product obtained from the dimerization of acetonitrile with sodium on the basis of its ultraviolet absorption spectrum. See J. J. Conn and A. Taurins, *Can. J. Chem.*, **31**, 1211 (1953).

[6] J. C. Westfahl and T. L. Gresham, *J. Org. Chem.*, **21**, 319 (1956).

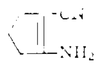
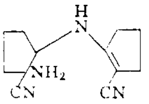
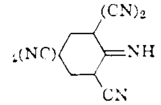
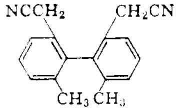
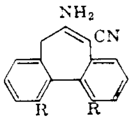
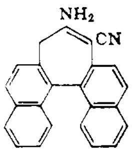
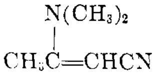
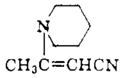
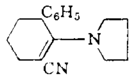
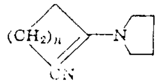
[7] (a) P. Newman, P. Rutkin, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 465 (1958); (b) K. Mislow and F. A. McGinn, *J. Am. Chem. Soc.*, **80**, 6036 (1958).

[8] M. E. Kuehne, *J. Am. Chem. Soc.*, **81**, 5400 (1959).

[9] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954); H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

[10] The detailed discussion of the infrared spectral data which support this contention will be presented at an appropriate point later in the paper.

TABLE I. INFRARED ABSORPTION BANDS OF ENAMINONITRILES (CM.$^{-1}$)

N-Unsubstituted Acyclic Compounds	Phase	NH_2	C≡N	C=C
1. $CH_3C(NH_2)=CHCN$[a]	[b]	3450, 3350, 1645	2180	1600
2. $C_2H_5OC(NH_2)=C(CN)_2$[c]	[b]	3279, 3135, 1653	[d]	1543
3. $(NH_2)_2C=C(CN)_2$[c]	[b]	3300, 3175, 1656	[d]	1555
4. $NCCH_2(NH_2)C=C(CN)_2$[e]	[f,g]	3356, 3226, 1664[g]	2370, 2217, 2198	1555[g]
Cyclic Five-Membered Compounds				
5.  [h]	[i]	3512, 3420, 1645	2189	1605
6.  [j]	[k]	3520, 3440, 1640	2180 (conjd.) 2240 (unconjd.)	1608, 1575
Cyclic Six-Membered Compounds				
7. I	[l]	3448, 3356, 1645	2169	1608
	[m]	3378, 3279, 1645	2165	1616
8. II	[l]	3436, 3333, 1637	2179	1616
	[n]	3460, 3390, 1642	2188	1610
9.  [o]	[p]	3425, 3356, 3236, 1631	2212[q]	1650[r] (C=N)
Cyclic Seven-Membered Compounds				
10.  [s,t]	[m]	None	2255	None
11.  [s] (±) R = NO_2	[m]	3325, 1635	2190	[d]
12. (+) R = CH_3[s]	[m]	3333, 1635	2174	[d]
13. (±)  [u]	[m]	3266, 3170, 1646	2167	[d]
N-Disubstituted				
14.  $CH_3C(N(CH_3)_2)=CHCN$ [a]	[b]	None	2190	1590
15.  [a]	[b]	None	2185	1570
16.  [v]	[b]	None	2170–2180	1570–1580
17.  [v] n = 5,6	[b]	None	2170–2180	1570–1580

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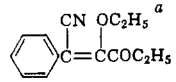
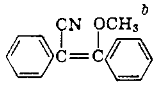
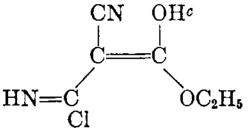
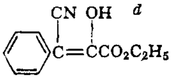
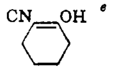
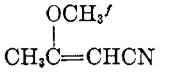
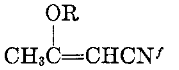
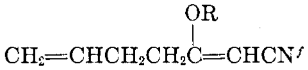
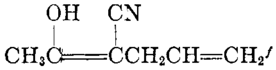
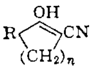
[a] Ref. 3c. [b] Phase not specified. [c] Ref. 3a. [d] No value reported. [e] Ref. 3b except where otherwise noted. [f] Nujol mull. [g] Private communication from Dr. R. A. Carboni. [h] Ref. 4a. [i] 2.5% by wt. in chloroform. [j] Ref. 4b. [k] Dilute chloroform solution. [l] Mineral oil mull. [m] Potassium bromide pellet. [n] 3% (w/v) in chloroform. [o] Ref. 6. [p] Fluorlube mull. [q] Ref. 21. [r] Probably C=N rather than C=C stretching. [s] Ref. 7a. [t] This compound is included to demonstrate that the normal unconjugated C≡N stretching frequency is unaffected by incorporation into the potassium bromide pellet. The shifts observed for enaminonitriles in this medium are therefore directly comparable to those obtained from a solution or mull. See also C≡N value for I in potassium bromide. [u] Ref. 7b. [v] Ref. 8.

TABLE II

INFRARED FREQUENCIES FOR β-ALKOXY- AND HYDROXY-α,β-UNSATURATED NITRILES

Compound	Phase	C≡N (Cm.$^{-1}$)
1.  [a]	Pure liquid	2174
2.  [b]	$CHCl_3$ solution	2169
3.  [c]	Not specified (NS)	2198
4.  [d]	NS	2200
5.  [e]	Dilute $CHCl_3$ solution	2190 2240 (unconjd.)
6.  $CH_3\overset{\overset{OCH_3}{\vert}}{C}=CHCN$ [f]	NS	2210
7.  $CH_3\overset{\overset{OR}{\vert}}{C}=CHCN$ [f] R = C_2H_5, n-C_4H_9, $CH_2=CHCH_2$, C_6H_5, C_6H_4Cl, 2,4-$C_6H_3Cl_2$	NS	2210–2220
8.  $CH_2=CHCH_2CH_2\overset{\overset{OR}{\vert}}{C}=CHCN$ [f] R = C_2H_5, n-C_4H_9	NS	2210
9.  $CH_3\overset{\overset{OH}{\vert}}{C}=\overset{\overset{CN}{\vert}}{C}CH_2CH=CH_2$ [f]	NS	2200 2240 (unconjd.)
Compound		
10.  [g] R = H, n = 2, 3, 4, 5, 6 (trace)	NS	2220–2210 2265–2255 (unconjd.)
R = CH_3, n = 3 R = C_6H_5, n = 3	NS	2215 2265–2260 (unconjd.)
11. VII[h]	3% (w/v) $CHCl_3$	2198 2252 (unconjd.)

[a] G. S. Skinner, J. A. Gladner, and R. F. Heitmiller, *J. Am. Chem. Soc.*, **73**, 2230 (1951). [b] P. B. Russell and E. Csendes, *J. Am. Chem. Soc.*, **76**, 5714 (1954). [c] Ref. 3a. [d] B. H. Chase and J. Walker, *J. Chem. Soc.*, 3518 (1953). [e] Ref. 18. [f] Ref. 3c. [g] Ref. 8. [h] Present study.

Perhaps the most compelling infrared spectral evidence in favor of the enaminonitrile structure for the compounds in Table I is the unusually low C≡N stretching frequencies observed for all of them. It is reported[11] that 2218 cm.$^{-1}$ is the lowest frequency observed for an α,β-unsaturated alkyl nitrile and 2221 cm.$^{-1}$ is the lowest frequency observed for a benzonitrile-type structure. Bellamy[12] lists 2215 cm.$^{-1}$ and 2220 cm.$^{-1}$ as the lower limits for C≡N stretching frequencies of α,β-unsaturated alkyl nitriles and benzonitriles respectively. The values of the nitrile frequencies in Table I have been depressed by 17–38 cm.$^{-1}$ below 2215 cm.$^{-1}$, the lowest value for normally conjugated aliphatic nitriles quoted above. This additional lowering is roughly equivalent to the average decrease (25 cm.$^{-1}$) observed in going from an unconjugated aliphatic to a conjugated aliphatic nitrile, that is, from 2250 cm.$^{-1}$ to 2225 cm.$^{-1}$.[11,12] Therefore this abnormally large shift by a factor of two must be due to some influence other than simple conjugation with the α,β-double bond. It has been stated[4a] that the amino group was presumably responsible for the further shift of the nitrile frequency to 2189 cm.$^{-1}$ in compound 5, Table I, but no further explanation

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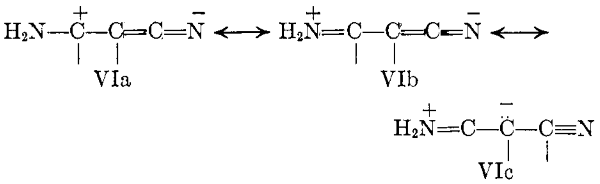
(11) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 343 (1952).

(12) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., Methuen & Co., Ltd., London, 1958, p. 263.

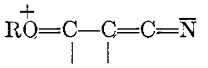
was offered. It is proposed here that this abnormal shift can be explained in terms of the enaminonitrile structure III with the resultant increased interaction between the p-electrons on the nitrogen atom with the π-electrons of the double bond and in turn with the π-electrons of the nitrile group itself. That is to say, the enaminonitrile structure allows charge-separated resonance forms such as VIa, VIb, and


$H_2N—\overset{+}{C}—C=C=\overset{-}{N} \longleftrightarrow H_2\overset{+}{N}=C—C=C=\overset{-}{N} \longleftrightarrow H_2\overset{+}{N}=C—\overset{-}{C}—C\equiv N$

VIa VIb VIc

VIc to contribute to the ground state of the molecule.[13,14] It would be difficult to reconcile this observed shift in the C≡N frequency with the iminonitrile structure IV.

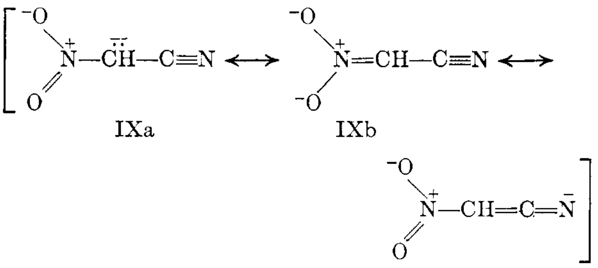
Similar lowering of the nitrile stretching frequency has been recorded for the related β-hydroxy- and β-alkoxy-α,β-unsaturated nitriles listed in Table II. The extreme charge-separated resonance form VIII analogous to VIb can be written to ac-


$R\overset{+}{O}=C—C=C=\overset{-}{N}$

VIII

count for the pronounced shift. In general, it appears that the shift of C≡N frequencies for the compounds in Table II is less pronounced than that for the corresponding β-amino compounds in Table I. This may be due to the greater electronegativity of oxygen compared to nitrogen. Consequently, the p-electrons in the oxygen-containing group may not be as delocalized as those in an amino group resulting in a less pronounced shift.

Another example of nitrile frequency lowering occurs in the anions of nitroacetonitrile.[16] The data are recorded in Table III. Again the resonance form IXc corresponding to VIa can be written for the ground state of these molecules to account for this shift. Here the shift is not as pronounced as


IXa IXb IXc

in enaminonitriles because there are competing resonance forms IXa and IXb which do not contribute to the nitrile frequency lowering. There must, however, be sufficient contribution from form IXc to produce the lowering observed.

TABLE III

INFRARED FREQUENCIES FOR C≡N IN NITROACETONITRILE ANIONS[a]

$[O_2NCHC\equiv N]^- H_3\overset{+}{N}R$

R	C≡N (cm.$^{-1}$)
H	2210
C_6H_5	2200
$CH_3OC_6H_4$	2200
$2,4(CH_3)_2C_6H_3$	2205

[a] All data from ref. 16 and determined as Nujol mulls.

Further support for the enaminonitrile structure III is obtained from the following observations. The appearance of two bands in the NH stretching region is compatible only with a primary amino group (—NH_2).[17] If an imino group (=NH) were present, only one band should appear in this region.[17] Furthermore, it appears that these molecules exist almost entirely as the enaminonitrile tautomer III and not as an equilibrium mixture of III and IV. If the molecule were actually an equilibrium mixture of the two tautomers, then two C≡N stretching frequencies should result, one for the unconjugated C≡N of tautomer IV and one for the conjugated C≡N of tautomer III. Thus, for the 2-cyanocyclanones in Table II, two C≡N stretching frequencies appear, one for the unconjugated C≡N in the keto tautomer and one for the conjugated C≡N in the enol tautomer.[8,18] Since no unconjugated C≡N band is observed for the compounds in Table I,[19] it is concluded they are essentially in the enaminonitrile form. The absence of an unconjugated band in the C≡N stretching region for I confirms that it is a monomer rather than a dimer (*cf.* Table I, 6).[1b]

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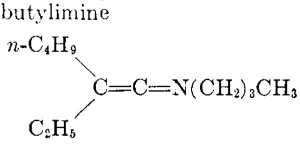
(13) Conn and Taurins (ref. 5) used resonance structures VIa and VIb to explain the ultraviolet spectrum of β-aminocrotononitrile.

(14) In this connection it is interesting to note the strong band at 2045 cm.$^{-1}$ reported for the ketenimine, ethyl-n-butylketen-n-butylimine



assigned to the >C=C=N-group (ref. 15). The latter is isoelectronic with the >C=C=$\overline{N}$ moiety appearing in resonance forms VIa and VIb. It is therefore inferred that these forms are making appreciable contributions to the ground state of the enaminonitrile molecule.

(15) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954).

(16) J. C. Grivas and A. Taurins, *Can. J. Chem.*, **37**, 1266 (1959).

(17) Ref. 12, p. 249.

(18) L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 4487 (1954).

(19) The exception, of course, is compound 6 where the unconjugated C≡N produces a band at the normal frequency.

In Table I bands appearing at 1645–1637 cm.$^{-1}$ in compounds I and II have been assigned to NH_2 deformation,[17] while those at 1646–1635 cm.$^{-1}$ in compounds 11–13 are probably also due to NH_2 deformation rather than $C=N$ stretching.[7a,b] The bands occurring at 1616–1608 cm.$^{-1}$ in compounds I and II have been assigned to endocyclic $C=C$ stretching by analogy with compounds 14–17 in Table I. It was recently observed that conjugated double bonds in cyclic six-membered enaminoketones have $C=C$ stretching frequencies in the range 1573–1560 cm.$^{-1}$ [20]

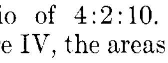
The infrared spectral data reported for compound 9[6] in Table I are difficult to interpret. Since three bands are present in the NH stretching region, it appears that there is a tautomeric equilibrium between the enaminonitrile form III and iminonitrile form IV.[21] The bands at 3425 cm.$^{-1}$ and 3356 cm.$^{-1}$ can be ascribed to the $—NH_2$ group, arising from free NH and intermolecularly bonded NH respectively.[22] Since intramolecular hydrogen bonding is impossible in enaminonitriles owing to the linearity of the $C\equiv N$ group, the third band at 3236 cm.$^{-1}$ is most logically assigned to the $=NH$ group.[17,23] However, as noted previously, in a tautomeric equilibrium, one should expect to find two $C\equiv N$ frequencies, but only one band at 2212 cm.$^{-1}$ was observed.[24] This value is not particularly low in comparison with the other $C\equiv N$ frequencies in Table I. Moreover, there is apparently no $C\equiv N$ stretching band for the *gem*-dicyano groups in the ring. The band at 1631 cm.$^{-1}$ has been assigned to NH_2 deformation[6] while the band at 1650 cm.$^{-1}$ is probably better assigned to $C=N$ stretching rather than $C=C$ stretching.[25]

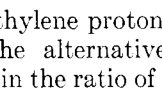
The alternative formulation of the tautomer as V does not seem attractive because of the following reasons. First, it would be difficult to reconcile the bands observed at 2198–2165 cm.$^{-1}$ for the compounds in Table I with structure V since the $—C=C=N—$ group absorbs at about 2045 cm.$^{-1}$ [14,15] Second, unsubstituted ketenimines with the $>C=C=NH$ structure have not been previously reported in the literature. Furthermore, the known substituted ketenimines are low-melting solids or liquids and usually have characteristic colors and odors.[15] In this study, compounds I and II as well as the rest of the enaminonitriles in Table I are high-melting solids. Moreover, compounds I and II are odorless and colorless, while I is unusually resistant toward hydrolysis.[1b]

The intensity of the absorption bands for the $C\equiv N$, NH_2, and $C=C$ groups is strong for compounds I and II and many others in Table I. This may be somewhat surprising for the $C=C$ group which is normally a relatively weak to medium absorber in this region. It appears, however, that the enhanced conjugation mentioned previously produces a strong intensity band for $C=C$ in this case.

NMR spectra. The NMR spectrum[26] was determined for II in deuterochloroform solution with added tetramethylsilane as internal reference. The tautomeric structure III is supported by the following data: (1) the NH_2 signal which appears at 266 cps. is in a position typical for this type of group, and (2) the areas of the signals for aromatic protons, amino protons, and methylene protons are in the ratio of 4:2:10. For the alternative imino structure IV, the areas would in the ratio of 4:1:10. There is a possibility that the imino proton and the proton on the carbon atom attached to the $C\equiv N$ group might have the same chemical shift. The absorption spectrum, however, shows no evidence of fine structure due to spin coupling with the neighboring methylene group, thus definitely ruling out structure IV. The insufficient solubility of I in a suitable solvent precluded the determination of its NMR spectrum.

Ultraviolet absorption spectra. The ultraviolet absorption maxima for some enaminonitriles are listed in Table IV. Since I contains the fluorene chromophore and the enaminonitrile chromophore which both absorb strongly in the same region of the spectrum, it is necessary to subtract the spectrum of X from that of I and the spectrum of XI from that of II to obtain the value for the enaminonitrile chromophore.[27]


X



XI

These data further substantiate the assignment of the enaminonitrile structure III to these compounds with the attendant resonance structures

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[20] N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

[21] Stuart-Briegleb scale models of these two tautomeric forms of this compound show that there is internal steric strain in both forms due especially to the bulkiness of the $C\equiv N$ groups as well as their mutual electrostatic repulsion. From a purely qualitative (visual) inspection, it appears that the enaminonitrile form is somewhat less strained than the iminonitrile form. The compound may then be an equilibrium mixture of the two tautomeric forms with equilibrium favoring the enaminonitrile form. The exchange of deuterium for the active hydrogen in this sterically crowded system (ref. 6) might shift the tautomeric equilibrium as well as affect their conformations. The reported wide difference in the infrared spectra of the deuterated and undeuterated compounds (ref. 6) may thus be qualitatively explained on this basis.

[22] J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).

[23] P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, **76**, 5169 (1954).

[24] Private communication from Dr. J. C. Westfahl.

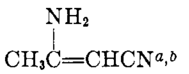
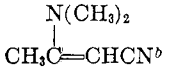
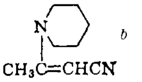
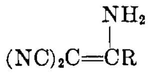
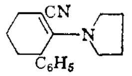
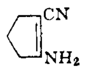
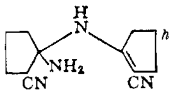
[25] In ref. 23, 1645–1639 cm.$^{-1}$ is given as the range of $C=N$ stretching in aliphatic imines.

[26] We are indebted to Varian Associates, Palo Alto, Calif. for the determination of the NMR spectrum.

[27] See ref. 1b, footnote 32.

TABLE IV

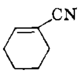
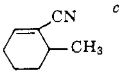
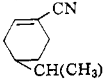
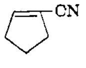
ULTRAVIOLET ABSORPTION DATA FOR ENAMINONITRILES

Compound	Solvent	λ_{max} (mμ)	ϵ_{max}
 $CH_3\overset{\overset{NH_2}{\vert}}{C}{=}CHCN$[a,b]	abs. C_2H_5OH[a]	258	13,600
	C_2H_5OH[b]	258	18,500
	CH_3OH[b]	258	19,800
 $CH_3\overset{\overset{N(CH_3)_2}{\vert}}{C}{=}CHCN$[b]	CH_3OH	267	23,200
 [b]	CH_3OH	270	23,800
 $(NC)_2C{=}\overset{\overset{NH_2}{\vert}}{C}R$			
R = OC_2H_5[c]	[d]	254	strong
R = NH_2[c]	[d]	251	strong
R = CH_2CN[e]	C_2H_5OH	276	14,000
	H_2O	273	15,700
 [f]	C_2H_5OH	289	17,470
 [g]	[d]	263	13,000
 [h]	C_2H_5OH	263	14,400
(I-X)	95% C_2H_5OH	267.5	12,700
(II-XI)	95% C_2H_5OH	261.5	12,200

[a] Ref. 5. [b] Ref. 3c. [c] Ref. 3a. [d] Not specified. [e] Ref. 3b, data courtesy of Dr. R. A. Carboni. [f] Ref. 8. [g] Ref. 4a. [h] Ref. 4b.

TABLE V

ULTRAVIOLET ABSORPTION MAXIMA OF CYCLIC CONJUGATED NITRILES

Compound	Solvent	λ_{max} (mμ)	ϵ_{max}
 [a]	95% ethanol	212	11,200
[b,c]	ethanol	211	11,200
 [c]	ethanol	210	9,500
 [d]	95% ethanol	212	8,900
 [a]	95% ethanol	217	9,900

[a] O. H. Wheeler, *J. Am. Chem. Soc.*, **78,** 3216 (1956). [b] E. A. Braude and O. H. Wheeler, *J. Chem. Soc.*, 320 (1955). [c] *J. Chem. Soc.*, 329 (1955). [d] R. L. Frank, R. E. Berry, and O. L. Shotwell, *J. Am. Chem. Soc.*, **71,** 3889 (1949).

VI a, b, c, in the excited state.[13] The alternative iminonitrile structure IV cannot explain the ultraviolet maxima observed for these compounds. Thus an unconjugated C≡N group absorbs between 160–180 mμ,[28,29a] while the unconjugated imino group likewise has no strong selective absorption above 200 mμ.[28,29b,30] Thus the λ_{max} and ϵ_{max} values are consistent only with the conjugated enaminonitrile structure III.

The absorption maxima for some alicyclic conjugated nitriles are presented in Table V. It is seen that there is a bathochromic shift of 46–55 mμ and a hyperchromic shift of 1500–4500 when the hydrogen atom on the β-carbon atom is replaced by an amino group to form an enaminonitrile. Similar bathochromic and hyperchromic effects caused by β-amino groups in conjugated systems have been reported.[28,31] Thus, enaminonitriles represent another example of strong π-p conjugation.

As a further test of the enaminonitrile structure III, the ultraviolet difference spectra (I-X) were determined in 95% ethanolic 0.1*N* hydrochloric acid and 0.1*N* potassium hydroxide respectively. The results are recorded in Table VI. It can be seen that in acid solution, the major maximum[32] formerly at 267.5 mμ has been shifted to 231 mμ and 226 mμ. Practically identical results were obtained in 95% ethanolic 0.2, 0.4 and 0.8*N* hydrochloric acid. Other workers[33] have reported that the ultraviolet spectrum of *N*-butenylpiperidine in acid solution reverts to that of the unconjugated olefin with only low intensity absorption above 210 mμ. Parallel results have been reported for aniline derivatives in strong acid solution.[31b,c,d] Quaternization of the amino group in acid solution prevents the *p*-electrons on the nitrogen from participating in excited states such as VI a, b, c, with a resultant hypsochromic shift. The subtraction spectrum of the enaminonitrile (I-X) should then revert to that of 1-cyanocyclohexene (Table V) in acid solution. The fact that the subtraction spectrum (I-X) differs from that of 1-cyanocyclohexene may be due to several factors. First, the failure of the model compound X to cancel all the absorption due to the fluorene chromophore may introduce spurious maxima at the observed wave lengths. Second, a hypsochromic shift occurs but not to the extent predicted because the proton may attach itself to other sites in the molecule, for example, to the

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(28) E. A. Braude, *Ann. Repts. on Progr. Chem. (Chem. Soc. London)*, 42, 105 (1945).

(29) A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Ltd., London, 1954, (a) p. 46; (b) p. 56.

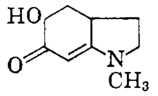
(30) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67,** 1017 (1945).

(31) (a) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952); (b) I. M. Klotz and D. M. Gruen, *J. Am. Chem. Soc.*, **67,** 843 (1945); (c) W. D. Kumler and L. A. Strait, *J. Am. Chem. Soc.*, **65,** 2349 (1943); (d) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69,** 2714 (1947).

(32) The term major maximum is used here to mean the maximum with the greatest oscillator strength.

(33) K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946).

nitrile nitrogen atom. Such limited hypsochromic shifts have been reported for the analogous enaminoketone XII in acid solution.[34] These workers



XII

proposed that the proton residues on the carbonyl oxygen atom rather than the amino nitrogen atom in XII, in analogy to amides of which it is a vinylog.[37] Thus, in acid solution the proton is prevented from exerting its maximum hypsochromic effect on XII with the resulting limited shift to 276 mμ. Complete resolution of this problem of proton location in enaminonitriles in acid solution is not possible at this stage with the limited data available. Nevertheless the results are compatible only with the enaminonitrile structure of I and II.

TABLE VI

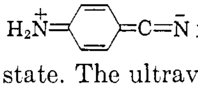
Ultraviolet Absorption Bands of (I-X) in 95% Ethanol

Medium	λ_{max} (mμ)	ϵ_{max}
Neutral	267.5	12,700
	231	5,400
	226	4,800
0.1*N* HCl	231	11,900
	226	10,800
0.1*N* KOH	267	13,300
	229 (infl.)	7,500
	224 (infl.)	12,200

The ultraviolet data for (I-X) in 0.1*N* potassium hydroxide in 95% ethanol agree with that observed for (I-X) in ethanol above. The slight hyperchromic effect in the alkaline medium may not be significant, but could be due to the conversion of a small equilibrium amount of iminonitrile form present in neutral ethanol to the enaminonitrile form in alkaline ethanol. Thus, it is well known that allyl cyanide (structure analogous to the iminonitrile IV) tautomerizes to crotononitrile (structure analogous to the enaminonitrile III) in basic solution.[38]

There is an interesting side light to the assignment of the enaminonitrile structure to the compounds discussed above. Enaminonitriles are vinylogs of cyanamides. Therefore, cyanamides might well be expected to exhibit a lowered C≡N stretching frequency in their infrared spectra. That this is in fact the case is revealed in Table VII. Here the C≡N frequency is approximately intermediate between that for conjugated nitriles and enaminonitriles (*cf.* Table I and previous discussion thereof). Analogous resonance forms such as $R_2\overset{+}{N}{=}C{=}\overset{-}{N} \longleftrightarrow R_2N{-}\overset{+}{C}{=}\overset{-}{N}$ can be written for these substituted cyanamides to explain the decrease in nitrile absorption frequency. In this connection it was found[39] that the C≡N absorption frequency increased to 2300 cm.$^{-1}$ in the decaborane diethylcyanamide complex, $B_{10}H_{12}.2(C_2H_5)_2NCN$. This frequency increase is attributed to the decreased availability of the *p*-electrons on the amino nitrogen of the diethylcyanamide moiety for participation in the resonance forms shown above, thereby indicating a boron-amino nitrogen bond. Apparently, the contribution of these resonance forms to the ground state is not appreciable enough to effect a frequency lowering equal to that for the vinylogous enaminonitriles in Table I.

The ultraviolet absorption data for these substituted cyanamides support this view for the excited states as well. Thus diethylcyanamide shows only weak end absorption at 210 mμ (ε 400),[40] while diallylcyanamide shows weak absorption in the near ultraviolet region increasing with shorter wave lengths to ε 855 at 210 mμ.[41] These values should be contrasted with those for the vinylogous enaminonitriles in Table IV where the large bathochromic and hyperchromic effects are operative.

In Table VII, there is also shown a decrease in the C≡N frequency, relative to benzonitrile, of *p*-aminobenzonitrile, an aromatic vinylog of cyanamide. It appears that here too resonance structures such as  must be contributing to the gound state. The ultraviolet spectrum of *p*-aminobenzonitrile has been reported as $\lambda_{max}^{C_2H_5OH}$ 277.5 mμ (ε 24,000)[42] and $\lambda_{max}^{95\%\ C_2H_5OH}$ 278 mμ (ε 22,390)[43],

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[34] J. Austin, J. D. Chanley, and H. Sobotka, *J. Am. Chem. Soc.*, **73**, 5299 (1951). From Woodward's rules (ref. 35) a λ_{max} value of *ca.* 244 mμ (corrected to water as solvent) has been calculated for XII in aqueous acid solution on the assumption that the proton is attached exclusively to the amino nitrogen atom. Actually these workers observed that the λ_{max} value for XII is shifted from 293 mμ in neutral aqueous solution to 276 mμ in acid aqueous solution, 32 mμ higher than the calculated λ_{max} of 244 mμ. See also ref. 36.

[35] R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); *J. Am. Chem. Soc.*, **64**, 76 (1942).

[36] E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 28 (1959), and references therein. It is pointed out that a quaternary nitrogen atom bearing a formal positive charge causes a significant decrease in the position of the short wave length maximum of a bicyclic α,β-unsaturated ketone. Thus the value calculated from Woodward's rules in footnote 34 above should be even somewhat less than 244 mμ, say 234 mμ.

[37] See, however, E. Skinner, *Spectrochim. Acta*, 95 (1959), who concludes that the infrared and Raman spectra of the hydrochlorides of urea and acetamide indicate that the proton resides on the nitrogen atom rather than the oxygen atom.

[38] B. Belleau, *J. Am. Chem. Soc.*, **73**, 5149 (1951); H. A. Bruson, *J. Am. Chem. Soc.*, **64**, 2457 (1942).

[39] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **80**, 6685 (1958).

[40] G. W. Stevenson and D. Williamson, *J. Am. Chem. Soc.*, **80**, 5943 (1958).

[41] New Product Bull., Coll. Vol. I, American Cyanamid Co., New York 20, N. Y., p. 76.

[42] A. Burawoy and J. P. Critchley, *Tetrahedron*, **5**, 340 (1959).

[43] P. Grammaticakis, *Bull. Soc. Chim., France*, [5] **20**, 207 (1953).

while that for benzonitrile as $\lambda_{max}^{C_2H_5OH}$ 225 mμ (ε 12,000)[42] and $\lambda_{max}^{alcohol}$ 225 mμ (ε 12,600).[44] Again the role of the amino group is clear in producing a large (53 mμ) bathochromic shift as well as an appreciable hyperchromic effect.

TABLE VII

NITRILE FREQUENCIES FOR SUBSTITUTED CYANAMIDES

	$C\equiv N$ (cm.$^{-1}$)	
Compound	Pure Liquid	$CHCl_3$ Soln.
Dimethylcyanamide	2200,[a] 2212[b]	2218[c]
Diethylcyanamide	2202,[a] 2210[d]	2209[c]
Diallylcyanamide		2215[c]
p-Aminobenzonitrile	2221[e]	
Benzonitrile	2230[e]	

[a] Private communication from Dr. G. H. Dorion, American Cyanamid Co., Stamford, Conn. [b] M. Davies and W. J. Jones, *Trans. Faraday Soc.*, **54**, 1454 (1958). [c] J. P. Jesson and H. W. Thompson, *Spectrochim. Acta*, **13**, 217 (1958). [d] Ref. 39. [e] Ref. 11.

EXPERIMENTAL[45]

4-Aminospiro[Δ^3-cyclohexene-1,9'-fluorene]-3-carbonitrile (I). This compound was prepared as described previously.[1b]

4-Amino-1'-oxo-3',4'-dihydrospiro[Δ^3-cyclohexene-1,2'(1'-H)-naphthalene]-3-carbonitrile (II) *and 1'-oxo-3',4'-dihydrospiro[cyclohexane-1,2'(1'H)-naphthalene]*(XI). The preparation of these compounds will be fully described in a subsequent communication.

3-Cyanospiro[cyclohexane-1,9'-fluoren]-4-one (VII). This compound was prepared by the published procedure.[46] It was found that dilute solutions of VII in chloroform or methanol decomposed within 2–3 days to produce a yellowish brown color with an unmistakable cyanide odor. Refrigeration and/or exclusion of air and moisture retarded this decomposition only for a day longer than before. These decomposition products were not investigated further. $\bar{\nu}_{max}^{CHCl_3}$: 2252 (unconjd. $C\equiv N$), 2198 (conjd. $C\equiv N$), 1736 ($C=O$ in six-membered ring with $C\equiv N$ substitution on α-carbon)[8], and 1639 cm.$^{-1}$ (conjd. $C=C$). It appears that this compound is essentially in the enolized form VII for the following reasons: The absorption band at 2198 cm.$^{-1}$ is much more intense than that at 2252 cm.$^{-1}$. The appearance of a well-defined band at 1639 cm.$^{-1}$ indicates a conjugated $C=C$ group while the intensity of the $C=O$ band at 1736 cm.$^{-1}$ is relatively weak for this group.

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(44) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

(45) All melting points were taken on a Fisher-Johns apparatus with a calibrated thermometer. Infrared spectra were determined on a Perkin-Elmer Model 21 Spectrophotometer. Ultraviolet spectra were determined on a Cary Model 11MS Spectrophotometer in 95% ethanol (distilled) solutions *ca.* $5 \times 10^{-5}M$.

(46) D. A. Stauffer and O. E. Fancher, U. S. Pat. **2,647,896** (1953); *cf. Chem. Abstr.*, **48**, 9405 (1954) and *J. Org. Chem.*, **25**, 935 (1960).

[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BRUNEL COLLEGE OF TECHNOLOGY, LONDON, AND THE UNIVERSITY OF PUERTO RICO AT MAYAGUEZ]

Absorption Spectra of Aromatic Azo and Related Compounds. III. Substituted Azobenzenes[1]

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Received May 31, 1960

The ultraviolet and visible spectra of a number of mono- and dihalogeno azobenzenes are reported. The changes in wave length and intensity produced by the substituents are correlated with their electronic and steric effects, and are compared with analogous results previously obtained for azoxybenzenes.

Although the spectra of individual substituted azobenzenes can be found in the literature, there have been few attempts at a systematic study of the effects of substituents on the light absorption of the azobenzene system.[3] In this paper results have been obtained for a series of mono- and dihaloazobenzenes (see Table I) and the spectra are discussed and compared with our previous data on substituted azoxybenzenes.[4] Our measurements were determined in absolute ethanol solutions [in which solvent the photochemical (*trans* → *cis*) isomerization is most suppressed[5a]] after standing overnight in the dark, and there is little doubt that the data refer to solutions containing negligible amounts of the *cis*-isomers.[5b]

The azobenzenes showed three distinct regions of absorption in the ultraviolet and visible parts of the spectrum, with bands at 220–240 mμ, 320–360 mμ, and 430–460 mμ. The first two bands were relatively intense (A_M 10,000–20,000), whereas the visible band was considerably weaker (A_M 400–1000). This low intensity band has been assigned by Burawoy[3a] to a radical transition in the azo

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(1) Part II, *J. Am. Chem. Soc.*, **78**, 3363 (1956).

(2) (a) Brunel College of Technology, London, W. 3; (b) University of Puerto Rico at Mayaguez.

(3)(a) A. Burawoy, *J. Chem. Soc.*, 1865 (1937); (b) A. H. Cook, D. G. Jones, and J. B. Polya, *J. Chem. Soc.*, 1315 (1939).

(4) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956).

(5)(a) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **75**, 1856 (1953); (b) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952).