Molecular Structure of the Nitrile Yilde Derived from 3-Phenyl-2H-azirine in a Nitrogen Matrix

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Nitrile ylides derived from 3-phenyl-2H-azirine and five of its isotope-labeled counterparts were generated photochemically in 12 K nitrogen matrices and examined by FTIR. A prominent 1926-cm⁻¹ feature in the unlabeled ylide's spectrum undergoes a 66-cm⁻¹ shift with ¹⁵N substitution, and this effect is interpreted as being consistent only with the asymmetric stretching fundamental of a linear C = N = C skeleton. The spectra of the ¹³C- and D-labeled nitrile ylides corroborate this conclusion and clarify spectral regions where Fermi multiplets and overlapping absorptions complicate the interpretation. The allene-like nitrile ylide C_s geometry is retained over the temperature range 12-82 K, which suggests that this geometry is also adopted in solution where nitrile ylides have been implicated as 1,3-dipolar reactive intermediates from the photolysis of 2H-azirines.

The photochemically induced ring opening of 2H-azirines produces the reactive species nitrile ylides.¹ In solution these ylides undergo stereo- and regioselective 1,3-dipolar cycloadditions with unsymmetrical dipolarophiles forming five-membered heterocycles.² Theoretical treatments have interpreted the stereoselectivity in terms of a concerted process,³ and predictions of regioselectivity have been based on calculations of optimized geometries for the 1.3-dipoles.4

While numerous studies have examined synthetic and mechanistic aspects of the reaction of nitrile ylides with dipolarophiles,^{2,5} reports on direct spectroscopic observations of nitrile ylides have been limited. Two groups characterized nitrile ylides substituted with strongly electron-withdrawing fluorocarbon groups,^{6,7} but experimental results and theoretical predictions^{4c} indicate these ylides are structurally atypical. Photochromic behavior was demonstrated by ultraviolet absorption spectroscopy for several alkyl- and aryl-substituted azirine-nitrile ylide pairs in cryogenic glasses,⁸ and a single infrared absorption frequency was noted for a nitrile ylide in an argon matrix.⁹ Thus, the paucity of spectroscopic evidence has left the structure of nitrile ylides a matter of conjecture and ambiguity. In the course of an investigation of 2H-azirines as possible model systems for molecular energy storage we sought to resolve the nitrile vlide structure question. We will now report the results of matrix studies in which infrared frequency shifts due to specific isotope substitutions are used to determine the structure of the nitrile ylide derived from 3phenyl-2*H*-azirine (1a in Figure 1).

Experimental Section

The apparatus used for these experiments has been described recently.¹⁰ Difference spectra were recorded on the IBM Model IR97 infrared spectrophotometer with a resolution of 0.5 cm^{-1} . The azidostyrenes 2a-f and phenylazirine 1a at their vapor pressures were codeposited with N_2 at a total rate of 0.4 mmol/h onto the CsI window maintained at 12 K; typically 2-3 mmol of the matrix mixture was so deposited. The photolysis light source was a GE Model AH4 medium-pressure Hg lamp focused on the matrix with a 5-cm plano-convex quartz lens. The 350-nm filter was a Corning 7-59 color filter transmitting the spectral range 310-480 nm, and the 250-nm band-pass filter was an Optics Technology Inc. interference filter transmitting in the spectral range 242-258 nm.

The azidostyrenes 2a-f and phenylazirine 1a were synthesized by the method of Hortmann et al.¹¹ The ¹⁵N-labeled azidostyrene 2b was synthesized with Na¹⁵N¹⁴N¹⁴N (97.5% mono end label, Amersham Corp.). Azidostyrenes 2c-e were synthesized, respectively, from styrene- β - d_1^{12} (from D₂O, 99.8%, ICN Corp.), from styrene- $\beta_1\beta_2$ (from CD₃I, 99.6% D, Aldrich Chemical Co.), and from styrene- β -¹³C¹³ (from ¹³CH₃I, 99.7% ¹³C, MSD Isotopes). The azidostyrene- d_5 2f was prepared from benzene- d_6 (99.96% D, Aldrich Chemical Co) by acetylation with acetic anhydride,¹⁴ NaBH₄ reduction,¹⁵ and then dehydration.¹³ The labeled styrenes were analyzed as their (1,2-dibromoethyl)benzene derivatives by 200-MHz ¹H NMR and high-resolution mass spectrometry. Nitrogen (99.998%, Pacific Oxygen Sales) was used without purification.

Results

The reversible phototautomerization of phenylazirine la (PA) to its nitrile ylide was studied in N2 matrices by Fourier transform infrared spectroscopy. In order to determine the structure of the nitrile ylide, the effects of several isotopic substitutions on its infrared absorption frequencies were examined. In this section we will describe the wavelength dependency of product absorption growth and the isotope-induced shifts of the nitrile ylide absorption bands.

Access to the azirine-nitrile ylide system is available either directly by depositing phenylazirine or indirectly by photolyzing matrix isolated azidostyrene 2a (AS) in which case a second, nonphotochromic product also appears. For the isotope-labeling studies, we found that synthetic considerations necessitated the use of the azidostyrene method.

Matrix Photolysis of Phenylazirine 1a (PA). The spectrum of phenylazirine in N_2 at 12 K is shown in Figure 2A. All of the significant absorption frequencies were readily associated with spectral features assigned to PA in room-temperature solution spectra. After 2.5 h of photolysis through a 250-nm band-pass filter, the PA spectrum diminished by 95% and a new spectrum

- (1) Padwa, A.; Carlsen, P. H. J. In Reactive Intermediates; Abramovitch,

- (a) Cataliella, F., Houk, K. N. J. Am. Chem. Soc. 1976, 95, 0597.
 (b) Carmella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. J. Am. Chem. Soc. 1977, 99, 385.
 (c) Houk, K. N. Top. Curr. Chem. 1979, 79, 2.
 (f) Padwa, A. Acc. Chem. Res. 1976, 9, 371 and references therein.
 (g) Janulis, E. P.; Wilson, S. R.; Arduengo, A. J. Tetrahedron Lett. 1984,
- 25. 405.
- (7) Wentrup, C.; Fischer, S.; Berstermann, H.-M.; Kuzaj, M.; Luerssen, H.; Burger, K. Angew. Chem., Int. Ed. Engl. 1986, 25, 85. (8) (a) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heinzelmann, W.
- *Helv. Chim. Acta* 1975, 58, 2662. (b) Sieber, W.; Gilgen, P.; Chaloupka, S.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* 1973, 56, 1679.
- (9) Chapman, O. L.; LeRoux, J.-P. J. Am. Chem. Soc. 1978, 100, 282.
 (10) Collins, S. T., Pimentel, G. C. J. Phys. Chem. 1984, 88, 4258.
- (11) Hortmann, A. G.; Robertson, D. A.; Gillard, B. K. J. Org. Chem. 1972, 37, 322.
- (12) Yoshino, T.; Manabe, Y.; Kikuchi, Y. J. Am. Chem. Soc. 1964, 86, 4670
- (13) Gilson, T. R.; Hollas, J. M.; Khalilipour, E.; Warrington, J. V. J. Mol. Spectrosc. 1978, 73, 234.
- (14) Adams, R.; Noller, C. R. In Organic Syntheses; Gilman, H., Blatt,
- A. H., Eds.; Wiley: New York, 1941; Collect. Vol. I, p 109.
 (15) Schlesinger, H. I.; Brown, H. C.; Hoekstra, H. R.; Rapp, L. R. J. Am. Chem. Soc. 1953, 75, 199.

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Figure 1. Structures of phenylazirine 1 and azidostyrene 2 showing positions of isotopic enrichment compounds 3–8 and C_8H_7N candidate nitrile ylide structures.



Figure 2. Spectra of 12 K N_2 matrices: (A) phenylazirine 1a (absorption marked X is due to H₂O impurity); (B) difference product spectrum from 250-nm photolysis of phenylazirine 1a: (C) difference spectrum showing regeneration of phenylazirine 1a by 350-nm photolysis of the matrix shown in 2B.

grew in as shown in the difference spectrum in Figure 2B. The frequencies and relative intensities of these new features are listed in Table I. Their uniform growth behavior suggests that they are due to a single product, the nitrile ylide. A subsequent irradiation for 21 h through a 350-nm band-pass filter caused the ylide features to decrease by 95% in intensity and the PA absorptions to reappear (see Figure 2C). These changes were, then, completely reversible except for a loss of a few percent per cycle and the slow accumulation of a third product K characterized by absorptions at 2049.9 and 2029.4 cm⁻¹.

Matrix Photolysis of Azidostyrene 2a (AS). After 10 min of photolysis with the unfiltered Hg arc, the infrared spectrum revealed the loss of all the parent AS and a product spectrum

TABLE I: Absorptions of Unlabeled (d_0) , Monodeuterated (d_1) , and Dideuterated (d_2) Nitrile Ylides from the Photolysis of the Corresponding Labeled Azidostyrenes 2a, 2c, and 2d in 12 K N₂ Matrices

d_0/cm^{-1}	rel int."	d_1/cm^{-1}	rel int. ^a	d_2/cm^{-1}	rel int. ^a
605.2	(100)	561.7	13		·
		603.4	(100)	604.2	(100)
694.3	91* ^b	653.4	27		
770.8	42*	657.7	29	694.1	35*
773.2	34*	768.4	44*		
785.7	67*	770.5	36*		
		785.2	72*	782.6	46*
930.4	3*			896.4	9
1002.0	6*	931.6	9*		
1027.5	5*	1003.4	5*	1004.3	7*
1073.1	27	1027.5	7*	1029.0	8*
1114.3	44	1073.6	18	1071.9	29
		1113.8	14		
				1153.4	9
1270.9	14				
1287.8	9	1270.3	13		
1308.0	6			1289.6	30
1367.7	8			1337.1	9
1374.9	5				
1449.5	7*	1449.7	15*	1449.7	15*
1496.2	9	1493.5	18*	1493.5	9*
1569.3	6				
1580.7	19*	1580.8	29*	1580.8	16*
1597.4	11*				
1873.4	9	1870.4	7	1870.6	7
1885.2	16			1888.0	50
1896.6	14			1898.8	62
1903.3	30	1908.0	98		
1926.2	80	1926.3	17		
				1948.3	15
				2010.1	5
				2024.8	3
				2205.2	5

^a Intensities are peak optical densities normalized to the most intense feature in the spectrum. ^bAsterisks (*) indicate bands which appear as positive features superimposed on negative features of disappearing parent bands.

identical with that of the ylide as listed in Table I and as shown in Figure 2B, except for a weak absorption at 1746.2 cm⁻¹ (revealing that a few percent of the product was in the form of PA), and new features at 2049.7, 2029.5, 1597.4, 1494.0, and 763.1 cm⁻¹ attributable to product K.

Subsequent photolysis of this sample for 26 h through the 350-nm filter caused the ylide features to diminish gradually with concomitant growth of the PA spectrum (see Figure 2A). Thus, we verified⁹ that azidostyrene can serve as a precursor to the azirine-ylide photochromic pair and, in addition, that species K is produced in both the AS photolysis and during the interconversion of the ylide and PA.

Matrix Photolysis of Isotope-Labeled Azidostyrenes 2b-f. Each of the isotope-labeled azidostyrenes 2b-f ($\leq 99\%$ isotope enrichment except for the ¹⁵N isotope which contained ca. 48% ¹⁵N/52% ¹⁴N, see Experimental Section) was irradiated in N₂ at 12 K as described above for the azidostyrene 2a. The absorptions due to the corresponding labeled ylide species are listed in Tables I and II. Interconversion of the isotope-substituted PA and ylide phototautomers by filtered irradiation (vide ante) showed that in each case the absorptions attributed to a labeled ylide in Tables I and II displayed the same uniform kinetic growth and reversible photolysis behavior. For each isotope the absorptions due to the labeled product K species were unequivocally distinguished by their lack of photochromic behavior and are not included in Table I or Table II.

Discussion

The spectra of the several isotopic molecules provide a strong basis for determining the structure of the ylide, long a subject of controversy and ambiguity. Two spectral regions are of special interest: the region near 1900 cm^{-1} where a variety of triple

TABLE II: Absorptions of ¹⁵N-Labeled (¹⁵N), ¹³C-Labeled (¹³C), and Perdeuteriophenyl-Labeled (d_5) Nitrile Ylides from the Photolysis of the Corresponding Labeled Azidostyrenes 2b, 2e, and 2f in 12 K N₂ Matrices

$^{15}N/cm^{-1}$	rel int.ª	$^{13}C/cm^{-1}$	rel int.ª	$d_{5}/{\rm cm}^{-1}$	rel int.ª
				537.7	20
				542.5	15
599.9	75			592.0	18
604.8	67	604.2	(100)	595.2	62
		684.5	37	687.8	24
689.0	67	688.8	27*	691.9	19
694.1	(100)* <i>^b</i>	694.3	73*		
770.8	46	770.8	34*	746.7	45
773.2	38	773.2	34		
785.5	85*	784.5	39	818.5	14*
		786.7	34	836.6	29*
930.6	6*	930.0	4*	960.0	12*
1002.0	12*	1001.8	9*		
1027.5	10*	1027.1	10*	1035.2	12*
1073.1	30	1072.2	24	1083.2	29*
1114.6	43	1108.5	42		
1270.3	15	1269.2	18	1261.1	11*
1286.9	7	1305.1	5	1287.2	25
1366.3	10	1355.8	6	1324.3	15
1374.0	7	1361.9	6	1365.3	3
				1542.7	21*
		1448.9	11*		
1496.2	12	1494.0	20*		
1570.0	6				
1580.6	23*	1582.5	22*		
				1597.2	13
1860.0	37			1851.3	5
1872.8	14	1869.0	13		
1885.6	13	1881.8	13		
1895.2	11	1889.5	14		
1903.6	21	1901.8	25		
1910.1	16			1911.5	(100)
1926.3	48	1920.3	75		

^a Intensities are peak optical densities normalized to the most intense feature in the spectrum. ^bAsterisks (*) indicate bands which appear as positive features superimposed on negative features of disappearing parent bands.

bonded and cumulene structures display characteristic absorptions and the region $800-500 \text{ cm}^{-1}$ where cumulene structures have characteristic bending modes. The upper region is complicated somewhat by multiplet structures that we are able to associate with Fermi resonance. The low-frequency region is made difficult to interpret by the presence of characteristically intense absorptions of the aromatic unit. We will discuss these in turn.

In overview, the product of photolysis of phenylazirine in N_2 exhibits 24 distinct and reproducible absorptions (see Figure 2). Eleven of these bands have frequencies and intensities attributable to and highly characteristic of vibrational modes of a monosubstituted benzene ring system.¹⁶ None of these bands is shifted by isotope substitutions on the azirine ring, and many of them are within one or two wavenumbers of the corresponding vibrations in the phenyl group of the phenylazirine photoisomer. Therefore, these absorptions appear in the difference spectra as positive features superimposed on the negative features of the disappearing parent bands.

We can identify bands in the range $1600-1500 \text{ cm}^{-1}$ as predominantly aromatic ring stretching motions (1597.4, 1580.9, 1496.2, and 1449.5 cm⁻¹) and those near 1110-1070 cm⁻¹ as largely aromatic in-plane C-H deformations (1073.1, 1114.3, 1027.5, and 930.4 cm⁻¹), while the region near 770-730 cm⁻¹ is where monosubstituted aromatic out-of-plane deformations fall (785.7, 773.2, 770.8, and 694.3 cm⁻¹). Assuming no photofragmentation, this leaves C₂H₂N as the substituent of the aromatic ring.

The 1800-2200-cm⁻¹ Spectral Region. The strong absorption at 1926.2 cm⁻¹ falls within the spectral region encompassing



Figure 3. Difference spectra in the 1825-1975-cm⁻¹ regions for (A) unlabeled (d_0) , (B) ${}^{15}N/{}^{14}N$ -labeled $({}^{15}N/{}^{14}N)$, (C) monodeuterated (d_1) , (D) dideuterated (d_2) , (E) ${}^{13}C$ -labeled $({}^{13}C)$, and (F) pentadeuteriophenyl-labeled (d_5) azirine photolysis products.

absorptions of triply or cumulatively bonded structures such as $C \equiv N$, C = C = N, and $^{-}C = ^{+}N = C$. Figure 1 presents six structures of molecules which could plausibly be associated with the 1926.2-cm⁻¹ feature. Each structure consists of a phenyl group with a multiply bonded C_2H_2N substituent. Two other such structures not shown, benzyl cyanide and benzyl isocyanide, can be dismissed on the basis of their well-known infrared spectra, most notably by the absence of their intense features, respectively, at 2250¹⁷ and 2150¹⁸ cm⁻¹.

Figure 3A shows the ylide spectrum in the region near 1900 cm^{-1} The most prominent feature at 1926.2 cm^{-1} is accompanied by satellites, listed in the order of decreasing intensity, at 1903.3, 1885.2, and 1873.4 cm^{-1} . These weaker features complicate the interpretation of the spectrum. Such a pattern might be due to multimers, various sites, different molecular species, or Fermi resonance between fundamental and combination modes. The four features seen in Figure 3A show uniform kinetic growth and photolysis behavior, which tend to disfavor the third explanation, more than one product contributing to the spectrum.

The spectrum of the monodeuterated species produced by the photolysis of the azidostyrene 2c in a N₂ matrix gives substantial evidence regarding the origin of the 1926.2-cm⁻¹ band splitting. As is clear from Figure 3C, the single deuterium label has eliminated the multiplet splitting seen in Figure 3A, reducing it to a single strong absorption at 1908.0 cm⁻¹. This result indicates that neither multimer clusters nor different site environments cause the splitting since the monodeuterated compound would be equally susceptible to these effects. The possibility of different molecular species contributing to the spectrum is still more unlikely in view of the uncomplicated monodeuterated spectrum.

The spectrum of the perdeuteriophenyl ylide (see Figure 3F) corroborates this result. The 1911.5-cm⁻¹ absorption is not accompanied by significant features nearby, again disfavoring multimer clusters, different site environments, or different molecular species. We conclude that the multiplets near 1900 cm⁻¹ seen in Figure 3 parts A, B, D, and E are due to Fermi resonance.

Further insight into the structure of the ylide is gained from the spectrum of the monodeuterated counterpart. Monodeuteration of structures 4 and 6 (Figure 1) which do not have geminal hydrogens would result in the D label being distributed approximately equally between the two nonequivalent positions. This would give rise to two skeletal stretching frequencies in the

⁽¹⁶⁾ Bellamy, L. J. The Infrared Spectra of Complex Molecules; Chapman and Hall: London, 1975; pp 72-96.

⁽¹⁷⁾ Pouchert, C. J. The Aldrich Library of Infrared Spectra; Aldrich: Milwaukee, 1975; p 970.

⁽¹⁸⁾ Unpublished observation from this laboratory: benzyl isocyanide exhibits a strong absorption at 2134.9 cm⁻¹ in a 12 K Ar matrix.

TABLE III: Asymmetric Stretching Mode Fermi Resonance Coincidences (cm⁻¹)

isotope	CNCD ₂	CNCH ₂	CN ¹³ CH ₂	C ¹⁵ NCH ₂	D ₅ CNCH ₂	CNCHD
obsd [°] ν's	1898.8	1926.2	1920.3	1860.0	1911.5	1908.0
	1888.0	1903.3	1901.8	1872.8		
unperturbed v	1893.4	1914.7	1911.2	1866.4	1911.5	1908.0
closest combination	1289.6	1308.0	1305.1	1270.3	1324.3	1295.6
	604.2	605.2	604.2	599.9	595.2	603.4
	1893.8	1913.2	1909.3	1870.2	1919.5	1899.0
discrepancy, $\Delta \nu$	+0.4	-1.5	-1.9	+3.8	+8.0	-9.0

1900-cm⁻¹ region and would also imply two different C-H and two different C-D bending absorptions. The data in Table I do not support these expectations, the most distinctive evidence probably being the single skeletal absorption band at 1908.0 cm⁻¹. Thus, we can eliminate two of the possible structures, 4 and 6, in Figure 1.

In addition to 3-phenyl-2H-azirine, N-phenylketenimine (7 in Figure 1) has been reported to be a product of the pyrolysis¹⁹ but not the photolysis^{9,20} of azidostyrene. We have, however, identified product K (absorptions at 2049.9, 2029.4, 1597.4, and 1494.0 cm^{-1}) from the photolysis of azidostyrene **2a** in a 12 K N₂ matrix as N-phenylketenimine. We base this assignment on both the comparison of the matrix values with those published for 7 in a room-temperature solution spectrum (2040, 2020, 1600, 1500, and 700 cm⁻¹)²¹ and on the agreement of the small ($\Delta \nu = 16.1$ and 14.7 cm⁻¹) observed ¹⁵N isotope shifts of the asymmetric stretching vibrations at 2049.9 and 2029.4 cm^{-1} with the ¹⁵N shift $(\Delta \nu = 12 \text{ cm}^{-1})$ calculated by a diatomic approximation in which the combined masses of the terminal atoms (C and N) vibrate against that of the central atom (C).

The ketenimine structure 8 in Figure 1 also contains the C= C=N vibrational chromophore. Therefore, it, too, is expected to experience only a small $^{15}\mathrm{N}$ isotope shift of its asymmetric stretching absorption (calculated $\Delta \nu = 12 \text{ cm}^{-1}$). The observed shift of the 1926.2-cm⁻¹ feature to 1860.0 cm⁻¹ for the ¹⁵N-labeled species is much too large to accommodate a ketenimine structure. The ¹³C spectrum (see Figure 3E) provides decisive confirmation. The central carbon position associated with a ketenimine structure would show a large ¹³C shift (calculated $\Delta v = 51 \text{ cm}^{-1}$), whereas the major peak at 1920.3 cm⁻¹ is only 6 cm⁻¹ below the corresponding absorption of the unlabeled ylide. Finally, structure 8 implies the presence of prominent N-H bending absorptions in the 1400- and 700-cm⁻¹ regions which would undergo marked ¹⁵N and D shifts.¹⁰ Thus, the data in Tables I and II rule out structure 8 as a candidate for the ylide structure.

To distinguish between structures 3 and 5 in Figure 1, we compare the observed ¹⁵N isotope shift ($\Delta \nu = 66.2 \text{ cm}^{-1}$) to the shifts calculated by diatomic approximations of each structure. The allene-like structure 3 would absorb near 1900 cm⁻¹ due to its asymmetric skeletal stretch for which the diatomic approximation combines the masses of the two carbon atoms as they vibrate together against the mass of the nitrogen atom. In contrast, for the propargyl-like structure 5, the triply bonded $C \equiv N$ stretch is the relevant motion, and its diatomic approximation simply involves the masses of C and N. In this fashion, we calculate ¹⁵N shifts of 42 cm⁻¹ for the allene-like structure **3** and only 30 cm⁻¹ for the nitrile structure 5. For the latter case, the calculated contribution of the N atom to the reduced mass of the C=N=C vibration is substantially smaller than observed. We conclude that structure 5 cannot be responsible for the observed ^{15}N isotope shift of 66.2 cm⁻¹.

In contrast, the significant discrepancy between the observed (66.2 cm^{-1}) and calculated $(42 \text{ cm}^{-1})^{15}$ N shifts for the allene-like structure 3 is reasonably attributed to Fermi resonance splitting (see Figure 3B) of the asymmetric skeletal stretch. To a first approximation this causes the fundamental to split into two bands, 1926.2 and 1903.3 cm⁻¹, equally shifted from the position the band would occupy in the absence of the Fermi resonance (near 1915 cm⁻¹). The spectrum of the perdeuteriophenyl ylide is in accord.

The asymmetric stretch of the ylide group is not expected to be noticeably affected by the phenyl deuteration. Hence, the 1911.5-cm⁻¹ singlet absorption of the d_5 ylide provides an estimate of the asymmetric stretching frequency in the absence of Fermi resonance. Turning to the ¹⁵N-labeled ylide molecule, in the absence of Fermi resonance, its fundamental would appear at about 1866 cm⁻¹, roughly equidistant from the observed 1872.8and 1860.0-cm⁻¹ features. Therefore, the ¹⁵N isotope shift is expected to consist of a contribution of about 42 cm⁻¹ calculated for the ¹⁵N reduced mass plus Fermi resonance shifts that add about $17-20 \text{ cm}^{-1}$ to the spacing. This is in quite good agreement with the observed 66-cm⁻¹ shift.

The dideuterated ylide's isotopic shift can be approximated by assuming that the deuterium atoms merely add to the mass of the terminal carbon atom. With this approximation, the shift in the asymmetric stretch should be about 24 cm⁻¹. Taking the average of the 1898.8/1888.0-cm⁻¹ Fermi doublet seen in Figure 3D, we obtain a frequency of 1893 cm⁻¹, shifted 22 cm⁻¹ from 1915 cm^{-1} .

The same approximation implies that the asymmetric stretching frequencies of the monodeuterio- and ¹³C-labeled ylides should be about equal and shifted ca. 13 cm⁻¹. Indeed, their frequencies are about the same (see Figure 3 parts C and E) but display somewhat smaller shifts than predicted.

We conclude that the splittings observed in the 1900-cm⁻¹ spectral region are due to Fermi resonance and that all of the isotopic data are in accord with a linear heterocumulene skeleton with double bonds of approximately equal strength and with the nitrogen atom in the center position. Furthermore, the apparent equivalence of the methylene hydrogens (as shown by the monodeuterated ylide spectrum) is consistent with the presence of a molecular plane of symmetry (C_S) defined by the phenyl group and the cumulene skeleton.

Of course, the postulate of Fermi resonance implies the existence of a near resonance between the fundamental asymmetric cumulene stretching vibration and a combination or overtone. Table III lists, for each isotope, the closest such combination. In each case, the location of the unperturbed stretching vibration is taken to be the average of the two most prominent features of the multiplet. The last row shows the discrepancy between the unperturbed stretching frequency and the closest resonance, listed in order of increasing discrepancy. There are two reassuring aspects of this comparison. First, the closest resonance, 0.4 cm⁻¹ for the dideuterio isotope, occurs for the molecule whose doublet features are most nearly equal in intensity. Second, the two isotopes with the largest discrepancies (poorest resonance) are the pentadeuterio and the monodeuterio isotopes, neither of which displays any multiplet splitting.

Earlier evidence about the structure of nitrile ylides comes from inferences based on product preferences and reactivities with dipolarophiles.⁵ There have also been several theoretical calculations at various levels of approximation.⁴ Padwa and Carlsen review these arguments well and point out the remaining disagreement and uncertainty.¹ There seems to be a consensus that the possible structures 4 and 6-8 in Figure 1 can be ruled out on chemical grounds. This conclusion is definitively corroborated here for the nitrile ylide formed photolytically from phenylazirine 1a. However, in earlier work, structures 3 and 5 have not been clearly differentiated. In fact, it is not uncommon to see these presented as resonant forms,9 despite the fact that they suggest different geometries. We believe that the data presented here remove this ambiguity. The isotopic shifts clearly place the nitrogen atom in the center of a linear skeletal structure, and they

⁽¹⁹⁾ Smolinsky, G. J. Org. Chem. 1962, 27, 3557.
(20) Hassner, A.; Fowler, F. W. J. Am. Chem. Soc. 1968, 90, 2869.
(21) Winter, H.-W.; Wentrup, C. Angew. Chem. 1980, 92, 743.



Figure 4. Difference spectra in the 800-500-cm⁻¹ regions of the (A) unlabeled and (B) pentadeuteriophenyl-labeled nitrile ylides.

require almost equal contribution of the terminal atoms to the reduced mass. The latter deduction implicitly requires that the two skeletal force constants be almost identical. Clearly, these conclusions describe the allene-like structure 3, and they are not compatible with the propargyl-like structure 5.

The 800-500-cm⁻¹ Spectral Region. The region below 800 cm⁻¹ contains, for every isotopic molecule studied, two of the three most intense features in the spectrum (the third being the 1900-cm⁻¹ absorption). This region is expected to contain two characteristic out-of-plane hydrogen motions of a monosubstituted aromatic structure.¹⁶ Usually, the more prominent of these is an intense feature in the range 770-730 cm⁻¹ accompanied by a second, somewhat less intense feature in the range 710-690 cm⁻¹. Fluorobenzene provides an example, with intense gas-phase absorptions at 754 and 689 cm⁻¹ that shift to 624 and 553 cm⁻¹ on perdeuteration.²² The combined deuteration shift, 1.50, shows that both absorptions are associated with out-of-plane hydrogen motions.

In our spectra, the two features at 785.7 and 694.3 cm⁻¹ are obvious candidates for this assignment. Both features are quite intense and, when the aromatic ring is perdeuterated, 785.7 cm^{-1} shifts to 746.7 cm⁻¹ while the 694.3 cm⁻¹ feature loses much of its intensity and a new absorption appears at 537.7 $\rm cm^{-1}$ (see Figure 4). In all of the other isotopic molecules studied, both the 785- and 694-cm⁻¹ features remain intense and unshifted. Thus, the perdeuterated aromatic molecule shows that there is both an aromatic and another absorption in the spectral region near 694 cm⁻¹.

The cumulene skeleton has two skeletal bending modes which are doubly degenerate in the isoelectronic triatomic counterparts, CO_{21} , N_3^- , NCO^- , and N_2O (whose absorptions fall, respectively, at 667,²³ 645,²⁴ 657,²⁵ and 589²⁶ cm⁻¹). Adding a terminal CH_2 ,

(23) Herzberg, G. Infrared and Raman Spectra; Van Nostrand Reinhold: (25) Herzberg, G. Infrared and Raman Spectra, van Rostrand Reinhold.
New York, 1945; p 272.
(24) Papazian, H. A. J. Chem. Phys. 1961, 34, 1614.
(25) Maki, A.; Decius, J. C. J. Chem. Phys. 1959, 31, 772.
(26) Smith, D. F.; Overend, J.; Spiker, R. C.; Andrews, L. Spectrochim.

as in ketene and diazomethane, adds a plane of symmetry and in-plane and out-of-plane CH₂ motions. The in-plane wag tends to occur at frequencies above 800 cm⁻¹ (ketene, 977 cm⁻¹; diazomethane, 1109 cm⁻¹), so this places a third vibrational mode, the CH₂ out-of-plane motion, in the low-frequency region. Thus, ketene in a N_2 matrix has a strong absorption at 591 cm⁻¹ due to the CH₂ out-of-plane mode that shifts to 432 cm⁻¹ on deuteration.²⁷ The out-of-plane skeletal mode for H₂CCO absorbs very strongly at 525 cm⁻¹ and shifts upward on deuteration to 542 cm^{-1} as the CH₂ mode crosses to lower frequency. For this molecule, the in-plane skeletal bend is found at 432 cm⁻¹, shifting to 371 cm⁻¹ on deuteration. The pattern is rather different for diazomethane. For H₂CNN the out-of-plane skeletal bend is the highest frequency, 564 cm⁻¹, and it shifts only to 528 cm⁻¹ on deuteration.²⁸ The out-of-plane hydrogen bend falls at much lower frequency, 427 cm⁻¹ in a N₂ matrix, and it shifts to 338 cm⁻¹ on deuteration. This low frequency is found to be due to quartic anharmonicity associated with relatively stable nonplanar conformations. The in-plane skeletal bend is at 420 cm⁻¹ (N_2 matrix) and shifts to 380 cm⁻¹ on deuteration.

Our spectra are dominated by a low-frequency absorption near 605 cm⁻¹. It might be analogous to the out-of-plane skeletal mode of ketone since it is shifted only 2 cm⁻¹ by deuteration, while ¹⁵N substitution causes a 5-cm⁻¹ downward shift. The out-of-plane CH₂ vibration is probably associated with the second absorption near 694 cm⁻¹ (at 689.0 cm⁻¹) which apparently shifts to 561.7 cm^{-1} upon monodeuteration and to 544 cm^{-1} on dideuteration. The in-plane skeletal mode might be associated with the absorptions at 657 cm⁻¹ shown by both the mono- and dideuterio molecules.

This assignment of the 605-cm⁻¹ feature attributes a rigidity to the cumulene skeleton close to that of N_2O (with bending frequency 589 cm⁻¹), and it places the out-of-plane CH₂ motion (689 cm⁻¹) at higher frequency than that observed either for ketene²⁷ or diazomethane²⁸ (591 and 427 cm⁻¹, respectively). We consider the remaining skeletal bending mode to be not well established in the absence of spectra below about 440 cm⁻¹.

In summary, the spectral absorptions below 800 cm⁻¹ are reasonably consistent with expectations based upon structure 3 (Figure 1) and the well-understood spectra of its several prototypes.

Conclusion

The infrared spectra of the nitrile ylides derived from phenylazirine 1a and its five isotope-labeled counterparts provide ample evidence to conclude that the nitrile ylide structure is associated with a linear, allene-like skeleton in which the nitrogen atom occupies the center position. This conclusion is deduced from an analysis of the isotopic shifts indicating that the two force constants of the heterocumulene (C=N=C) skeleton are approximately equal. In addition, the observation²⁹ that no new infrared absorptions appear on warming the nitrile ylide in xenon from 12 to 82 K suggests that the allene-like geometry is also adopted in solution where nitrile ylides are postulated as 1,3-dipolar reactive intermediates.

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- (28) Moore, C. B., Pimentel, G. C. J. Chem. Phys. 1963, 38, 2816.
- (29) Unpublished observation from this laboratory.

⁽²²⁾ Lipp, E. D.; Seliskar, C. J. J. Mol. Spectrosc. 1978, 73, 290.

Acta Part A 1972, 28A, 87.

⁽²⁷⁾ Moore, C. B.; Pimentel, G. C. J. Chem. Phys. 1964, 40, 342.