Gaseous 3,4-Pyridyne and the Formation of Diazabiphenylene

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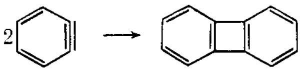
Abstract: Flash photolysis of pyridine-3-diazonium-4-carboxylate appears to yield 3,4-pyridyne (3,4-dehydropyridine) which dimerizes to diazabiphenylene in the gas phase. The rate of dimerization, measured by time-of-flight mass spectroscopy of the product, is approximately 1.3×10^9 l. mol^{-1} sec^{-1}, comparable to the reported rates of dimerization of benzyne. The dimer has been characterized by high-resolution mass spectrometry and infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. Fragmentation reactions of pyridyne and its dimer are analyzed in terms of the observed kinetics and products and the thermochemistry of the system.

Within the past decade, new precursors of benzyne made possible the generation of gaseous benzyne as well as allowing use of new solvents for studying solution reactions of benzyne. In this same period interest in hetarynes (dehydroheterocycles) bloomed. However, the vast majority of hetaryne studies were concerned with solution reactions.[1]

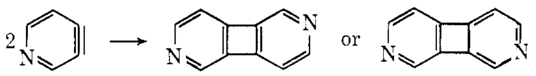
The intent of this work has been the study of gas-phase reactions and properties of the hetaryne, 3,4-pyridyne. We pursue the opportunity to compare the chemistry of benzyne and 3,4-pyridyne; the differences are many, but hopefully these differences will be clearer within the framework of a benzyne model than outside.

The principal reaction of gaseous benzyne is dimerization to form biphenylene, an example of a 1,2 cycloaddition.



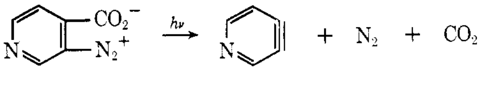
(1)

The analogous reaction of 3,4-pyridyne leads to the formation of 2,6- and/or 2,7-diazabiphenylene, one member of a heretofore unknown series of compounds.



(2)

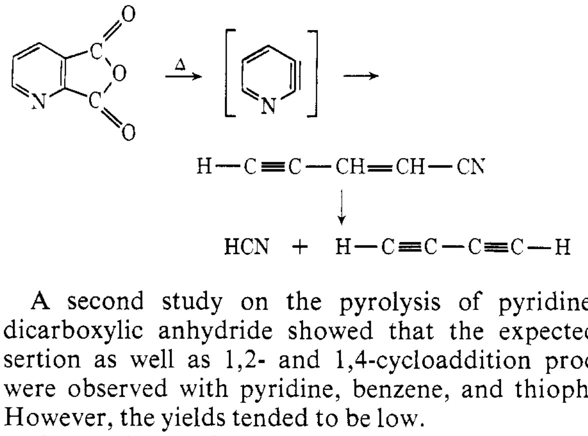
Pyridine-3-diazonium-4-carboxylate[2] was chosen as a precursor of 3,4-pyridyne. Gaseous 3,4-pyridyne was generated by flash photolytic decomposition.



(3)

This precursor seemed especially well suited for observing the 1,2 cycloaddition of 3,4-pyridyne with itself to form diazabiphenylene. In solution, cycloadditions to pyridyne are limited in number, in contrast to benzyne chemistry. Yet, in solution, with pyridine-3-diazonium-4-carboxylate as a precursor, the Diels–Alder cycloaddition between 3,4-pyridyne and furan[2] and the 1,2 cycloaddition between cyclopentadiene and 3,4-pyridyne[3] proceeded in relatively good yield.

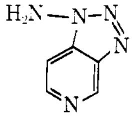
The first example of a gas-phase reaction of pyridyne was the thermolytic fragmentation of pyridine-2,3-dicarboxylic anhydride.[4] The reaction was proposed as proceeding through a 2,3-pyridyne intermediate which decomposed to β-ethynylacrylonitrile (8.4% yield). A substantial quantity of HCN was formed in the reaction and it was proposed that the HCN was a product of the decomposition of the β-ethynylacrylonitrile.



(4)

A second study on the pyrolysis of pyridine-2,3-dicarboxylic anhydride showed that the expected insertion as well as 1,2- and 1,4-cycloaddition products were observed with pyridine, benzene, and thiophene.[5] However, the yields tended to be low.

That neither of the above studies detected the dimerization product can probably be rationalized by such factors as thermal instability of the dimerization product, preferential reactions of the pyridyne intermediate, etc. As potential precursors of diazabiphenylenes, 1-aminotriazolo[4,5-*c*]pyridine (I) and 3-aminotriazolo[4,5-*b*]pyridine (II) were prepared.[6] Treatment in solution with lead tetraacetate in the presence of tetracyclone yielded the expected addition products of 3,4-pyridyne (63%) and 2,3-pyridine (4%). The authors stated that the reactions of the pyridyne precursor were being investigated in the absence of tetracyclone, but no further reports of a diazabiphenylene have appeared.



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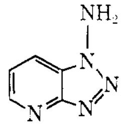

II

The study reported here attempts to explore the previously little-known gas-phase reactions of pyridyne.

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[1] For a general discussion of aryne chemistry, see R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967.

[2] T. Kauffmann and F. P. Boettcher, *Chem. Ber.*, **95**, 949 (1962).

[3] T. Kauffmann, J. Hansen, K. Udluft, and R. Wirthwein, *Angew. Chem., Int. Ed. Engl.*, **3**, 650 (1964).

[4] M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Lett.*, **26**, 2947 (1966).

[5] E. K. Fields and S. Meyerson, *Advan. Phys. Org. Chem.*, **6**, 1 (1968).

[6] G. W. J. Fleet and I. Fleming, *J. Chem. Soc. C*, 1758 (1969).

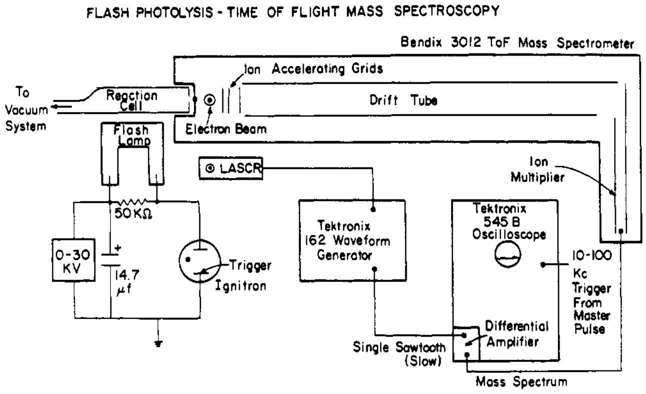

Figure 1. Schematic representation of time-of-flight mass spectrometer and coupled flash photolysis system.

The experimental methods employed in this research were principally time-of-flight mass spectroscopy and kinetic ultraviolet spectroscopy. Preliminary results of this study have been reported in a communication.[7]

Experimental Section

A. **Pyridine-3-diazonium-4-carboxylate.** Pyridine-3-diazonium-4-carboxylate was prepared in a five-step synthesis from the commercially available 3,4-dicarboxypyridine (Aldrich Chemical Co.). The 3-amino-4-carboxypyridine intermediate was prepared using the syntheses of Crum and Fuchsman.[8] The only modification involved the Hofmann degradation of the imide to the amino acid. The intermediate in this reaction, an isocyanate, when heated in a basic solution was converted to an amine. It proved important to have sufficient excess of base at the time of heating to maintain basic conditions until the amine has formed. Addition of glacial acetic acid to neutralize the solution after cooling gave the desired product. The preparation of pyridine-3-diazonium-4-carboxylate from 3-amino-4-carboxypyridine followed the syntheses of Kauffmann and Boettcher.[2]

B. **Time-of-Flight Mass Spectroscopy.** Time-of-flight mass spectra were obtained with a Bendix 3012 time-of-flight mass spectrometer (ToF). The only modification of the standard equipment was removal of a pumping baffle to obtain the maximum pumping speed (100 l./sec) of the diffusion pump. Reactions were initiated by an intense burst of radiation from a flash lamp. Time resolution of the reaction has been described previously.[9] Flash power was supplied by a 14.7-μF capacitor, typically charged to 10 kV. An ignitron trigger activated the flash lamp, which then turned on a slow sawtooth by photon action on a light activated, silicon controlled rectifier (LASCR). A schematic diagram of the apparatus is shown in Figure 1.

Three different reaction cells, shown in Figure 2, were employed. The cylindrical direct inlet system of the ToF was fitted with a cylindrical brass tube whose end held an aperture opening into the ion source of the spectrometer. Sample cells (2a and 2b) were held by O-ring fittings in the brass cylinder; they extended out beyond the spectrometer and were connected to a vacuum system by an O-ring fitting. A sample of pyridine-3-diazonium-4-carboxylate in water was deposited on the part of the tube exposed to the flash lamp. Prior to photolysis, the water was pumped away. The simplest cell was the straight tube, shown in Figure 2a. A variation of the straight tube reaction cell is one shaped like a coaxial trap, Figure 2a The bottom of the "trap" is open and allows molecules to effuse through the pinhole aperture into the spectrometer. The center tube is quartz beyond the "trap" and serves as a reaction cell.

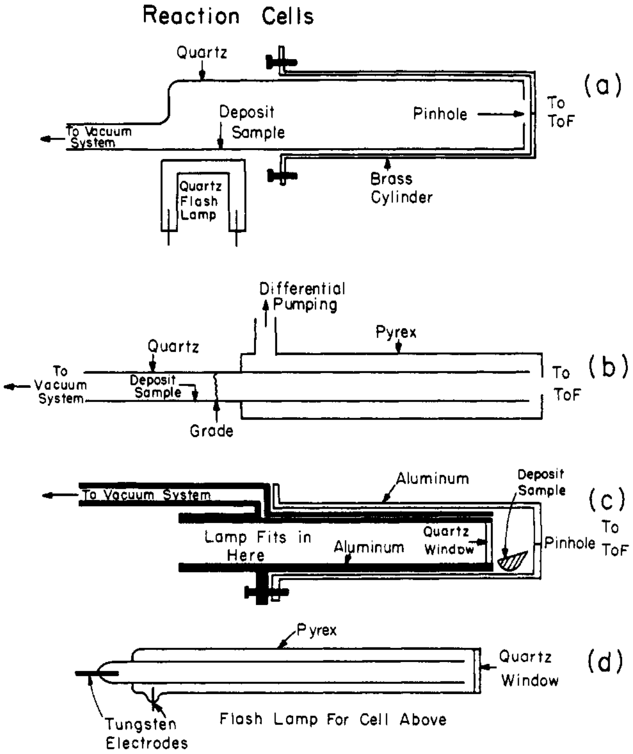

Figure 2. Reaction cells for flash photolysis monitored by time-of-flight mass spectrometer: (top) simple system, similar to that of ref 9; (middle) system with differential pumping; (bottom) system similar to that of ref 10, for photolysis near pinhole.

A third cell, as shown in Figure 2c, was adapted from one designed by Meyer.[10] In essence it consists of a clear quartz plate perpendicular to the cylinder axis and near the pinhole. A coaxial flash lamp is used to photolyze the reactant on a small piece of raised quartz. The sample is approximately 2 mm from the pinhole.

C. **Kinetic Ultraviolet Spectroscopy.** The essentials of the apparatus for kinetic ultraviolet spectroscopy have been described previously.[11] Absorption spectra were recorded on Kodak 103-O, 103-F and Spectrum Analysis No. 1 photographic plates, with a Hilger medium dispersion spectrograph. The electronic circuitry is similar to that described for the ToF mass spectroscopy work.

Three exposures (with a neutral density step wedge) were generally recorded on a photographic plate. First, to establish the background comparison, the spectral source was recorded. The second exposure recorded the decrease in transmission due to whatever species were present, reaction intermediates and/or products, at a preselected time after the reaction was initiated. The spectral source was then recorded again about 15–20 sec later to determine the extent of reaction.

The wavelengths of spectral lines were determined by interpolation between known wavelengths in the iron spectrum. Plate densities were measured with a recording microdensitometer. Intensity ratios were determined from plate densities corrected for the nonlinear response of the spectrographic plates.

D. **End Product Studies.** Samples for product analysis work were photolyzed in a quartz cell connected through a vacuum system to the ToF spectrometer. The gaseous end products were collected in a cold trap and after thermal equilibration at 77°K were separated and identified by low-temperature sublimation and ToF mass spectroscopy (used as a conventional mass spectrometer). It was possible to monitor continuously the gases effusing into the spectrometer. Successively warmer traps, starting with liquid N_2, were used and the mass spectra of the products were recorded as functions of temperature and electron bombardment energy (to help distinguish parent and fragment ions).

Ratios of reaction products were determined as a function of the amount of inert quenching gas. Because of the explosive nature of the reaction, only small quantities (~3 μmol) could be photolyzed at one time. The quantities of gaseous products were low enough to

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(7) J. M. Kramer and R. S. Berry, *J. Amer. Chem. Soc.*, **93**, 1303 (1971).

(8) J. D. Crum and C. H. Fuchsman, *J. Heterocycl. Chem.*, **3**, 252 (1966).

(9) R. S. Berry, J. Clardy, and M. E. Schafer, *J. Amer. Chem. Soc.*, **86**, 2738 (1964); M. E. Schafer and R. S. Berry, *ibid.*, **87**, 4497 (1965).

(10) R. T. Meyer, *J. Chem. Phys.*, **46**, 967 (1967); *J. Sci. Instrum.*, **44**, 422 (1967).

(11) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Amer. Chem. Soc.*, **84**, 3570 (1962).

show that the materials were being pumped away through the mass spectrometer; plots of mass peak intensities *vs.* time showed first-order decreases, indicating molecular effusion. Therefore, the relative concentrations of products were obtained by extrapolation of intensities back to the zero of time, corresponding to the time of opening the sample, at a particular temperature, to the mass spectrometer. The intensities of the mass peaks were fitted to a log I *vs.* t graph, and intercepts at $t = 0$ were taken as the initial concentrations. Intercepts and slopes were determined by a least-squares method.

Photolysis reactions run with about 10 atm of N_2 or CH_4 were conducted in a high-pressure uv absorption cell consisting of a Teflon-gasketed brass cylinder with two sapphire windows held by screw-on flanges. A Hoke valve with Swagelok adapter completed the cell The sample was deposited on one of the sapphire windows and flash photolyzed neat.

Solid products were separated by glc, first washed with acetone or chloroform and then injected into a Varian 202B gas chromatograph with an SE-30 column. Further purifications were carried out on a Carbowax column.

To determine yields of solid products as a function of inert gas, known quantities of starting material were photolyzed and washed with measured volumes of acetone. Absolute yields were determined by injection of samples of known concentration.

Results

A. Gaseous End Products. After photolysis, the gaseous products were trapped out at liquid N_2 temperatures and the N_2 produced in the reaction was allowed to effuse through the mass spectrometer. When the cold trap bath was changed to *n*-pentane–liquid N_2 (-130.5°) copious quantities of CO_2 sublimed into the spectrometer. At the same time a product of mass 26 appeared. Two successively smaller peaks were present at 25 and 24. This product is assigned to acetylene[12] (1 mm vapor pressure at -143°).[13] After most of the CO_2 sublimed away (and perhaps the trap had warmed) a product of mass 50, with fragments at 49, 48, 38, 37, and 36, appeared. At low electron voltage (30 eV) 50 remained and the fragments disappeared. Mass 50 is diacetylene[14] (1 mm vapor pressure at -83°[13]).

In a number of runs, appearing at about the same time as diacetylene were masses at 68, 52, 40, and 24. The intensities of 68 and 40 were approximately equal and mass 68 was assigned to carbon suboxide[15] ($O{=}C{=}C{=}C{=}O$, 1 mm vapor pressure at -95°[13]). However, the peak at 52 is equal to or greater than 40 in intensity. The intensity of the fragment of carbon suboxide at mass 52 is 2% of the intensity of mass 40. Therefore 52 cannot come only from carbon suboxide. If mass 52 were butatriene[16] (C_4H_4) a large fragment would be expected at 51 (80%). No fragment at 51 is seen. Mass 52 is probably cyanogen (1 mm vapor pressure at -95.8°) formed as a secondary product of the reaction.

After diacetylene has started to effuse into the spectrometer, two new products appear: mass 27, which was assigned to HCN[17] (1 mm vapor pressure at -70.8°[13]), and a peak at 51. It was impossible to eliminate diacetylene when mass 51 appeared, but the appearance of 51 was not accompanied by any detectable change in the intensities of fragments of lower mass. In the mass spectrum of cyanoacetylene[18] ($HC{\equiv}CCN$), the parent at 51 is the base peak, 50 is 22% of base peak, and all other fragments are less than 8% (the fragments of cyanoacetylene correspond exactly to the fragments and parent of diacetylene). The vapor pressure of cyanoacetylene is 1 mm at -56°.[19] From these facts and a consideration of the unimolecular decomposition of 3,4-pyridyne, mass 51 was concluded to be cyanoacetylene.

As the temperature is raised further, cyanoacetylene and diacetylene start to disappear and peaks at 53 and 52 appear. With the total disappearance of cyanoacetylene and diacetylene there appear peaks at masses 53, 52, 51, and 50, descending in intensity with decreasing mass. These peaks are assigned to acrylonitrile, $H_2C{=}CHCN$[20] (1 mm vapor pressure at -51°[13]). Acrylonitrile has a base peak at mass 26, but this coincides with the principal product of fragmentation of HCN. About the same time mass 78 appears. Its intensity is weak and there are no fragments intense enough to give a clue to its identity. No structure is assigned.

The last product observed shows a parent at mass 77 with a prominent fragment at mass 50. There are other fragments at 76, 75, and 74, indicating the loss of three hydrogens. Fragments at 52, 51, and 49 are also seen. On the basis of chemical arguments the product at mass 77 would not be expected to be free 3,4-pyridyne but some more stable rearrangement product. Possible rearrangement products are β-ethynylacrylonitrile (1-cyanobuten-3-yne), cyanobutatriene, and 2-cyanobuten-3-yne.

B. Diazabiphenylene. The solid products from the photolysis of pyridine-3-diazonium-4-carboxylate were washed with acetone or chloroform and injected into a glc with an SE-30 column. One peak represented 70% of the products and this was the only compound collected and analyzed. It was further purified on a Carbowax column. The compound is a white solid with mp 169–169.5°.

A high resolution mass spectrum shows a parent (100% base peak) at 154.0544 ($C_{10}H_6N_2$ = 154.0531). There are fragments at 127.0429 (C_9H_5N = 127.0422), 100.0301 (C_8H_4 = 100.0313), and 74.0134 (C_6H_2 = 74.0156) as well as metastables at 104.8, 78.8, and 54.8. The mass spectrum is shown in Table I.

The ultraviolet spectrum of the principal solid product in methanol contains maxima at 338 nm (log ϵ 3.08), 325 (3.15), 312 (3.17), 297 (3.18), 283 (3.16), and 241 (5.10). Shoulders are present at 320 nm (log ϵ 3.05), 304 (3.12), 289 (3.14), and 234 (4.98). On the long-wavelength side of the first band at 338 nm are two and possibly three weak shoulders, 388 nm (log ϵ 1.58), 370 (2.18), and possibly 355 (2.47). Addition of HCl shifts the long-wavelength bands about 500 cm^{-1} to the blue. The band contour and intensities remain the same except for an increase in the intensity of the shoulder at 320 nm. With HCl it is equal in intensity to the band at 325 nm. The shoulder at 370 nm also picks up intensity. The peak at 241 nm is shifted about 200 cm^{-1} to the red and the shoulder at 234 nm disap-

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(12) Mass Spectral Data, American Petroleum Institute Research Project 44, No. 72.

(13) R. C. Weast, Ed., "Handbook of Chemistry and Physics," Vol. 51, Chemical Rubber Co., Cleveland, Ohio, 1970, pp D146–172.

(14) Reference 12, No. 74.

(15) K. D. Bayes, *J. Amer. Chem. Soc.*, **84**, 4077 (1962).

(16) W. M. Schubert, T. H. Liddicoet, and W. A. Lanka, *ibid.*, **76**, 1929 (1954).

(17) Reference 12, No. 94.

(18) V. H. Dibeler, R. M. Reese, and J. L. Franklin, *J. Amer. Chem. Soc.*, **83**, 1813 (1961).

(19) W. Dannhauser and A. Flueckinger, *J. Chem. Phys.*, **38**, 69 (1963).

(20) Reference 12, No. 238.

Table I. Mass Spectrum of Diazabiphenylene[a]

m/e	Intensity relative to $C_{10}H_6N_2$, m/e 154	m/e	Intensity relative to $C_{10}H_6N_2$, m/e 154
155	12.06	77	5.89
154[b]	100.00	76	5.19
153	3.29	75	6.09
		74	23.38
128	6.78	63	4.68
127	46.15	62	4.30
126	2.60	61	3.23
101	3.90	52	3.70
100	18.82	50	22.89
99	7.42	48	3.09
98	5.63		

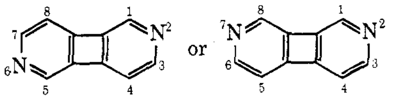
[a] Ionizing voltage 70 eV. [b] Parent peak.

pears. Addition of more HCl produced no further shifts.

The nuclear magnetic resonance spectrum (in $CDCl_3$) shows three groups of protons in the ratio 1:1:1. The peaks are situated at (relative to TMS) δ 8.3 and 8.0 (doublets, possibly quartets) and 6.8 (sextet, possibly octet).

The infrared spectrum (KBr pellet or collected directly on a salt plate from the glc) shows its strongest band at 838 cm^{-1} with a shoulder at 830 cm^{-1}. Bands around 1600 cm^{-1} as well as two bands at 733 and 720 cm^{-1} were present. No C≡N stretching vibrations were apparent, nor were C—H stretching vibrations observed. The base line showed a slowly rising transmittance with increasing wavelength.

The compound described above is assigned the structure 2,6- or 2,7-diazabiphenylene.



C. Time-of-Flight Mass Spectra. The products of the reaction started to reach the pinhole and be detected ~100–150 μsec after the photolysis flash began. In this initial product spectrum masses 28 and 44 were most prominent. They correspond to N_2 and CO_2. Unless noted all other products appeared in the first or second product spectrum. All the various products reached the pinhole at the same time. However, N_2 and CO_2 were present in such large quantities that the smaller products appeared to be absent in the initial spectrum. By the next spectrum their intensity would grow sufficiently to be detected.

Mass 77 appeared, as a parent, together with 51, 50, 27, 26, and others in the first or second product spectrum. At ionizing energies of 25 and 50 eV, masses 51, 50, 27, and 26 all appeared prominently. Thus mass 77 at early times may correspond to 3,4-pyridyne, any of the three stable rearrangement products of mass 77, or a combination of the possibilities. Likewise, 51, 50, 27, and 26 may be parents (cyanoacetylene, diacetylene, hydrogen cyanide, and acetylene), fragments, or both.

To determine if the reaction proceeded directly to HCN and C_4H_2 or C_2H_2 and HC_3N without going through the 3,4-pyridyne intermediate, spectra were taken at 50-μsec repetition rates and ionizing energies of 25 eV. Masses 51, 50, 27, and 26 still appeared at the same time as mass 77.

Mass 154, corresponding to diazabiphenylene, reached the pinhole at the same time as mass 77. It was easily identified by its parent ion, as well as prominent fragments at 127, 100, and 74.

The change in concentration of products as a function of time depended upon which sample cell was used and the time between mass spectra. The coaxial reaction cell with differential pumping showed an initial product concentration rise (perhaps due to the velocity distribution of the products); after ~300 μsec the differential pumping would take over and the intensities of the mass spectral peaks would decrease rapidly. The straight tube reaction cell shows the same initial behavior, but products tend to remain longer, as expected.

The reaction gives off large amounts of N_2 and CO_2. In the straight tube, the rate of effusion through the pinhole is limited and pressure builds up with the primary reaction so that the products suffer many collisions and normally nonvolatile products tend to condense on the wall before reaching the pinhole. This, of course, complicates the interpretation of the kinetic data. The cell with differential pumping solved some of these problems, but substituted complication of a second rate process, the loss due to pumping.

In general with the coaxial and straight tube reaction cells, products showed no dramatic change of concentration with time. Almost all the products appeared at the same time. A few mass peaks were late in arrival (one sweep) but the result was not reproducible. One result, however, was of interest. Mass 121 showed a definite decrease in concentration with time, while mass 120 remained essentially the same.

The third reaction cell, adapted from Meyer,[10] was used for kinetic studies. With the sample about 2 mm from the pinhole, velocity distribution should be minimized. Mass 77 may correspond to a stable product even at early times and not to the intermediate 3,4-pyridyne. Therefore, mass 154 (diazabiphenylene) was used to measure the rate of formation of diazabiphenylene.

Mass 154 appears at the same time as mass 77, increases in intensity for approximately 100 μsec, and then levels off. In the same interval, 77 is either approximately constant or rises more slowly than 154. The rate constant for dimerization of 3,4-pyridyne to diazabiphenylene was determined to be 1.3×10^9 l. mol^{-1} sec^{-1}. Time-resolved mass spectra are shown in Figure 3.

D. Kinetic Ultraviolet Spectroscopy. In general the photographic plate shows three exposures: (a) the spectral source, (b) the reaction at the delay time selected (photolysis exposure), and (c) the spectral source 10–20 sec after the initiation of the reaction (post exposure). With small amounts of reactant (approximately 1 μmol) there is no difference between the spectral exposure and the photolysis exposure until about 35 μsec after initiation. With large amounts of starting material, (approximately 16 μmol) the photolysis exposure shows a large decrease in transmission at 15 μsec.

The decrease in transmission in the photolysis exposure starts at the long-wavelength cutoff of the 103-O plate (500 nm) and extends to the short wavelength cutoff (230 nm). Because of the decreasing sensitivity of the plate, the short wavelength region often appears

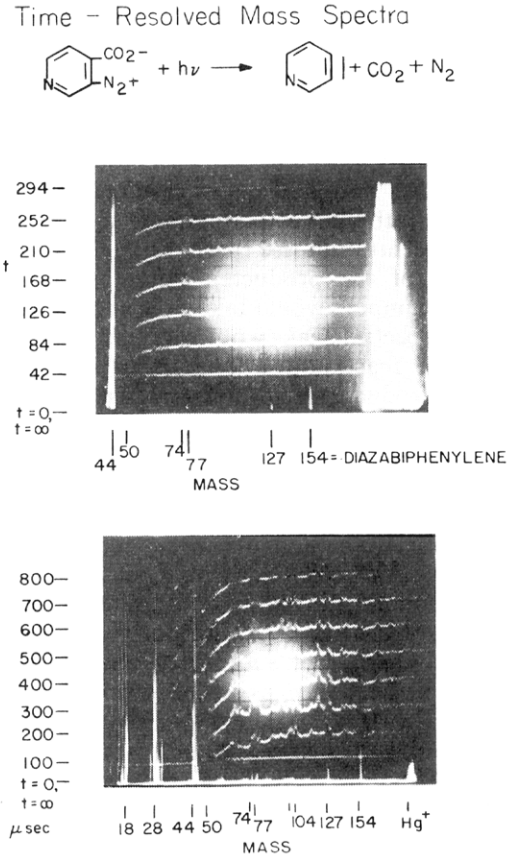


Figure 3. Time-of-flight mass spectra of photolysis products from pyridine-3-diazonium-4-carboxylate: (top) high mass range; (bottom) mass range 16–200.

Table II. Lines from Kinetic Ultraviolet Spectroscopy

nm	nm	nm
248.4	302.2	359.3 (?)
258.5 (?)	312.2	361.5
259.9 (?)	312.9	362.6
271.9 (?)	327.2 (?)	364.2 ?)
274.1 (?)	328.1	388.8 (?)
276.5	334.0	390.3 (?)
283.4	334.9	421.8
284.0	338.3	425.2
285.3	344.6	436.1
285.7 (?)	352.8 (?)	439.2
286.3	353.8	490.0
297.6 (?)	357.5	501.5

Table III. Ratio of Reaction Products *vs.* Added N_2

Ratio	No N_2	15 Torr of N_2	$^1/_3$ atm of N_2	$^2/_3$ atm of N_2	Average of all pressures
27/50[a]	2.2 ± 0.4[e]	3.1 ± 0.4	6.0 ± 1.2	5.6 ± 0.7	
50/77[b]	6.9 ± 0.9	6.0 ± 1.4	6.0 ± 0.8	6.9 ± 1.6	6.5
26/51[c]	1.22 ± 0.14	1.44 ± 0.46	1.60 ± 0.18	1.58 ± 0.43	1.46
50/51[d]	2.13 ± 0.34	2.04 ± 0.47	2.15 ± 0.49	1.93 ± 1.31	2.04

[a] 27/50 = hydrogen cyanide/diacetylene. [b] 50/77 = diacetylene/cyanobutatriene, or 1- or 2-cyanobuten-3-yne. [c] 26/51 = acetylene/cyanoacetylene. [d] 50/51 = diacetylene/cyanoacetylene. [e] 95% confidence values.

to be opaque. The transmission decreases almost monotonically toward shorter wavelengths. The microdensitometer curves show that the spectral exposure has a contour similar to the photolysis exposure. No broad bands attributable to either the pyridyne intermediate or the diazabiphenylene product are observed.

The decrease in transmission, especially at early times (45 μsec, 1.33 μmol), shows a λ^{-4} dependence. At longer times (70 μsec) the fit is not quite as good.

The opacity of the reaction mixture increases with increasing time. At longer times (concentration dependent) the opacity decreases slightly and levels off as the products condense out. With about a 1.5-μmol sample the opacity levels off at about 500 μsec.

The plate densities were used in an attempt to determine the rate constant for dimerization. Various wavelengths were chosen. The apparent rate constant was calculated to be $\sim 12 \times 10^9$ l. mol^{-1} sec^{-1} based on data at 360.0 nm; a lower value of $\sim 7 \times 10^9$ was obtained from data at 268.0 nm and a value of $\sim 9 \times 10^9$ with data at 262.5 nm. These values are five to ten times the rate constant obtained by ToF mass spectroscopy. We infer that the increase in the overall optical density is probably due to scattering and not to absorption by products.

With larger samples ($\sim$3 μmol), the photolysis exposure shows many rather sharp absorption lines. The lines are listed in Table II. The lines appeared at early times (15 μsec) and persist at least 800 μsec. The lines at wavelengths below 370 nm correlate with the solution spectra of diazabiphenylene and are assigned to diazabiphenylene. Because diazabiphenylene is completely formed in 200 μsec in the ToF work, it is impossible to assign the lines below 3700 Å to 3,4-pyridyne. The same reasoning applies to the lines above 3700 Å which also persist for at least 800 μsec. The lines at wavelengths above 3700 Å are left unassigned.

An attempt was made to determine the rate constant for dimerization from the strength of the absorption at 328.1 nm. The results as a function of time showed too much scatter to give a meaningful rate of dimerization. Time-resolved ultraviolet spectra are shown in Figure 4.

E. Pressure Studies. To test the unimolecular reaction hypothesis, products were studied as a function of the partial pressure of added inert gas. The results are presented in Tables III–V.

Discussion

The results of the previous sections are compatible with the formation to 3,4-pyridyne. Once formed 3,4-pyridyne may undergo any of three related unimolecular reactions as well as dimerization to diazabiphenylene. The three related unimolecular reactions are (a) rearrangement to a stable product of mass 77 with a prominent fragment at 50 [77 is either β-ethynyl-

Table IV. Diazabiphenylene as a Function of Pressure

Pressure	Starting material $\times 10^5$ mol	% diazabiphenylene
No N_2	6.31	3.9
No N_2	7.32	3.6
$^1/_3$ atm of N_2	7.92	5.8
$^2/_3$ atm of N_2	8.59	5.6
	Fresh sample	
$^1/_3$ atm of N_2	6.04	12.2
$^2/_3$ atm of N_2	9.20	11.2
No N_2	8.72	5.3
10 atm of N_2	7.25	4.7

Table V. High Pressure Studies

Pressure	HCN[a]	C_4H_2[a]
No N_2	90	17.5
10.75 atm of N_2	11.2	0.66
No N_2	106	15.5
10.75 atm of N_2	29	0.9
9 atm of CH_4	~4.7	
$^2/_3$ atm of CH_4	62	7.9

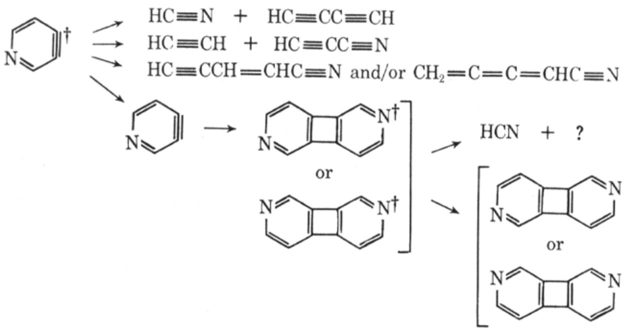
[a] Ion current in units of 10^{-8} A.

acrylonitrile (1-cyanobuten-3-yne), 2-cyanobuten-3-yne, or cyanobutatriene] (one bond broken in the pyridine ring); (b) decomposition to HCN (27) and $HC{\equiv}C$-$C{\equiv}CH$ (50) (two bonds broken); and (c) decomposition and rearrangement to C_2H_2 (26) and $HC{\equiv}CCN$ (51) (two bonds broken).

Also compatible with the experimental results is the production of HCN in a second reaction. Two other possible sources of HCN are another primary reaction or unimolecular decomposition of diazabiphenylene. No stable product compatible with an additional primary reaction was observed. Even with samples photolyzed in *ca.* 10 atm of N_2 or CH_4, excess HCN was still present and there was no increase in diazabiphenylene with ~10 atm of N_2. Diazabiphenylene initially contains ~137 kcal/mol as the following discussion of heats of reaction will show. This suggests the possibility of an immediate loss of HCN in some dimerizations, as well as direct decomposition of 3,4-pyridyne.

A. Thermochemical Considerations and Product Formation. The reactions of 3,4-pyridyne are apparently those shown in Scheme I (daggers indicate vibrational excitation).

Scheme I



To understand the experimental results it will be necessary to estimate some of the heats of reaction for various processes. The estimates are obtained from bond energy considerations. Estimates will be made for analogous benzyne reactions for comparison.

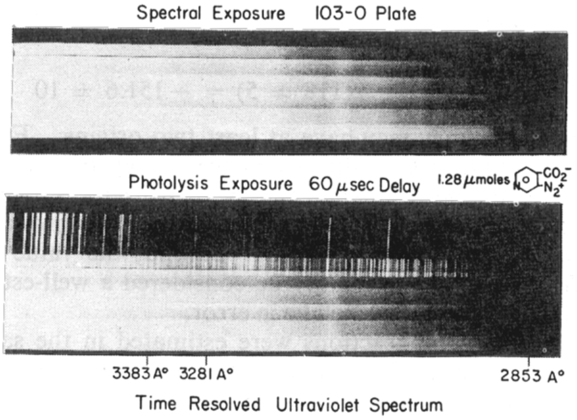
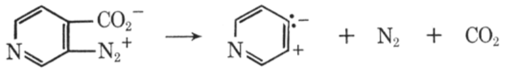


Figure 4. Time-resolved ultraviolet spectra showing bands assigned to diazabiphenylene.



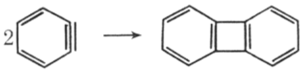
$$\Delta H = \Sigma \text{ bonds broken} - \Sigma \text{ bonds formed} = (C{-}C) + (C{-}N) + (C{-}O) - (C{=}O) = 82.6 + 72.8 + 85.5 - 192.0 = 48.9 \text{ kcal/mol}$$

$$\Delta H = -111 \text{ kcal/mol}$$

The energy difference between the analogous structures in benzyne was estimated to be 111 kcal/mol by Simmons.[21] The nature of the calculations makes it equally applicable to 3,4-pyridyne.

$$C_5H_3N(CO_2^-)(N_2^+) \longrightarrow C_5H_3N + N_2 + CO_2$$
$$\Delta H = +49 - 111 = -62 \text{ kcal/mol}$$

Thus the reaction to form 3,4-pyridyne, CO_2, and N_2 from pyridine-3-diazonium-4-carboxylate is exothermic by about 62 kcal/mol. The heat of reaction for the formation of benzyne from benzenediazonium-2-carboxylate should be the same within the approximations of the calculations.



$$\Delta H = \Sigma \text{ bonds broken} - \Sigma \text{ bonds formed} = 2(\text{C–C yne bonds}) - 2(\text{C–C}) = 2(18.4) - 2(82.6) = -128.4 \text{ kcal/mol}$$

The energy of the benzyne type bond (C–C yne bond) was estimated from the exchange integral to be 18.4 kcal/mol (see Simmons[21]). There is also a loss of resonance energy in this reaction (resonance energy of two benzene rings minus the resonance energy of biphenylene) which must appear as heat. ΔH for loss of resonance $= 2(38) - 59 = 17$ kcal/mol.[22] Therefore

$$\Delta H = -128.4 + 17 = 111 \text{ kcal/mol}$$

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(21) H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961).

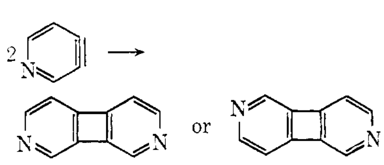
(22) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, pp 243–246.

To compare with this, ΔH_f of biphenylene[23] = +84.4, ΔH_f of benzyne[24] = 118 ± 5

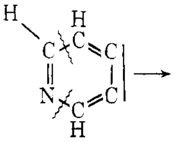
$$\Delta H = 84.4 - 2(118 \pm 5) = -151.6 \pm 10$$

This discrepancy may have at least two origins. First, the assumption that the resonance energy of benzyne is equal to the resonance energy of benzene is clearly an oversimplification; the strain in benzyne probably reduces the resonance energy. Second, the value for ΔH_f of benzyne can hardly be considered a well-established figure and may well be in error.

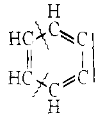
The following reactions were estimated in the same way as above. The unknown resonance energy of the 3,4-pyridyne dimer was estimated from the relationship (resonance energy of benzene):(resonance energy of pyridine) as (resonance energy of biphenylene): (resonance energy of diazabiphenylene). The value obtained was 33 kcal/mol. The bond energies used were[25] C—C 82.6, C=C 145.8, C≡C 199.6, C—N 72.8, C=N 147, C≡N 212.6, C—O 85.5, and C=O 192.0. Where applicable C≡N for HCN = 207 and C≡C for HC≡CH = 194.3. C—H bond breaking and formation cancels out in first approximation and was not included.



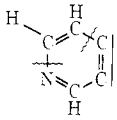
+ 119 kcal/mol (2b)



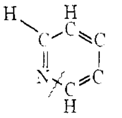
$\longrightarrow HCN + HC{\equiv}C{-}C{\equiv}CH - 27$ kcal/mol (5a)



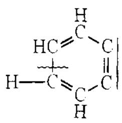
$\longrightarrow HC{\equiv}CH + HC{\equiv}C{-}C{\equiv}CH - 66$ kcal/mol (5b)



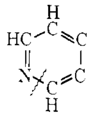
$\longrightarrow HC{\equiv}CH + HC{\equiv}C{-}CN - 27$ kcal/mol (5c)



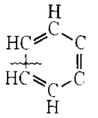
$\longrightarrow HC{\equiv}C{-}CH{=}CH{-}CN$ or $H_2C{=}C(C{\equiv}C{-}CN)(CN)$ + 7 kcal/mol (6a)



$\longrightarrow HC{\equiv}C{-}CH{=}CH{-}C{\equiv}CH - 31$ kcal/mol (6b)



$\longrightarrow H_2C{=}C{=}C{=}CHCN + 17$ kcal/mol (7a)



$\longrightarrow H_2C{=}C{=}C{=}CHC{\equiv}CH - 22$ kcal/mol (7b)

An alternative sequence would break the dehydro bond of 3,4-pyridyne and then the fragment would further decompose to $HC{\equiv}CCN$ and C_2H_2 or HCN and $HC{\equiv}CC{\equiv}CH$. The heat of reaction for this mechanism would of course be the same as that of (5a) or (5c).

This alternative scheme is proposed because of pyrolysis studies on the 2,3-dicarboxylic anhydrides of pyrazine,[26] pyridine,[4] quinoxaline,[27] and quinoline.[27] All proceed to give products which can be envisioned as proceeding through a hetaryne intermediate followed by fragmentation of the dehydro bond. There is only one problem with the scheme for the fragmentation of 3,4-pyridyne. To obtain the proposed products β-ethynylacrylonitrile (1-cyanobuten-3-yne) and/or cyanobutatriene by fragmenation of the dehydro bond requires a shift of an ethynyl group from one end of the molecule to the other. The formation of 2-cyanobuten-3-yne requires something more than hydride shifts no matter what skeletal bond is broken.

One may try to use analogies with the C_4H_3Cl halocarbons to elucidate the problem, but, as we shall see, this is not terribly enlightening. The mass spectra of the four isomers of C_4H_3Cl, chlorobutatriene, *cis*- and *trans*-1-chlorobuten-3-yne, and 2-chlorobuten-3-yne are very similar.[28] At best, it would be difficult to identify one isomer even with standard mass spectra of all the isomers taken on the same machine as the unknown. The substitution of a cyano group for the chlorine should not change the situation. There was no marked difference in stability between the four chloro isomers and they were separated by glc at temperatures up to 150°. Thus, one would expect any instability in the cyano series to be due to the nature of the nitrile itself. The 1-cyanobuten-3-yne isomer (β-ethynylacrylonitrile) is known[4] and the other isomers to a first approximation should have similar stabilities.

The distribution of chloro isomers from the dehydrochlorination of 1,4-dichloro-2-butyne with alkali in homogeneous ethanol was found to depend in a complicated way on temperature, solvent, concentration, and degree of completion of the reaction.[28] The isomeric propargyl ($HC{\equiv}CCH_2X$), allenic ($H_2C{=}C{=}CHX$) system also might serve as an analog. Bromoallene can be prepared from the rearrangement of propargyl bromide with suitable catalyst.[29] The rearrangement is reversible. However, the uncatalyzed thermal rearrangement did not occur in either direction. From these results it would seem impossible to draw an analogy to indicate which cyano isomers of C_5H_3N are formed.

The requirement of shifting more than hydrogens to form 2-cyanobuten-3-yne should make it a less likely product than 1-cyanobuten-3-yne or cyanobutatriene. It might be argued that since 1-cyanobuten-3-yne is formed in the fragmentation of 2,3-pyridine[4] with no mention of cyanobutatriene that the same would be true for 3,4-pyridyne. However, a single bond-breaking mechanism in 2,3-pyridyne requires one hydrogen shift to form 1-cyanobuten-3-yne and two hydrogen shifts to form cyanobutatriene. In

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(23) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, p 288.

(24) Reference 1, p 268.

(25) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958, pp 270–289.

(26) R. F. C. Brown, W. D. Crow, and R. K. Solly, *Chem. Ind. (London)*, 343 (1965).

(27) M. P. Cava and L. Bravo, *Chem. Commun.*, 1538 (1968).

(28) R. Vestin, A. Borg, and T. Lindblom, *Acta Chem. Scand.*, **22**, 685, 687 (1968).

(29) T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, **75**, 1314 (1953).

3,4-pyridyne the same mechanism requires one hydrogen shift or two for *each* product depending upon which single bond is broken. Therefore, the product of mass 77 with a prominent fragment at 50 is β-ethynylacrylonitrile (1-cyanobuten-3-yne) and/or cyanobutatriene.

The exothermicity of the reaction to form 3,4-pyridyne is approximately the same as for the formation of the benzene analog (benzyne). The heat of reaction to form the dimerization product is also about the same for pyridyne and benzyne. However, the heats of reaction for the decomposition of the intermediates and their dimers are quite different. This difference can be traced to the schematic decomposition process. It requires about 10 kcal/mol less energy to break a C–N bond than a C–C bond.[25] The resultant breakage of the π-electron system removes the resonance energy of the ring system. Thus, it requires ~17 kcal/mol less energy to break the pyridine ring than the benzene ring.[22] The formation of triple bonds such as C≡N and C≡C favors the nitrile type bond, and this process in the nitrogen system is ~12 kcal/mol more favorable.[25] The net effect, amounting to ~39 kcal/mol, makes the decomposition of 3,4-pyridyne to any given products a more favorable process than decomposition to the same type products from benzyne.

The reaction of pyridine-3-diazonium-4-carboxylate decomposing to 3,4-pyridyne, N_2, and CO_2 is exothermic by ~62 kcal/mol. The enthalpy of the reaction plus the activation energy of the reaction minus the heat loss to the walls will be contained in the products of the reaction. As a crude estimate of the initial temperature rise of the products, let us say that the energy of activation approximately equals the heat loss to the walls. Then $\Delta H = \Sigma C_p(T)\Delta T$ and $C_p(T)$ is known for N_2 and CO_2 and we can estimate $C_p(T)$ for 3,4-pyridyne from the heat capacity of benzene.[30] A value of T is chosen, $C_p(T)$ calculated, and ΔT determined. The calculation is continued until $T - 300°K = \Delta T$. The calculated ΔT is 825°.

This calculation can be used to estimate the temperatue rise when inert gas is added. The principal uncertainty comes in estimating the effective volume of the reaction. The estimated volume and the pressure are related to the number of moles of inert gas through the ideal gas law. The effective volume was estimated to be a cylinder 5 cm long with a diameter equal to the inner diameter of the quartz tube. This volume was chosen because this was approximately the volume of visible products initially in the form of a smoke. For a pressure of 15 Torr of N_2, $\Delta T \approx 760°$; for $^1/_3$ atm of N_2, $\Delta T \approx 225°$; and for $^2/_3$ atm of N_2, $\Delta T \approx 125°$.

From the calculated temperature rise we can estimate the enthalpy initially retained in the pyridyne molecule. With no added N_2, $\Delta H \approx$ 44 kcal/mol; for 15 Torr of N_2, $\Delta H \approx$ 40 kcal/mol; for $^1/_3$ atm of N_2, $\Delta H \approx$ 7.5 kcal/mol; and for $^2/_3$ atm of N_2, $\Delta H \approx$ 3.5 kcal/mol. Within the approximation of the calculations, the same values for temperature rises and retained enthalpy would be obtained for benzyne.

The values for the calculated temperature rises and the enthalpy initially retained in the pyridyne intermediate are crude at best. They will only be used to show that qualitatively the results are compatible with a model of unimolecular decomposition. The nature of the decomposition of the pyridine-3-diazonium-4-carboxylate, *i.e.*, explosion, means that intimate mixing of reaction products with inert gas is not possible. Also the problem of lack of complete reproducibility in explosions is very much present.

All three modes of unimolecular decomposition of 3,4-pyridyne have calculated heats of reaction less than or equal to 27 kcal/mol. Double ring breakage requires 27 kcal/mol and single bond breakage gives up 7 or 17 kcal/mol depending on the product formed. The heat of reaction to form 3,4-pyridyne is exothermic by ~62 kcal/mol and crude calculations suggest that the pyridyne is left with 44 kcal/mol initially. Therefore, if the activation energy to decompose 3,4-pyridyne is not large (especially in the case of double bond breakage), unimolecular decomposition should be possible.

As long as 3,4-pyridyne has energy in excess of the activation energies for decomposition, the products should be controlled kinetically and not thermodynamically. As the pressure of inert gas is increased, the pyridyne intermediate should be stabilized, unimolecular decomposition should be quenched, and the dimer yield should increase. All absolute concentrations of unimolecular decomposition products decreased with added gas. However, it was not possible to completely quench the unimolecular decomposition products, probably because of lack of intimate mixing in the reaction. The yield of dimer increased, but not as much as expected for a homogeneous system without polymerization. Changing the pressure of added N_2 from zero to $^2/_3$ atm of N_2 decreased the yield of unimolecular decomposition products by a factor of ~6–7, while the dimer concentration rose by a factor of ~2.

If 3,4-pyridyne decomposes unimolecularly with double bond breakage of the ring the ratio of C_2H_2 to HC≡CCN should be approximately 1 and be independent of added inert gas. That this is the case can be seen by observing the ratio of products. C_2H_2/HC≡CCN is 1.2 at no added gas, 1.4 at 1.5 cm of N_2, 1.6 at $^1/_3$ atm, and 1.6 at $^2/_3$ atm.

3,4-Pyridyne decomposes with double bond breakage to a second set of products, HCN + C_4H_2. The ratio of C_4H_2/HC≡CCN is approximately 2 at all pressures. Thus the two decomposition modes are about equally likely and affected similarly by pressure.

Single bond breakage yields HC≡CCH=CHCN and/or NCCH=C=C=CH_2 (mass 77). The reactions corresponding are 7 and 17 kcal/mol exothermic, respectively. Therefore, the products may be formed with excess energy and further decompose or be stabilized by collisions. The ratio of C_4H_2/77 was found to be approximately constant at all pressures studies. This ratio was not found to be statistically different for any pressure, and within that accuracy it appears that HC≡CH=CHCN and/or CH_2=C=C=CHCN does not unimolecular decompose. If 77 were to decompose, the ratio of 50/77 should be high at low pressure and low at high pressure.

Were the decomposition of 77 the only source of HCN and diacetylene, the ratio of HCN/C_4N_2 should behave like the ratio of C_2H_2/HC≡CCN. However, it does not—with no added N_2, the ratio is 2.2; the ratio is 3.1 at 15 Torr of N_2, 6.0 at $^1/_3$ atm, and 5.6

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(30) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Englewood Cliffs, N. J., 1962, p 63.

at $^2/_3$ atm. This change was due far more to the decrease in the yield of C_4H_2 with added N_2, than to a change in the yield of HCN. Since the C_4H_2/HC≡CCN ratio remains approximately constant, HCN must be produced in another reaction.

No evidence was found for a second primary reaction. Diazabiphenylene, however, shows two metastable peaks in its mass spectrum corresponding to loss of two molecules of HCN. This suggests a possible loss of HCN from diazabiphenylene at some stage soon after it is formed. The dimerization reaction producing diazabiphenylene is exothermic by ~119 kcal/mol. Therefore, even if the reacting pyridyne molecules contain no excess energy, the resulting dimer must be about 119 kcal/mol above its ground state initially.

A unimolecular decomposition rate for diazabiphenylene was estimated and compared with the calculated bimolecular collision frequency at $^2/_3$ atm and 10 atm of N_2. The rate constant was estimated[31-33] as

$$k = A\left(\frac{E - E_0 + E_z}{E + E_z}\right)^{n-1}$$

where n is the total number of oscillators, and not from $k = A[(E - E_0)/E]^{m-1}$, where m is the effective number of oscillators. The calculated rate was 5 × 10^{10} l./sec, based on these parameters: $A = 10^{13}$, $E = 119$ kcal/mol, $E_0 = 25$ kcal/mol, $E_z = 113$ kcal/mol, and $n = 48$. This rate is probably a good estimate of the upper limit. The value 25 for E_0 is a minimum, since it does not include any strain energy in the product. The assumed collision frequency was taken as 7×10^{10} sec^{-1}, based on a conservative estimate of 4 Å as the collision diameter. With a partial pressure of 10 atm of N_2, the average energy contained in a diazabiphenylene molecule should be comparable to ΔH_f for diazabiphenylene. At $^2/_3$ atm, the collision frequency is about $^1/_{10}$ the estimated unimolecular decomposition rate, but at 10 atm the rates are approximately equal. Therefore at $^2/_3$ atm the unimolecular decomposition rate might predominate, but at 10 atm of N_2 the rates would be approximately equal and an increase in dimer yield should be noted. The fact that no increase is seen at 10 atm seems to indicate that collisions are not effective in quenching diazabiphenylene, or that the unimolecular decomposition rate is higher than estimated, or that HCN is produced in still another reaction. It should be noted, however, that the yield of diazabiphenylene is twice as great with $^2/_3$ atm of N_2 as it is with no added inert gas.

The yield of HCN was also monitored at high pressure. The ratio of HCN/C_4H_2 remained larger than expected (1:1) with 10.75 atm of N_2. CH_4 (9 atm), with nine internal vibrational modes, was also used as a quenching gas. Large amounts of HCN were still observed.

That there is a large difference between gaseous benzene chemistry and 3,4-pyridyne chemistry is obvious. Benzyne, under similar conditions, dimerizes to biphenylene in good yield (~35%)[11] and shows no unimolecular decomposition. Most of the differences seem to be explainable in terms of energetics. Unimolecular decomposition of biphenylene to yield C_2H_2 seems unreasonable because of the high endothermicity of the reaction. Double bond breakage of the benzyne ring requires more energy than is initially contained in the benzyne. Single bond breakage should be energetically allowable, but may not be observed because of a high activation energy or because it cannot compete with the dimerization reaction which shows no activation energy.[34]

B. Kinetic Considerations. Time-of-Flight Mass Spectra. The time-of-flight mass spectra are compatible with a scheme of unimolecular decay of 3,4-pyridyne. Masses corresponding to the fragmentation products of 3,4-pyridyne reach the pinhole at the same time as mass 77 even at high repetition rates and low ionizing energies. This is reasonable for unimolecular decay which should be fast compared to the time scale of observation at low pressure. Strong supporting evidence for the formation of 3,4-pyridyne is the formation of diazabiphenylene.

The rate of formation of diazabiphenylene was calculated from the change in concentration of mass 154 with time using the cell with sample 2 mm from the pinhole. The data were consistent with either first- or second-order dependence on 3,4-pyridyne. Since pressure was effective in quenching the unimolecular decomposition products of 3,4-pyridyne, and, since pressure increased the yield of diazabiphenylene (at least to $^1/_3$ atm of N_2), 3,4-pyridyne must exist in the gas phase. Inert gas would have little effect on reaction in the solid phase. For the reaction to be first order, 3,4-pyridyne must either react with the starting material or $C_5H_3N \cdot CO_2$ (to be discussed in detail later). The starting material is an ionic solid which would be expected to have high melting and sublimation temperatures. Also the heat evolving reaction is unimolecular and therefore "combustion" would be expected to occur directly in the solid. It would be difficult to explain the large rate constant by reaction of solid starting material and gaseous 3,4-pyridyne. The concentration of $C_5H_3N \cdot CO_2$ (30–45% of the intensity of mass 154) decays over approximately a 300-μsec period while diazabiphenylene reaches its maximum after 100–150 μsec. Therefore, it is concluded that the formation of diazabiphenylene is a dimerization process. This is expected from the dimerization of benzyne to biphenylene.

Mass 77 is either approximately constant or rises more slowly than 154 with time. This is compatible with the measurement of the dimerization rate and not a velocity distribution (especially in the case of 77 being approximately constant). Measurement of the rate constant entails knowing the absolute concentration of diazabiphenylene. This was estimated from the known sample sizes, and the observation of a 5% yield for fresh samples (starting material slowly decomposes with time, even stored in a freezer). The rate of dimerization, 1.3 × 10^9 l. mol^{-1} sec^{-1} compares quite reasonably with the two measured rates for dimerization of benzyne,[34,35] ≥7 × 10^8 and 4.6 ± 1.2 × 10^9 l. mol^{-1} sec^{-1}.

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(32) B. S. Rabinowitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

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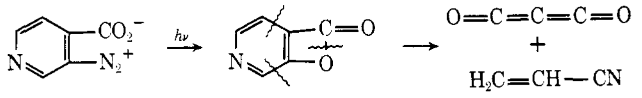
(35) M. Schafer and R. S. Berry, *J. Amer. Chem. Soc.*, **87**, 4497 (1965).

Decomposition of benzenediazonium-2-carboxylate produces benzoic acid in low yield.[36] Decomposition of benzenediazonium-4-carboxylate in the presence of water vapor produced large quantities of *p*-hydroxybenzoic acid.[36] Other examples can be found in the literature for removal of N_2 but no CO_2 from a diazonium carboxylate. It is tempting to assign mass 121 to $C_5H_3N \cdot CO_2$, *i.e.*, loss of N_2 only. This substance would be expected to be unstable and decompose with time. Mass 121 drops in intensity over ~300 μsec while mass 120 remains essentially constant. Also of importance is the observation of carbon suboxide (68) and acrylonitrile (53) as products in low yield. It is proposed that $C_5H_3N \cdot CO_2$ can lose CO_2 as well as decompose to carbon suboxide and acrylonitrile.



Bond energy calculations indicate that the formation of the bicyclic intermediate would be exothermic by 13 kcal/mol. The net reaction would be endothermic by 14 kcal/mol. Alternatively the reaction of CO_2 and 3,4-pyridyne to form the intermediate drawn would be exothermic by 43 kcal/mol and the net reaction exothermic by 16 kcal/mol.

Finally it is observed that mass 127 does not appear to be abnormally intense in relation to 154. If diazabiphenylene were unimolecularly decomposing to HCN, an intermediate of mass 127 (154 − 27) might be expected. That mass 127 is not observed means either HCN is eliminated very quickly or diazabiphenylene does not unimolecularly decay.

Kinetic Ultraviolet Spectroscopy. It appears that at early times Rayleigh scattering is interfering with the ultraviolet spectra. The λ^{-4} dependence offers good proof for this interpretation. With large concentrations (~12 μmol) the walls and windows are covered with an opaque coating at the end of the reaction. When inert gas is added a thick smoke is seen which lasts for 10–20 sec before condensing out on the walls.

The rate constants calculated from the optical densities would appear to be derived from the rate of appearance of scattering centers and not from the rate constant for dimerization. Assuming a temperature of 1100°K (calculated for no added gas) and a mass of 154, the average velocity of molecules leaving the bottom of the cell is 4×10^4 cm/sec. The molecules expand into a vacuum and with a cell diameter of 2 cm the molecules should fill the cell in ~50 μsec. With the concentrations of reactants used, the appearance of scattering centers would yield an apparent rate constant of $\sim 10^{10}$ l. mol^{-1} sec^{-1} which is very close to the rate observed for the increase in cell opacity by kinetic ultraviolet spectroscopy.

Were the rate constant measured from the ultraviolet data really the rate of dimerization to diazabiphenylene, it would present an interesting paradox, because such a rate would mean that the increase in concentration of diazabiphenylene would be unobservably fast in the ToF, which, of course, is not the case. It is concluded that the apparent rate observed by kinetic ultraviolet spectroscopy is not the dimerization rate at all.

The lines observed in the flash photolysis exposure were not observed in the post-photolysis exposures or in the attempts at taking the gas-phase ultraviolet spectrum of pure diazabiphenylene. (Suggestions of absorption were present, but nothing definite could be found.) Gas-phase spectra were attempted from room temperature to 120°. In general there was no absorption (perhaps a problem of sublimation) and where some was present (broad), there seemed to be no good correlation between the solution spectra and the observed absorption. With biphenylene, by contrast, there was no problem in obtaining the gas-phase spectrum at long or short wavelengths.

On the basis of the transient gas-phase spectra and the solution spectra of the purified product, the lines below 370.0 nm are assigned to gaseous diazabiphenylene. Failure to see the lines in the past probably indicates that the diazabiphenylene condensed on the walls and has a vapor pressure too low to give significant absorption in our cells.

In conclusion it has been possible to observe the gas-phase ultraviolet spectrum of diazabiphenylene. Because of Rayleigh scattering the 3,4-pyridyne intermediate was not observed, nor was the rate of dimerization obtained from the ultraviolet spectra.

C. Diazabiphenylene. Diazabiphenylene (the 2,6 and/or 2,7 isomer) is the dimerization product of 3,4-pyridyne. All the spectroscopic data presented in the previous section are compatible with the assigned structure (diazabiphenylene). A strong case can be made that the diazabiphenylene is a pure compound; a weaker case can be made that the diazabiphenylene is the 2,6 isomer.

Diazabiphenylene was separated first on a nonpolar SE-30 column and then on a polar Carbowax column. The melting point range was 0.5°. It would be highly unlikely that a eutectic mixture was involved. It is concluded that diazabiphenylene is a pure compound.

The nitrogen atom in 3,4-pyridyne acts like an electron-attracting substituent on benzyne.[37] If the dehydro bond is polarized significantly, a 2,6 isomer would be expected.[38] Calculations by Hoffmann, *et al.*,[39] show the total electron density on carbon 3 as 4.35 and 3.97 on carbon 4. Four examples of substituted benzynes dimerizing predominantly to 2,6 isomers are known.[40] Three of the examples were in the liquid phase; the last was formed by explosion by thermal decomposition. In all four cases the substitutions were methyl groups (both the 2,6[41] and 2,7[42] isomers of dimethylbiphenylene have been prepared and characterized). Therefore, by analogy with these four examples we expect that the compound under discussion is 2,6-diazabiphenylene.

Mass Spectrum. A high resolution mass spectrum at 70 eV shows a parent (100% base peak) at 154.0544

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(36) Unpublished results.

(37) Reference 1, p 300.

(38) Reference 23, pp 262–263.

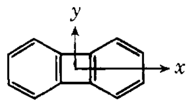
(39) W. Adam, A. Grimison, and R. Hoffmann, *J. Amer. Chem. Soc.*, **91**, 2590 (1969).

(40) C. D. Campbell and C. W. Rees, *Chem. Commun.*, 192 (1965); C. R. Harrison, J. F. W. McOmie, J. B. Searle, J. P. Smith, J. O. Jenkins, and J. W. Smith, *J. Chem. Soc. C*, 1769 (1966); F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 3939 (1957); G. Vargas, Nunez, *Bol. Soc. Quim. Peru*, **31**, 6 (1965).

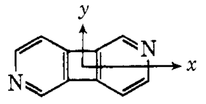
(41) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 3939 (1957).

(42) D. G. Farnum, E. R. Atkinson, and W. C. Lothrop, *J. Org. Chem.*, **26**, 3204 (1961); W. C. Lothrop, *J. Amer. Chem. Soc.*, **63**, 1187 (1941).

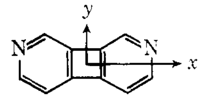
Table VI. Predicted Changes in Electronic Transitions



D_{2h}



C_{2h}



$C_{2v}{}^{a}$

Trans	Symm	Polariz	Trans	Symm	Polariz	Trans	Symm	Polariz
$6 \rightarrow 7$	B_{1g}	Forbidden	$6 \rightarrow 7$	A_g	Forbidden	$6 \rightarrow 7$	B_1	x axis
$6 \rightarrow 8$	B_{3u}	x axis	$6 \rightarrow 8$	B_u	x and y	$6 \rightarrow 8$	B_1	x axis
$5 \rightarrow 7$	B_{3u}	x axis	$5 \rightarrow 7$	B_u	x and y	$5 \rightarrow 7$	B_1	x axis
			$n_1 - n_2 \rightarrow 7$	A_u	z axis	$n_1 + n_2 \rightarrow 7$	B_2	z axis
			$n_1 + n_2 \rightarrow 8$	A_u	z axis	$n_1 + n_2 \rightarrow 8$	B_2	z axis

[a] C_2 axis about y.

(diazabiphenylene = $C_{10}H_6N_2$ = 154.0531). Three metastables are present at 104.8, 78.8, and 54.8 corresponding to $154^+ \rightarrow 127^+ + 27$, $127^+ \rightarrow 100^+ + 27$, and $100^+ \rightarrow 74^+ + 26$, respectively. Fragments at 127.0429 (C_9H_5N = 127.0422), 100.0301 (C_8H_4 = 100.0313), and 74.0134 (C_6H_2 = 74.0156) show conclusively that the metastables correspond to loss of two molecules of HCN and one of C_2H_2. Successive losses of molecular HCN from the parent ion correspond to the HCN groups in each outer ring of diazabiphenylene. The fragment at 77.0246 corresponds to C_5H_3N (77.0265) and/or $(C_{10}H_6N_2)^{+2}$.

A comparison with the biphenylene mass spectrum[43] shows that, qualitatively, they are similar. Both show parents that are 100% of base peak. Biphenylene has its most prominent fragments at 126, 77, 63, and 50 with relative intensity under 15%. The diazabiphenylene fragments at 127, 100, 74, and 50 show greater intensity relative to the parent ion.

Infrared Spectrum. The ir spectrum of diazabiphenylene shows it strongest band at 838 cm^{-1} characteristic of a 1,2,4 trisubstituted benzene[44] (two free H's). The medium intensity band expected for one free H is not present. Characteristic of heterocyclic aromatic compounds are the bands around 1600 cm^{-1} (C=C and C=N stretching) as well as two bands at 733 and 720 cm^{-1} (C—H ring vibrations). Significantly, no C≡N stretching vibrations were present, hence no nitrile groups. No C–H stretching vibrations at 3000 cm^{-1} were observed (very weak in biphenylene) and the base line showed a slowly rising transmittance with increasing wavelength as in biphenylene.[45]

Ultraviolet Spectrum. A discussion of the uv spectrum of diazabiphenylene will be preceded by a discussion of the uv spectrum of biphenylene. Biphenylene is a planar molecule of symmetry group D_{2h}. Hückel molecular orbital theory generates 12 molecular orbitals, 6 of which are double filled in the ground state. Electronic transitions arise from promotion of an electron to a half-filled or unfilled molecular orbital. HMO predicts electronic transition ($6 \rightarrow 7$) should be of symmetry B_{1g} and forbidden. The second transition ($6 \rightarrow 8$) and the third transition ($5 \rightarrow 7$) are of symmetry B_{3u} and allowed with polarization along the long molecular axis (x).

The uv absorption of biphenylene shows three main absorptions at ~3900 Å (log ϵ 2.4), ~3600 (4), and ~2500 (5). Hochstrasser[46] has shown that the 3900-Å absorption is due to a symmetry-forbidden electronic transition. That the absorption is to a B_{1g} excited state was supported by the perturbing vibration. Hochstrasser[47] has also shown with mixed crystals that the 3600 Å absorption corresponds to an allowed transition along the x axis (B_{3u}).

Introduction of two N atoms into biphenylene in the 2 and 6 or 2 and 7 positions (a) lowers the symmetry of the molecule and (b) opens up $n \rightarrow \pi^*$ type transitions where the lone-pair orbital must be expressed as a linear combination, $n_1 + n_2$ or $n_1 - n_2$, for symmetry reasons. Assuming that diazabiphenylene is planar the 2,6 isomer belongs to the symmetry group C_{2h} and the 2,7 isomer to C_{2v}.

Table VI illustrates the changes in the predicted electronic transitions of biphenylene as the symmetry is lowered to that of 2,6- and 2,7-diazabiphenylene. The 2,6 isomer should have a $\pi \rightarrow \pi^*$ spectrum very similar to biphenylene while in the 2,7 isomer the lowest electronic transition becomes allowed. The $n \rightarrow \pi^*$ transitions in the 2,6 isomer originate from each lone pair state while in the 2,7 isomer they only originate from the $n_1 + n_2$ state. All allowed $\pi \rightarrow \pi^*$ transitions are polarized in the molecular plane while all allowed $n \rightarrow \pi^*$ transitions are polarized perpendicular to the molecular plane.

In discussing the uv spectrum let us start with the $n \rightarrow \pi^*$ transitions. A blue shift of 500 cm^{-1} with the addition of HCl is too small to attribute the long-wavelength bands (below 338 nm) to an $n \rightarrow \pi^*$ transition. Addition of HCl enhances the shoulders at 370 and 320 nm. These two shoulders are probably related. The separation is of the order 4000 cm^{-1}. The only possibilities left for an $n \rightarrow \pi^*$ transition are the two other shoulders at 388 and 355 nm which are not present in acid (either "lost" under the increase in the shoulder at 370 mμ or shifted to higher energy ($n \rightarrow \pi^*$)) or the $n \rightarrow \pi^*$ system is buried under the $\pi \rightarrow \pi^*$ system.

The long-wavelength bands below 338 nm are assigned to a $\pi \rightarrow \pi^*$ transition. It is not possible to get accurate vibrational spacings because of solution broadening. It would be tempting to assign the long wavelength bands to the allowed B_u transition in the 2,6 isomer and the weak shoulders on the long wavelength side to the forbidden A_g transition. A

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(43) L. Friedman and D. F. Lindow, *J. Amer. Chem. Soc.*, **90**, 2324 (1968).

(44) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).

(45) Reference 23, p 288; G. Wittig and G. Lehman, *Ber.*, **90**, 875 (1957).

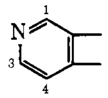
(46) R. M. Hochstrasser, *Can. J. Chem.*, **39**, 765 (1961).

(47) R. M. Hochstrasser, *J. Chem. Phys.*, **33**, 950 (1960).

comparison of the available uv spectra of 2,6 and 2,7 isomers of substituted biphenylenes[41,42] reveals little because the transitions are essentially localized in the π system. Therefore, with the limited information at hand it is unclear whether the spectrum belongs to the 2,6 or 2,7 isomer.

The transition at short wavelength (240 nm) is probably analogous to the biphenylene transition in the same region.

Nuclear Magnetic Resonance. A first order nuclear magnetic resonance spectrum of diazabiphenylene can be deduced by treating diazabiphenylene as a 3,4-disubstituted pyridine. The problem becomes a three-proton system. Using the numbering system in 2,6- or 2,7-diazabiphenylene we are concerned with the H_1, H_3, and H_4 protons.

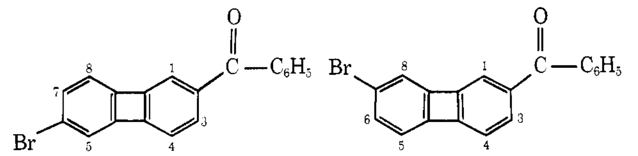


In pyridine[48] both α protons (H_1 and H_3) absorb at δ 8.6 and the β proton absorbs at δ 7.2 (H_4). Addition of two methyl groups at the 3 and 4 positions of pyridine[49] gives $H_\alpha = 8.18$, $H_\alpha = 8.14$, and $H_\beta = 6.88$. Therefore to a first approximation we should expect an ABX system. There would be an eight-line pattern for the AB part and a six-line pattern for the X part.

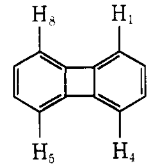
The proton at δ 6.8 was assigned to H_4. It is a sextet (possibly octet) as would be expected for the X proton; however, the intensity of one line is too great. The expected eight-line AB pattern, however, does not appear. Instead we see a doublet at δ 8.3 and a doublet at δ 8.0 (both possibly quartets). The splitting at δ 8.3 is 4 cps while at δ 8.0 it is 1.4 cps. In pyridine[50] $J_{\alpha\alpha'} = 0.4$ cps, $J_{\alpha'\beta} = 0.9$ cps, and $J_{\alpha\beta} = 5.5$ cps. Therefore the larger interaction between H_α and H_β (or H_3 and H_4) suggests that $H_3 = \delta\ 8.3$ and $H_1 = \delta\ 8.0$.

It appears that instead of an ABX system we really have an AMX system. We should expect three well separated doublets of doublets. H_1 and H_3 are consistent with this; however, H_4 has a six-line pattern. The diazabiphenylene structure is also consistent with the 1:1:1 ratio of hydrogens.

It might be argued that the 2,6 and 2,7 isomers are contributing to the spectrum. As a model let us consider 2-benzoyl-6-bromobiphenylene and 2-benzoyl-7-bromobiphenylene. The nmr spectra have been published[51] and the two different substituents allow us to see effects in both rings. (The frequency at which the spectra were taken was apparently omitted, unfortunately; however, the results as presented suffice for our purposes.) All protons are found to be doublets of doublets. The centers of absorption for H_1, H_3, and H_4 in both isomers are found to differ by 1.8 to 3 cps. The coupling constants are found to differ by 1.8 to 3 cps. The coupling constants are found to differ by 0 to 0.5 cps. The differences are small but should be observable in a mixture. The two α protons in the Br ring also have absorption centers differing by ~3 cps. However, the β protons (or H_4 in diazabiphenylene) differ by 6.6 cps. This suggests that the B proton is most affected by a change in isomers. *If* the second isomer of diazabiphenylene is present in substantial amount and *if* the centers of absorptions for H_1 and H_3 in both isomers are substantially the same and *if* the absorptions for H_4 differ by the right amount to give a reasonably symmetric six-line pattern, then the two isomers might explain the spectrum. It seems highly unlikely.

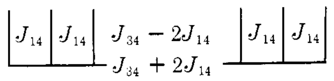


The descriptions of the nmr spectrum of biphenylene[52] do not mention the values of coupling constants between H_1 and H_8 and H_4 and H_5, the peri hydrogens. Drawing one of the Kekulé structures for biphenylene shows that the peri hydrogens are separated by five alternating single and double bonds just as between para hydrogens H_1 and H_4. (However, the geometry of the hydrogens is different.) H_1 and H_4 should be coupled through the ring, but if the interaction between the two rings is substantial, then peri coupling should be observed (probably less than 1 cps). Even though there is, in fact, interaction between the rings in biphenylene (consider the uv spectrum), conclusions differ about the π electron delocalization as determined from nmr spectral data.[52]



If one naively assumes that in diazabiphenylene the para coupling constant J_{14} is equal to the peri coupling constant J_{18} ($=J_{45}$), then the H_4 spectrum will be further to a six-line pattern (Chart I). The same pattern should emerge for H_1, and H_3 should remain a quartet. From H_3, $J_{34} = {\sim}5.5$ cps and $J_{13} = {\sim}0.5$. From H_4, $J_{34} + 2J_{14} = 7.3$ cps and $J_{14} = {\sim}0.9$. From the spacing in H_4, J_{14} is found to be ~1.2, but $J_{34} - 2J_{14}$ which should be 3.7 cps is, in fact, 1.8 cps, half of what it should be. For H_1 the total six-line pattern should be condensed to $J_{13} + 2J_{14} = 2.3$ cps which would make it difficult to resolve.

Chart I



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[49] Reference 48, No. 2854.

[50] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 266.

[51] J. M. Blatchly, D. V. Gardner, J. F. W. McOmie, and T. P. Prabhu, *J. Chem. Soc. C*, 2789 (1969).

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