Electronic Absorption Spectra of Methanal Azine and the Methyleniminyl Free Radical

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pairs separated by twice the TA energy and combinations involving the TO_1 and TO_2 modes usually overlap. Also, the lowest-energy peak is a TA overtone which remains intense even at low temperatures. In contrast, the TA and TO_1 modes of $SrTiO_3$ are near degenerate at the zone boundary with energy 117 cm^{-1} and the TO_2 mode has an energy of 194 cm^{-1}. Because of the higher TA energy, the spectra appear to consist of groups of peaks rather than combination pairs. One higher-energy group around 600 to 750 cm^{-1} is temperature insensitive and consists of sum combination bands, and the lower-energy group around 300 to 400 cm^{-1} is partially temperature sensitive and consists of difference combination bands together with some overlapping sum bands. The differences between the $KTaO_3$ and $SrTiO_3$ spectra are due to phonon energy differences at the zone boundary rather than drastic changes in the scattering efficiencies or selection rules.

The three sharp lines which appear in the pure sample below the 110°K phase transition are attributed to scattering from local modes. These lines do not have the same energies as the polar TO modes. Also, in an impure $SrTiO_3$ sample at low temperatures, Raman scattering is found from both the local modes and the polar TO modes. The absence of ferroelectricity and first-order Raman scattering in the tetragonal phase makes it probable that the point group of this phase is C_{4h} or D_{4h}. The impure $SrTiO_3$ undergoes different types of phase transitions as the sample is cooled to liquid-helium temperatures. This is clearly seen in the different spectra observed at low temperatures and illustrates how sensitive Raman scattering is to crystal symmetry. The point group of the impure sample at 78°K is either S_4, C_4, or C_{4v} with the latter most likely. At lower temperatures the symmetry is undoubtedly lower than tetragonal.

ACKNOWLEDGMENTS

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Electronic Absorption Spectra of Methanal Azine and the Methyleniminyl Free Radical

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The methyleniminyl free radicals, H_2CN, HDCN, and D_2CN have been produced from flash photolysis of their stable dimers, the methanal azines H_2CNNCH_2, HDCNNCHD, and D_2CNNCD_2. The electronic absorption spectra of both radicals and parent substances are presented and discussed in terms of simple molecular orbital descriptions of the transitions. The photochemical processes are related to these transitions, and applications to the corresponding hydrocarbon diene, butadiene-1,3, are noted.

A brief report[1] has already summarized some principal results concerning the participation of methanal azine, $H_2C=N-N=CH_2$, in the photodecomposition of diazomethane in cryogenic matrices. It was stated that methanal azine (previously termed formaldazine), formed by the combination of methylene radicals with diazomethane, was subsequently photolyzed to produce methylenimine and hydrogen cyanide, via the disproportionation reaction of a pair of methyleniminyl ($H_2C=N$) radicals.

The evidence cited for the discrete existence of the H_2CN radicals in that reaction consisted of the direct detection of an absorption spectrum, in the ultraviolet, assigned to an electronic transition of this species after flash photolysis of methanal azine in the gas phase. The same spectrum has also been observed during the flash photolytic decomposition of gaseous methanal oxime, $H_2C=NOH$.[2] Absorption bands at similar wavelengths have also been obtained during the flash photolysis of both ethanal azine, $CH_3CH=N-N=CHCH_3$, and propanone azine, $(CH_3)_2C=N-N=C(CH_3)_2$.[2] Thus methyleniminyl would seem to be the first member of a new homologous series of free radicals, of which the near-ultraviolet electronic transitions are conveniently situated to be employed for monitoring concentrations during investigations of their reaction kinetics.

Methanal azine is itself of some interest in that its electronic absorption spectrum is comparable to that of butadiene-1,3, its hydrocarbon analogue. Like butadiene, methanal azine is the first member of a series of conjugated acyclic dienes, but the nitrogen atoms present in the azines confer special properties on these molecules. Further members of this series have been

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[1] J. F. Ogilvie, Chem. Commun. 1965, 359.

[2] D. G. Horne and R. G. W. Norrish (to be published).

characterized chemically for many years, but their electronic spectra have not been studied.

In this article we are concerned with the presentation and descriptive analysis of the ultraviolet absorption of the methyleniminyl free radical and its parent dimer, methanal azine. The experimental results require for their interpretation assignments of transitions not previously applied to similar systems, and an application to butadiene-1,3 resolves an anomaly in the extinction coefficients and photochemistry of this molecule.

EXPERIMENTAL

Methanal azine was prepared[3] by depolymerization (at approximately 475°K, *in vacuo*) of the dried white solid which was precipitated from solution when hydrazine hydrate (Whiffen Co.) was added to formalin solution (or to solid polyoxymethylene) stoichiometrically, according to the equation:

$$n\ N_2H_4+2n\ H_2CO \rightarrow (H_2CN)_{2n}+2n\ H_2O.$$

In the case of the deuterated methanal azines, the corresponding deuterated polyoxymethylenes (from Merck, Sharpe and Dohme, Montreal) were employed. Purification was effected by vacuum distillations, and was checked by infrared and ultraviolet absorption spectra of the gas. (Minor impurities containing no nitrogen, rather than methanal azine, are believed to have been responsible for the microwave absorption reported earlier.[1]) Samples were stored at 77°K, and operations with the gas were performed at pressures less than 20 torr to reduce polymerization on surfaces. The diluent gas in the flash-photolysis experiments was "oxygen-free" nitrogen (British Oxygen Company), dried by passage through a trap at 77°K. Ultraviolet absorption spectra of methanal azine and its decomposition products were recorded on a Unicam SP800C double-beam prism spectrophotometer with fused-silica optics. The range was 14 000 to 52 500 cm^{-1}, with spectral slitwidths less than 50 cm^{-1} and false radiation less than 0.5% (for frequencies less than 50 000 cm^{-1}) when the best spectra were obtained. Unicam SP100G and Perkin–Elmer 521 double-beam recording infrared spectrophotometers with diffraction gratings were also used for analysis of methanal azine and its decomposition products.

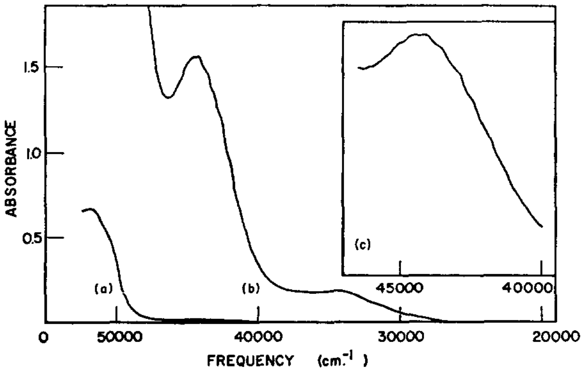

Fig. 1. Electronic absorption of methanal-h_2 azine. Gas pressure is 15.0 torr, path length in (a) 1 mm, (b) and (c) 100 mm. 1(c) is expanded portion to illustrate diffuse structure of second band.

Table I. Electronic transitions of methanal azine (H_2C=N–N=CH_2).

Maximum absorption frequency	Extinction coefficient	Oscillator strength
~34 500 cm^{-1}	35 liter $mole^{-1}\cdot cm^{-1}$	$\sim 0.5\times 10^{-3}$
44 150	275	$\sim 3.0\times 10^{-3}$
~51 700	8700	$\gtrsim 1.6\times 10^{-1}$

The apparatus for flash photolysis and kinetic spectroscopy experiments was of the usual pattern developed in this laboratory.[4,5] The fused-silica reaction vessel was of internal dimensions 2.0-cm diameter and 50-cm length. The photolysis lamp, also 50-cm effective length, lay parallel to the reaction vessel within an aluminium reflector. This lamp was fired to produce a light pulse of 19-μsec half-width upon discharging two 33.3-μF condensers from 7.8 kV, dissipating 2000 J. The spectroscopic source was a horizontal flash lamp on the axis of the reaction vessel, fired by the discharge of one 2-μF condenser charged to 10 kV (100 J) with a half-width of 6 μsec. Both lamps contained 100 torr of pure krypton. The delay between the two lamps was controlled electronically and could be varied in intervals progressively increasing from 0.5 μsec. Transient absorption spectra were photographed by means of a Hilger E478 Littrow spectrograph; the effective spectral slitwidth at 35 000 cm^{-1} was 5 cm^{-1}. Optical densities were measured on Ilford HP3 plates (with iron arc wavelength calibration) with a Joyce Loebl E12 Mark III recording microdensitometer. Frequencies presented in this article are vacuum wavenumbers (cm^{-1} units). Further details of the flash photolysis apparatus are presented in the dissertation of Horne (Cambridge, 1966, unpublished).

RESULTS

Spectra of Methanal Azines

The electronic absorption spectrum of methanal azine is presented in Fig. 1. It consists of three principal absorption features specified by the data in Table I.

The small frequency band is completely diffuse, showing no discernible vibrational structure under our conditions of measurements both photoelectric and

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[3] N. P. Neureiter, J. Am. Chem. Soc. 81, 2910 (1959).

[4] R. G. W. Norrish, Bakerian Lecture (1966); Proc. Roy. Soc. (London) **A301**, 1 (1967).

[5] G. Porter, *Technique of Organic Chemistry* (Interscience Publishers, Inc., New York, 1961), Vol. 8, Part 2, p. 1055.

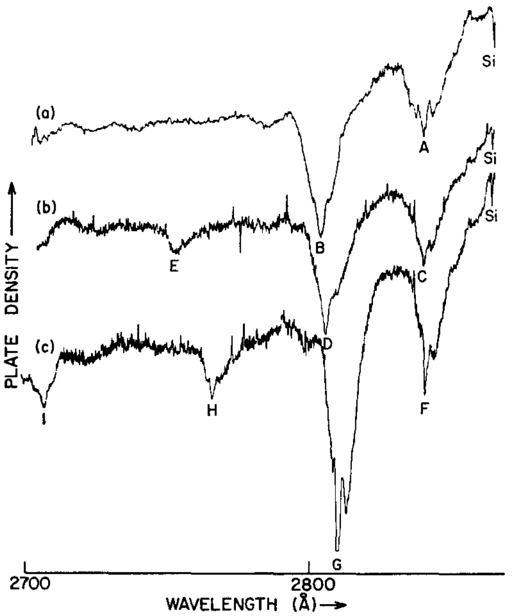

FIG. 2. Microdensitometer traces of transient absorption spectra photographed after flash photolysis of (a) methanal-h_2, (b) methanal-*hd*, and (c) methanal-d_2 azines. Scans have been displaced vertically. Source absorption line at right is SiI, 2882 Å; wavelength scale is nonlinear.

photographic, and it has a weak tail extending to frequencies less than 30 000 cm^{-1} ($\epsilon \sim 1$ at 28 000 cm^{-1}). The middle band has traces of diffuse structure, illustrated in curve 1(c), with apparent maxima or inflection points at 39 700, 40 250, 40 800, 41 300, 41 900, 42 450, 43 100, 43 600, 44 200, 44 600, and 45 200 cm^{-1}, a progression of vibrational interval approximately 550 cm^{-1}. (The accuracy of frequency measurement was limited to 100 cm^{-1} by the diffuse nature of the structure.) The remaining band, the most intense, has an apparent shoulder near 50 400 cm^{-1}. The values of the oscillator strengths, estimated from twice the product of the extinction coefficient at the maximum absorption and the frequency difference between the frequencies at the maximum and half-maximum (on the small frequency side), are necessarily approximate because of the overlapping nature of the bands.

Ultraviolet absorption spectra of the deuterated methanal azines HDCNNCHD and D_2CNNCD_2 have also been recorded, but the data are less reliable than before, because of the small samples available. However the intensity ratios of the three bands are equal, within experimental error, for all three isotopic species. Structure is present in the second bands of both methanal-*hd* and -d_2 azines, but seems to be as diffuse as for methanal-h_2 azine; the frequency intervals are again approximately 550 cm^{-1}.

Flash Photolysis of Methanal Azines

Flash photolysis was effected under conditions maintained isothermal by the presence, in the reaction vessel mixed with the methanal azine, of a large excess pressure of transparent diluent gas. When a mixture of 3 torr H_2CNNCH_2 and 240 torr nitrogen was subjected to flash photolysis, a transient absorption near 2800 A was produced; the absorption was most intense at the instant of maximum photoflash intensity and disappeared within 200 μsec. A microdensitometer trace of this absorption, photographed at 6-μsec delay, is presented in Fig. 2, curve (a). No other transient spectra were detected between 2100 and 6500 A, except on one occasion a weak methyl radical signal at 2150 Å, photographed at 20 μsec delay. In Fig. 2, curves (b) and (c), are shown the spectra obtained on flashing HDCNNCHD and D_2CNNCD_2, respectively; they had similar decay characteristics to the previous transient spectrum, curve (a). The frequencies of the central maxima of each band in these spectra are listed in Table II. Flash photolysis of butadiene-1,3 under comparable conditions produced no detectable transient absorption between 2400 and 6000 Å.

The products obtained after flash photolysis of several samples of methanal-h_2 azine were collected and analysed by their gas-phase vibration–rotation spectra. The major products, in order of decreasing abundance, were hydrogen cyanide, ammonia, ethene, methane, and ethyne. Ultraviolet spectra showed a trace of diazomethane to be also present. Hydrogen and nitrogen were not detectable by these techniques.

The oscillator strength of the transient ultraviolet absorption spectrum was estimated by the following procedure. The optical density of the transient absorption was compared with that of a calibrated step-wedge on the same photographic plate. On the assumption that the transient spectrum is due to the methyleniminyl free radical H_2CN (*vide infra*), the oscillator strength f was calculated according to the equation,

$$f=4.3\times10^{-9}\int\log[I_0(\nu)/I(\nu)]d\nu/(cd),$$

in which $\log[I_0(\nu)/I(\nu)]$ is the optical density of the transient absorption at frequency ν, c is the concentration of H_2CN, and d is the optical path length. On the same photographic plate, the optical density of the

TABLE II. Frequencies of absorption band central maxima in the transient spectra detected after flash photolysis of the isotopic methanal azines; $\Delta\nu$ is the separation of bands from the first in each case, and the letters refer to the bands similarly labeled in Fig. 2.

H_2CNNCH_2		HDCNNCHD		D_2CNNCD_2	
ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
A 35 080	0	C 35 045	0	F 35 040	0
B 35 610	530	D 35 550	505	G 35 485	445
		E 36 310	1265	H 36 115	1075
				I 36 930	1890

methanal azine continuum at 34 100 cm^{-1} was measured before, and several microseconds after, the flash that produced photolysis of samples of 1.0 torr methanal azine and 250 torr nitrogen. This method enabled a calculation of the absolute radical concentration, 0.155 ± 0.035 torr, corrections being applied to take account of the primary quantum yield of H_2CN (1.6 ± 0.2) and the (small) extent of reaction of H_2CN during the photolysis flash. The result is an oscillator strength for the H_2CN transition of $f=(4\pm2)\times10^{-4}$. (The statistical factor in the oscillator strength equation, omitted above, has been assumed to be unity.)

DISCUSSION

Methanal Azine

Methanal azine has been shown, from an analysis (Ogilvie, unpublished results) of the vibration–rotation structure of several infrared absorption bands, to have rotational parameters similar to those of butadiene-1,3.[6] The structure of this azine is hence best described by the name, in systematic nomenclature, *s-trans* 2,3-diazabutadiene-1,3. The symmetry point group of the equilibrium nuclear configuration of the ground state is therefore C_{2h}. The electronic structure of this molecule can then be represented in the following molecular orbital scheme, in order of increasing orbital energy, as

$$\begin{aligned}&K_NK_NK_CK_C(a_g,\sigma_{\mathrm{CH}})^2(b_u,\sigma_{\mathrm{CH}})^2(a_g,\sigma_{\mathrm{CH}})^2(b_u,\sigma_{\mathrm{CH}})^2\\&\quad(a_g,\sigma_{\mathrm{CN}})^2(b_u,\sigma_{\mathrm{CN}})^2(a_g,\sigma_{\mathrm{NN}})^2(a_u,\pi_1)^2(b_g,\pi_2)^2\\&\quad(a_g,n_{\mathrm{N}+})^2(b_u,n_{\mathrm{N}-})^2(\bar{a}_g,\sigma_{\mathrm{CH}}^*)^0(\bar{b}_u,\sigma_{\mathrm{CH}}^*)^0\\&\qquad\qquad(\bar{a}_u,\pi_3^*)^0(\bar{b}_g,\pi_4^*)^0,\ {}^1A_g.\end{aligned}$$

These orbitals are simply formed from those of a pair of H_2CN fragments, taken to be either symmetric or antisymmetric with respect to the inversion operation applied at the center of symmetry. The symmetric sigma orbitals are conventionally taken to have less energy than the corresponding antisymmetric ones, but they are essentially degenerate if the nuclei at their centers are well separated or if perturbing orbitals of the same symmetry type are not of similar energies. The pi orbitals are considered to have the usual properties as in Hückel theory. The nature of the $\bar{a}_g$ and $\bar{b}_u$ orbitals will be considered later. The $n_{\mathrm{N}+}$ and $n_{\mathrm{N}-}$ orbitals are defined, respectively, as the additive and subtractive combination of the lone pairs on the nitrogen atoms; accordingly they have slight bonding and antibonding properties, respectively.

We now proceed to the assignment of the electronic absorption bands of methanal azine. The $\pi^*\leftarrow\pi$ transition of some dienes is found in the region of 2000 A, and this transition of some alkyl-substituted azomethines has been assigned to bands with maxima near 57 000 cm^{-1}.[7] The first prominent absorption system of butadiene-1,3 has $\nu_{00}=46\,300$ cm^{-1}, $\epsilon_{\max}=2.75\times10^4$, $f=0.66$, and $\Delta\nu=1400$ cm^{-1} (our measurements). This transition is designated $\pi_3^*\leftarrow\pi_2$. The diffuse vibrational structure of interval 1400 cm^{-1} is identified with a symmetric skeletal (carbon atoms) valence-stretching vibration; this is of smaller frequency in the excited state than in the ground state (1600 cm^{-1}) because of the occupancy of the antibonding orbital in the excited state. The frequency decrease is accompanied by an increase of the outer carbon–carbon bond length, so this vibration is excited during the electronic transition. By analogy we can assign, for methanal azine, the similar $\pi_3^*\leftarrow\pi_2$ transition, $\nu_{00}=50\,400$, $\epsilon=8700$, $f=0.16$ and $\Delta\nu=1300$ cm^{-1}. Because of the presence of atoms other than carbon in the conjugated skeleton of methanal azine, this $\pi_3^*\leftarrow\pi_2$ transition, although allowed, is expected both to be less intense than for the corresponding hydrocarbon and to lie at greater frequencies, for the reason that the result of the transition is to decrease the pi-electron density at the more electronegative central nitrogen atoms. As the apparent absorption maximum of our band measurement is near the limit of our spectrometer, we can be certain neither that 51 700-cm^{-1} marks the frequency of the absorption maximum of the entire band, nor that the reported oscillator strength is not a serious underestimate. Also the inflection at 50 400 cm^{-1} is much less pronounced than the structure observed for butadiene-1,3, so the assignment of 50 400 cm^{-1} as ν_{00} can only be tentative. However, if the latter be accepted, the principal features of the $\pi_3^*\leftarrow\pi_2$ bands of these two molecules can be interpreted without invoking a gross change of molecular configuration in the excited state—both ground and excited states thus being planar and centrosymmetric. As a result of a preliminary theoretical calculation, the suggestion[8] of singlet excited states twisted at one double bond has been made for butadiene-1,3, but our observations provide no support for this hypothesis. In fact, both the presence of three (remaining) electrons in the bonding pi orbitals and the form of the antibonding pi orbital indicate that the excited ^1B states of both butadiene and methanal azine would retain coplanar nuclear equilibrium configurations.

We next consider the $\pi^*\leftarrow n$ excitation of methanal azine, of which there is no parallel for butadiene. Transitions of this type usually have energies of 25 000 to 40 000 cm^{-1} and oscillator strengths of magnitude $\sim10^{-4}$.[9] There is one distinct band with these characteristics ($\nu_{\max}\sim34\,500$ cm^{-1}, $f\sim10^{-4}$) observed for methanal azine. The two parity-allowed transitions of

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[6] D. J. Marais, B. P. Stoicheff, and N. Sheppard, Tetrahedron **17**, 166 (1962).

[7] D. A. Nelson and J. J. Worman, Tetrahedron Letters 507 (1966).

[8] L. Burnelle, J. Chem. Phys. **43**, S29 (1965).

[9] J. N. Murrell, *Theory of the Electronic Spectra of Organic Molecules* (Methuen and Co., Ltd., London, 1963).

this type are $\bar{a}_u \leftarrow a_g(\pi_3{}^* \leftarrow n_{\mathrm{N}+})$ and $\bar{b}_g \leftarrow b_u(\pi_4{}^* \leftarrow {}_{\mathrm{N}-})$. The $\pi_4{}^*$ orbital of the upper state in the latter transition is expected to lie at energies much greater than 27 000 cm^{-1} above the nonbonding (or possibly slightly antibonding) $n_{\mathrm{N}-}$ orbital, especially as the $\pi_3{}^*$ orbital is appreciably higher than for the corresponding hydrocarbon. The former alternative is thus the more reasonable choice. This assignment is allowed by symmetry, as the transition moment transforms like the z axis (figure axis) of the molecule. The alternative $\pi_3{}^* \leftarrow n$ transition which is not allowed by symmetry, $\bar{a}_u \leftarrow b_u$, would involve a smaller transition energy because the nonbonding orbitals are nondegenerate with the gerade combination at smaller energy. Vibronic interaction could give some intensity to this transition, if a nonsymmetric vibration were excited, and then the oscillator strength might approach 10^{-4} in magnitude. The effect of such a vibronic interaction is frequently to cause a distortion of the molecule in the excited state, in other words, to reduce the symmetry of the excited-state conformation such that the electronic transition becomes formally allowed. In this case, the allowed $\pi_3{}^* \leftarrow n$ transition should be also observed, at greater energies and having a greater oscillator strength. A band with maximum near 44 000 cm^{-1} is available for such an assignment. As a matter of fact, the two observed bands at 35 000 and 44 000 cm^{-1} lie on either side of 40 000 cm^{-1} near which absorption due to the $\pi^* \leftarrow n$ transition has been found[10] for simple azomethines, embodying the $\mathrm{R_2C{=}NR}$ chromophore. However, because of the relative decrease of energy of the $\pi_3{}^*$ antibonding orbital in the diene, according to Hückel theory, the mean of the corresponding pair of $\pi^* \leftarrow n$ transitions in methanal azine should be situated at appreciably smaller frequencies. Moreover, the vibrational structure on the 44 000-cm^{-1} band is not easily explained on the basis of such an assignment, for which valence-stretching modes of the skeleton would be expected to accompany the excitation of an essentially nonbonding electron into an antibonding orbital. Further, despite the dissimilar shapes of the 35 000- and 44 000-cm^{-1} bands, one would expect the former rather than the latter to be more likely to show vibrational structure, if they were both $\pi^* \leftarrow n$ transitions. Therefore we prefer the assignment of the 35 000-cm^{-1} band to the symmetry-allowed $\pi_3{}^* \leftarrow n_{\mathrm{N}+}(\bar{a}_u \leftarrow a_g)$ transition, and seek further an explanation of the 44 000-cm^{-1} band (*vide infra*); however as the present evidence is not conclusive, further theoretical or experimental confirmation is desirable. The ${}^1A_u{}'$ excited state is probably planar, but the gradual onset of absorption indicates a considerable change in geometry relative to the ground state. (Some part of the absorption between 27 000 and 30 000 cm^{-1} might also be due to a $\sigma^* \leftarrow n$ transition or to even the forbidden $\pi_3{}^* \leftarrow n_{\mathrm{N}-}$ transition; as no second band in this region is distinct, no further discussion of this possibility will be made.)

To enable an assignment of the remaining band of Table I, we have included, in the number of molecular orbitals of methanal azine, two antibonding sigma orbitals $\bar{a}_g$ and $\bar{b}_u$. Similar orbitals have been included as a basis of discussion of assignments for alkenes.[11a,b] The characteristics of the former orbitals are that they are antibonding between carbon and hydrogen atoms, but mildly bonding between the carbon and nitrogen atoms of the diene skeleton and that they have substantial Rydberg character.[11a] As this bonding effect partially compensates for the principal antibonding effect, the energy of this orbital is greatly reduced relative to what it would be in the absence of a bonding effect. For this orbital to be involved in an allowed transition involving no change in symmetry species of the equilibrium nuclear positions, the combining orbital must have ungerade parity. The suitable occupied orbitals having this property are $b_u(n_{\mathrm{N}-})$ and $a_u(\pi_1)$. The overlap of the former with $\bar{a}_g$ would be extremely small, whereas with the latter the overlap would be similar to that in the case of alkenes, in which the oscillator strength of the "mystery" band is similar.[11a] However the π_1 and π_2 orbitals are so much split in energy that, for the $\bar{a}_g$ orbital to be the terminus of the transition from π_1, that antibonding orbital would have to lie at lesser energy than at least the nonbonding orbitals representing the lone electron pairs of the nitrogen atoms, an untenable situation. Therefore we must use the adjacent $\sigma_{\mathrm{CH}}{}^*$ orbital $\bar{b}_u$ which according to both molecular orbital calculations[11a,b] for ethene is of similar energy and bonding properties. The essential difference between the $\bar{a}_g$ and $\bar{b}_u$ orbitals is that the latter has a node at the center of symmetry of the molecule. Because of this, the bonding effect of the corresponding $\bar{b}_{3u}$ orbital of ethene is greatly reduced and the orbital energy hence appreciably increased. In the dienes the bonding effect of both $\bar{a}_g$ and $\bar{b}_u$ orbitals can still be operative, despite a node between the nitrogen atoms. Therefore the $\bar{b}_u$ orbital is likely to have an energy not much greater than the $\bar{a}_g$ orbital. Hence the $\bar{b}_u$ orbital is well situated to account for the transition from the $\pi_2(b_g)$ orbital. The observed absorption band consists of a continuum with overlying diffuse structure of interval 550 cm^{-1}, apparently insensitive to deuterium substitution. Such a progression of at least 10 vibrational quanta indicates an appreciable change in molecular geometry in the excited state. The magnitude of the vibrational frequency is appropriate to a bending or torsional vibration, which must be of a totally symmetric species to be compatible

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[10] R. Bonnett, J. Chem. Soc. **1965**, 2313. M. B. Robin and W. T. Simpson, J. Chem. Phys. **36**, 580 (1962).

[11] (a) M. B. Robin, R. R. Hart, and N. A. Kuebler, J. Chem. Phys. **44**, 1803 (1966). The ethene transition should be written ${}^1A_g \rightarrow {}^1B_{1u}$ in the notation of these authors, not ${}^1A_g \rightarrow {}^1B_{2u}$. In the present article we use the notation recommended by Mulliken [J. Chem. Phys. **23**, 1997 (1955)] and this transition is still ${}^1B_{1u} \leftarrow {}^1A_g$. (b) H. Berthod, J. Chem. Phys. **45**, 1859 (1966).

with the allowed electronic transition proposed. The vibrational interval is inappropriately small for the N–N stretching vibration in the excited state unless the newly occupied orbital had a large antibonding effect in that (N–N) region, and such a long progression in a stretching vibration would be unusual. A more likely assignment of the 550-cm^{-1} vibration is to a torsional mode about the N–N bond. With the loss of a center of symmetry in the nonplanar excited state, the parity selection rule is no longer strictly applicable. The proof of Rydberg character of the upper electronic state could be furnished by the apparent disappearance of this transition in an argon matrix experiment.[11a] There is no separate band distinguishable for butadiene, but an enhanced tail can be discerned in the region of 41 000 cm^{-1}.[12] This additional region of absorption, almost covered by the adjacent overwhelming $\pi_3{}^* \leftarrow \pi_2$ band, can then give rise to the extinction coefficient and photochemical anomalies previously reported,[13] hence allowing the retention of 46 300 cm^{-1} as ν_{00} of the $\pi_3{}^* \leftarrow \pi_2$ transition. In methanal azine the energy of this transition is sufficiently different that there can be no doubt of the existence of a separate band. Whatever the nature of the transition in methanal azine, it would seem to correspond to the indicated ones of ethene and butadiene-1,3.

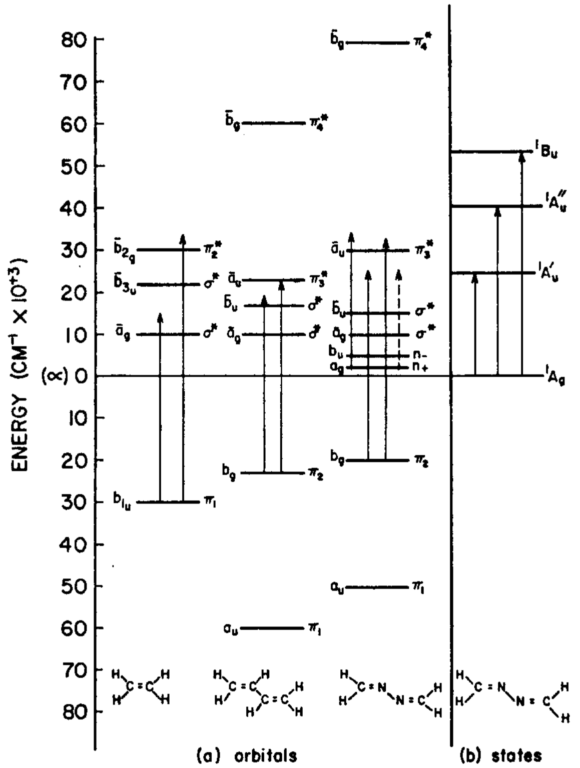

FIG. 3. Approximate energy levels of (a) orbitals of ethene, butadiene-1,3, and methanal azine, and (b) singlet states of methanal azine. Energy levels from simple Hückel calculations have been scaled to suit assigned transitions.

The approximate energy levels and assigned transitions are depicted in Fig. 3. The relative energies of the levels have been calculated from Hückel theory, and the frequencies have been scaled to fit the assigned $\pi^* \leftarrow \pi$ transitions. The Coulomb integral of a nitrogen atom was assigned the value $N = \alpha_c + \frac{1}{2}\beta$, and all bond integrals were assigned the value β. With this usage, the values of β for butadiene-1,3 and methanal azine were 37 400 and 39 300 cm^{-1}, respectively. The ethene $\pi^* \leftarrow \pi$ transition was assigned a frequency of 60 000 cm^{-1}, but this value does not matter greatly for the present purpose of comparison. The other energy levels in Fig. 3 were placed to be appropriate to the transitions as assigned, as well as to have qualitative compatibility with the earlier theoretical computations.[11a,b]

In ethanal and propanone azines, the spectra are similar, except that the $\pi_3{}^* \leftarrow \pi_2$ bands shift to smaller frequencies in the manner expected from Woodward's rules.[9] The $\sigma^* \leftarrow \pi_2$ band is hence increasingly overlapped by the former much more intense transition. This second band shows no sign of vibrational structure in either case. The band of least transition energy can be observed to extend, still lacking structure, to frequencies less than 27 000 cm^{-1} at the greater concentrations of gas usable with these substances.

Carrier of the Transient Spectrum

Chemical analysis of the reactant and the products of the flash-photolysis reaction indicates the presence of only carbon, nitrogen, and hydrogen. The large isotope effects in the transient spectrum produced on progressive deuterium substitution in the parent azine prove that the transient carrier contains at least two hydrogen atoms. The rovibronic branch separations indicate that at least two heavy atoms are present. (We have not prepared methanal azine substituted with nitrogen and carbon isotopes.) From the immediate appearance of the transient spectrum during the photolysis flash under isothermal conditions, and from its monotonically decreasing intensity after the flash, we conclude that the production of the carrier is the result of a primary photochemical process. That the spectrum does not belong to methanal azine itself is suggested by the fact that there is in the vibration–rotation spectrum of methanal-d_1 azine a consistent doubling of the bands which has no counterpart in the new vibronic spectrum. Further evidence that methanal azine is not the carrier is furnished by the detection of the transient spectrum when methanal oxime was flashed,[2] in which case the spectrum also appeared immediately and decayed monotonically. That the transient carrier has at least two functional substitution positions is proved by the detection of single vibronic bands centered at 34 350 and 34 005 cm^{-1} after ethanal and propanone azines,

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[12] American Petroleum Institute Research Project No. 44; Ultraviolet spectral data No. 65. Our spectrum shows no difference in form from this one, also cited in Ref. 13.

[13] R. Srinivasan and F. I. Sonntag, J. Am. Chem. Soc. 87, 3778 (1965).

respectively, were flashed.[2] The presence of only a single band or a single series of bands when ethanal and methanal-d_1 azines were (separately) flashed strongly indicates that only two, equivalent, substitution positions are present with the chromophoric group in the carrier. From all this evidence, we conclude that the carrier of the transient spectrum in Fig. 2(a) is the methyleniminyl free radical H_2CN. A rearranged structure H_2NC might also be compatible with the evidence but is, we feel, extremely unlikely. Further supporting evidence comes from the product analysis and from the rovibronic band shapes.

Nature of the Electronic Transition of the Transient Spectrum

The transient spectrum having been assigned to H_2CN, to relate the type of transition to the electronic structure of this species would now be appropriate. A transition commonly found in this region of the ultraviolet is described conveniently as $\pi^*\leftarrow n$. For methanal, this transition is characterized by an oscillator strength $f=2.4\times10^{-4}$ and an origin $\nu_{00}=28\ 193\ \text{cm}^{-1}$ [14]; however, the spectrum is abundant and complicated, and the band representing the purely electronic transition is of extremely small intensity. In contrast, the methyleniminyl spectrum in Fig. 2 is simple even though some detected bands had a considerable absorbance. Also, the smallest energy band of each isotopic species, showing small but significant deuterium shifts which are undoubtedly due to zero-point energy effects, bears a great resemblance to a zero–zero band (i.e., the band marking the transition from the vibrationally unexcited ground state to the vibrationally unexcited but electronically excited state). From the simplicity of the spectrum, we infer that there is only a small change of equilibrium structure in the two combining electronic states. Also, the presence of the zero–zero bands, as we interpret them, signifies a transition allowed by electric dipole selection rules. Again, the results are in contrast with the case of methanal. Thus we have apparently ruled out a $\pi^*\leftarrow n$ transition for the observed spectrum.

An allowed electronic transition has frequently associated with it vibrational structure if there be a change in molecular geometry, and the vibrations excited then consist principally of totally symmetric fundamental modes. The band contours should then indicate the direction of the transition moment. The central branch, strongly present in all the observed transient bands except possibly E (in Fig. 2) which is weakest in any case, indicates either type A or C bands. The latter usually have broader central branches than type A bands in rovibrational spectra of asymmetric rotors, but this generalization is applicable only when rotational constants are closely similar in both combining states. In an electronic transition, particularly one in which vibrations are excited in the terminal state, the structure, and therefore the rotational constants, will be slightly different. Thus the bands could be of type A contour. In fact, the shapes of bands A and B closely resemble, in both form and separation of unresolved branches, the ν_2 and ν_3 bands of the rovibrational spectrum of methanal-h_2 recorded under similar resolution. (This is further support for the preceding assignment of the carrier of the transient spectra. Also the regularity of the band shapes indicates only a small change in rotational constants, and therefore in geometric structure.) In these methanal bands, the transition moment is along the figure axis and hence the bands have type A contours. The type C band of methanal ν_4 has a broader, more easily resolvable rotational structure than the ν_2 and ν_3 bands resembled in the transient spectra. Thus we conclude that the transient bands have type A contours, which are, of course, consistent with an allowed electronic transition under the selection rules for C_{2v} species; the simplicity of the spectrum strongly indicates that the geometric structure is planar in both combining states, and therefore that C_{2v} selection rules are applicable.

The totally symmetric vibrations of a methanal-like species are: ν_1, methylene symmetric stretching mode; ν_2, heavy-atom valence-stretching mode, and ν_3, methylene symmetric deformation. For methanal-d_2 in the ground state, these vibrations are of frequency 2056, 1700, and 1106 cm^{-1}, respectively. In the $^1A_2$ ($^1A''$) and $^3A_2$ ($^3A''$) excited states, ν_2 decreases to 1174 and 1249 cm^{-1}, respectively. By comparison, we might then assign the intervals I–F = 1890 cm^{-1} and H–F = 1075 cm^{-1} to ν_1' and ν_2' or ν_3'. For the latter interval to represent ν_2', we should not expect a greatly different magnitude for the interval E–C which is 1265 cm^{-1}. On the other hand, the decrease from 1265 to 1075 cm^{-1} is entirely appropriate to a methylene deformation frequency affected by progressive deuteration. The assignment of the remaining bands (B, D, and G) to an excitation of ν_2' is not justifiable[15]. The anomalously large intensity of these bands also poses a formidable problem. The only explanation which we can offer that is possibly consistent with the preceding analysis is that these bands represent transitions from the ground to an excited vibronic state in which a quantum of the same vibrational mode is singly excited in each state. The direction of the zero–zero band shift, to smaller frequencies, signifies that the zero-point energy, half the sum of the fundamental frequencies, is less in the excited state than in the ground state. However, what we have tentatively suggested to be a "hot" band lies

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[14] J. R. Henderson and M. Muramoto, J. Chem. Phys. **43**, 1215 (1965).

[15] By comparison with the analysis of the recently discovered F_2CN radical ($\nu_2{}^1=1884$ cm^{-1}) [R. N. Dixon, G. Duxbury, R. C. Mitchell, and J. P. Simons, Proc. Roy. Soc. (London) **A300**, 405 (1967)], the interval I–F = 1890 cm^{-1} might alternatively be assigned to $\nu_2{}^1$ of D_2CN in our spectrum.

at greater frequencies than our assigned zero–zero bands. (An alternative vibrational assignment based on B, D, and G being the zero–zero bands is not tenable.) Thus the frequency of the vibrational mode involved in the "hot" band must increase in the excited state. It also shows an appreciable isotope effect. We therefore suggest that ν_4, the out-of-plane deformation mode, is involved, and would consequently seem to be of fairly small frequency in the ground state. The nature of the perturbation responsible for the intensity anomaly is unknown. An alternative assignment of a second electronic transition of a carrier with the same chemical composition and similar rotational constants is difficult to justify, but cannot be rejected on the available information. It is worth noting that two separate electronic transitions of diazirine have been deduced to occur within the small energy interval of 217 cm^{-1}.[16]

The measured oscillator strength is rather small for an electronically allowed transition, even one in which the overlap of combining orbitals is small. However the measured f value is based on an integrated intensity of the absorption in a spectrum for which the concentration of three samples of the radical has been deduced. The stated error associated with the obtaining of the f value in this way is nevertheless considered to be realistic. However, the band contours and the narrow nature of some features suggest that the spectrum consists of a large group of lines which are unresolved because of the limited resolution of our spectrograph. Under these conditions, the integrated intensity is only meaningful when the natural linewidth is increased, by such means as pressure broadening, to the same magnitude as the spectral slitwidth. As the line width of approximately 0.1 cm^{-1} caused by a total pressure less than one-half atmosphere in the reaction vessel is very much smaller than the employed spectral slitwidth, the computed f value may be too small by an order of magnitude. In this case, the oscillator strength could approach a value often associated with allowed electronic transitions.

A possible transition consistent with the preceding analysis would be the promotion of an essentially nonbonding nitrogen electron from the $2s$ orbital to the half-filled $2p_y$ orbital. Because of the nonbonding nature of these orbitals, only a small effect on molecular structure might result from the transitions. The corresponding excitation in the free nitrogen atom requires, however, an energy of 88 000 cm^{-1}. If therefore we take the source orbital to have some p_z character, then the energy is increased, and the expected oscillator strength is decreased correspondingly.

The final assignment of the orbitals affected in this electronic transition and the solution of the structure of the methyleniminyl radical will have to await the analysis of new spectra obtained with greatly increased dispersion.

Photodissociation Processes of Methanal Azine

In this section we discuss the processes which ultraviolet radiation induces in methanal azine in our system, employing the molecular orbital theory as a basis of explanation. We have observed three electronic transitions of methanal azine, all of different types, and each results in a different electronic state. Two different initial orbitals are involved in the transitions, π_2 and n_{N+}, and two different terminus orbitals, π_3^* and σ^*_{CH}. Of course each different combination of source and terminus orbitals constitutes a different electronic state or set of states. There are three different bonds, or sets of bonds, in this simplest azine molecule, C–H, C–N, and N–N, and dissociation at each of these linkages is energetically possible from the energy of the photons in the $\pi^*\leftarrow\pi$ absorption band. Finally, we note that, due to the optical thickness of the methanal azine in the reaction vessel and to the intensity distribution of both the absorption of the azine and the emission from the photolysis flash lamp, the great majority of the decomposed methanal azine, and therefore of the produced methyleniminyl free radical, must result from the $\pi_3^*\leftarrow\pi_2$ transition.

Because of the continuous nature of the absorption in the $\pi^*\leftarrow n$ band of methanal azine, there is indicated either a direct dissociation, or an efficient crossing to a perturbing state probably followed by direct dissociation (strong predissociation). The small frequency limit of the observed spectrum corresponds to an energy exceeding 70 kcal $mole^{-1}$. This energy probably exceeds that of the N–N bond in the ground state. In the excited state the loss of the partially bonding character of the n_{N+} orbital may be in part compensated by the small bonding character between the nitrogen atoms in the π_3^* orbital. The bond energy of the N–N linkage in hydrazine has been found to be approximately 55 kcal $mole^{-1}$ [17]; although the dissociation energy in methanal azine is expected to be greater, as a result of conjugation effects, the enhancement may not be large. Therefore the $\pi_3^*\leftarrow n_{N+}$ transition could lead to excitation above the dissociation limit to form methyleniminyl radicals, providing either that the $^1A_u'$ state (resulting from that transition) were entirely unstable, or, more likely, that a large change in either the N–N bond length or other structural parameter occurred in that state. An alternative explanation of the continuous nature of the absorption in the 35 000-cm^{-1} region would require predissociation by a perturbing state of less energy. This might be either a triplet state or the ground (singlet) state. A radiationless transition into the former state would be a relatively inefficient process as the spin–orbit coupling for first-row atoms is very

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[16] L. C. Robertson and J. A. Merritt, J. Mol. Spectry **19**, 372 (1966).

[17] S. N. Foner and R. L. Hudson, J. Chem. Phys. **29**, 442 (1958).

small. Although molecules with $\pi^* \leftarrow n$ transitions sometimes have anomalously rapid intersystem crossing processes, a crossing rate of $\sim 10^{12}$ sec^{-1}, as would be necessary to cause vibrational diffuseness, would be extremely great. Although the possibility for polyatomic molecules of nontotally symmetric vibrations renders ineffectual in practice the requirements of certain selection rules made formally applicable by the centrosymmetric equilibrium structure of various electronic states of these dienes, the transition energy between the ground state and the $^1A_u'$ state would cause Franck–Condon factors to be small. For these reasons, the smallest energy spin-allowed electronic transitions of many free unsaturated molecules consist of discrete absorption bands, or diffuse ones depending on the density of rovibronic energy levels and the dispersion of the spectroscopic instrument.

Thus the continuous nature of the 35 000-cm^{-1} absorption region seems best explained in terms of a direct dissociation mechanism. Consistent with this explanation, the diffuse nature of the absorption in the other two bands may be proposed to be due to symmetry-allowed predissociation into this $^1A_u'$ state. However other dissociation processes are also possible in the greater energy states; these will be considered below.

The excitation of an electron from the π_2 into the π_3^* orbital might be expected, from consideration of the positions of nodes in the relevant orbitals, to result in either symmetrical cleavage into molecular nitrogen and two methylene radicals during a symmetric skeletal stretching vibration or into one methylene radical and diazomethane during an antisymmetric vibration. (The diazomethane may require collisional deactivation for stabilization, as it would be formed vibrationally excited.) Diazomethane and some minor products typical of methylene radical reactions, such as ethene, methane, and ethyne, have been detected directly in the gas phase. The faint methyl radical signal also detected on occasion may have resulted from an efficient hydrogen abstraction reaction by methylene. However, although there can be offered a hypothetical mechanism of the methylene reaction products, verification is still required.

Limited data on the photochemistry of azines[18] suggest the dominance of an intramolecular process,

$$\mathrm{RCH{=}N{-}N{=}CHR}+h\nu\rightarrow\mathrm{RCN}+\mathrm{RCH{=}NH}.$$

In the case of methanal-h_2 and -d_2 azines, the corresponding products have been detected after photolysis both in pure solid films and argon matrices at cryogenic temperatures.[1] (The methyleniminyl radical itself has been detected by the ESR method[19] following the reaction of hydrogen atoms with hydrogen cyanide in argon matrices at 4°K.) If a considerable proportion of the methanal azine decomposed in our flash photolysis experiments reacted by such an intramolecular process, we might thereby explain the magnitude of the oscillator strength which seems small for an apparently allowed transition. However for the investigated rate of chemical reaction of the H_2CN radical,[2] the over-all rate constant, derived using $f=4\times10^{-4}$, is similar to the maximum possible rate calculated by assuming a steric factor for the disproportionation reaction equal to that of the ethyl radical.[20] This result enables us to place an upper limit of $\sim 10^{-3}$ on the oscillator strength of the methyleniminyl absorption spectrum, neglecting resolution effects here. The disparity, if significant, between the experimentally determined value of the oscillator strength and the calculated maximum value probably indicates a steric factor for disproportionation smaller for H_2CN than for C_2H_5, but could result from the occurrence, to a limited extent, of an intramolecular process in methanal azine photolysis. Thus we find no real support for the previous hypothesis of an intramolecular process.[18] Further chemical evidence supports this conclusion.[2]

Another consequence of the previous investigation of the photodecomposition of ethanal azine was the suggestion[18] that the dissociation process

$$\mathrm{CH_3CH{=}N{-}N{=}CHCH_3}+h\nu \rightarrow \mathrm{CH_3}+\mathrm{CH{=}N{-}N{=}CHCH_3}$$

was less important than the purported intramolecular process at all wavelengths (3340 to 2380 Å), but becomes more significant at the shorter wavelengths. The nature of the σ^* molecular orbital involved in the second transition, occurring at the shorter wavelengths referred to above, again furnishes an explanation of the photochemical result. The σ^* orbital has a node between the carbon atoms terminating the conjugated skeleton and the attached hydrogen atoms and methyl groups.[11] One of these attached groups might easily be separated in a direct dissociation process, involving an antisymmetric vibration, as the energy of the photon is adequate. Also, in butadiene-1,3, the corresponding process could eventually produce molecular hydrogen which is reported to be a major product.[21] Such a situation again supports the $\sigma^* \leftarrow \pi$ assignment to the 41 000-cm^{-1} absorption of butadiene-1,3, making unnecessary the hypothesis of the extension of the $\pi_3^* \leftarrow \pi_2$ system to this frequency.[13]

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[18] R. K. Brinton, J. Am. Chem. Soc. 77, 842 (1955).

[19] E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. 36, 1938 (1962).

[20] J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc. 1960, 1611.

[21] R. Srinivasan, J. Am. Chem. Soc. 82, 5063 (1960).