Photoelectron Spectra of Methanal Azine

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Résumé: *Les spectres de photoélectrons du méthanal azine ont été mesurés vers 300°K. Les ionisations de deux orbitales non-liantes importantes situées à 9.55 et 12.45 eV, et de deux orbitales* π *situées à 10.72 et 13.5 eV ont été identifiées à l'aide de la structure fine de vibration et de calculs semi-empiriques d'orbitales moléculaires. Aucune caractéristique spectroscopique n'est associée à des isomères de rotation moins stables que la forme* s-*transoïde. Les résultats sont discutés en relation avec trois autres molécules de type diènique: les butadiène-1, 3, éthanedial et propènal.*

Abstract: *Photoelectron spectra of methanal azine,* $H_2C{=}N{-}N{=}CH_2$, *have been measured at ~300 K. Ionisations from two essentially non-bonding orbitals, at 9.55 and 12.45 eV, and from two* π*-orbitals, at 10.72 and 13.5 eV, have been identified with the aid of vibrational fine structure and results of semi-empirical molecular orbital computations. No spectroscopic features are associated with rotational isomers less stable than the* s-*transoid form. The results are discussed in relation to three other diene-type molecules: butadiene-1,3, ethandial and propenal.*

Introduction

In previous articles, electronic absorption spectra of the simplest acyclic azine, methanal azine $H_2C{=}N{-}N{=}CH_2$, have been described[1] and the transitions assigned[2]. A remarkable feature of these spectra was a distinct band, having discernible vibrational structure, which was attributed to a rotational isomer less stable than the dominant *s*-transoid conformer. This conformation is energetically preferred for four diene-type molecules, ethandial, propenal and butadiene-1,3 in addition to methanal azine. For the first three of these molecules, already published photoelectron spectra[3,4] gave no evidence for the presence of the less stable *s*-cisoid rotamer, but the fraction of *s*-cisoid isomer present is believed to be very small. On the contrary, the less stable rotamer of methanal azine is deduced to be present to the extent of the order of 10% at temperatures ~300° K.[5] Π-molecular orbital computations[2] suggested that ionisation of electrons from π-type orbitals would probably not produce distinct photoelectron lines or bands for the less stable rotamers; because these ionisation energies were calculated to be similar to those of the dominant *s*-transoid rotamers, these photoelectron spectroscopic features would be expected to overlap considerably.

One possibility which was left open in the previous work[2] was the appearance of separate features in the photoelectron spectra of the different rotamers in the region corresponding to ionisation from non-bonding orbitals which are symmetric with respect to reflection in the molecular plane (of planar conformers) and are thus not treated in the π-electron approximation. In this paper, we present experimental results of photoelectron spectra of methanal azine and theoretical results of all-valence-electron semi-empirical molecular orbital calculations. We also make comparisons with related diene-type molecules.

Experimental

Methanal azine vapour was prepared from the polymer obtained by mixing hydrazine and methanal solutions in practically stoichiometric proportions. The polymer was degassed and pyrolysed to produce monomeric methanal azine, according to the established method[1,6], by controlled

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heating under vacuum in a flask attached directly to the inlet system of a Perkin-Elmer PS16 photoelectron spectrometer. Performance of this spectrometer was checked after operation with azine samples by use of argon; 40 meV resolution and 20 meV energy accuracy were confirmed in this way. Many spectra were scanned as the polymer was heated under different conditions. Although the polymer was heated above 400°K, the effective temperature of the azine in the spectrometer is believed to be ~300°K because of thermal equilibration attained in connecting tubing between the flask and ionisation chamber. Impurity vapours, previously discovered to be formed during thermal decomposition of this polymer[1, 6], were readily identified by their known photoelectron spectra.[4]

Results

The spectra obtained as described above showed the presence of water, methanal, ammonia and dinitrogen in addition to a substance (or substances) of which photoelectron spectra were not known. The relative constancy of the new spectral features under different production conditions indicates that only one (major) substance is the carrier of these features, at least in the region of energies less than 15 eV. Because methanal azine has been proved to be produced by this experimental method[2, 6], we attribute these features to this substance. As will be seen, the theoretical analysis is consistent with this attribution.

Five distinct regions of absorption maxima may be seen in the spectrum less than 15 eV, as shown in Figure 1. The second of these regions, ~11 eV, shows evidence of vibrational fine structure and is shown on an expanded scale in Figure 2. There was no particular evidence of fine structure in the other four regions of maxima. The characteristic features of onset of signal, associated approximately with adiabatic ionisation energy, and maximum of signal, associated with vertical ionisation energy, are listed in Table I. Spectral diffuseness and overlapping limit the accuracy of these data, in worst cases, to the extent of 0.2 eV.

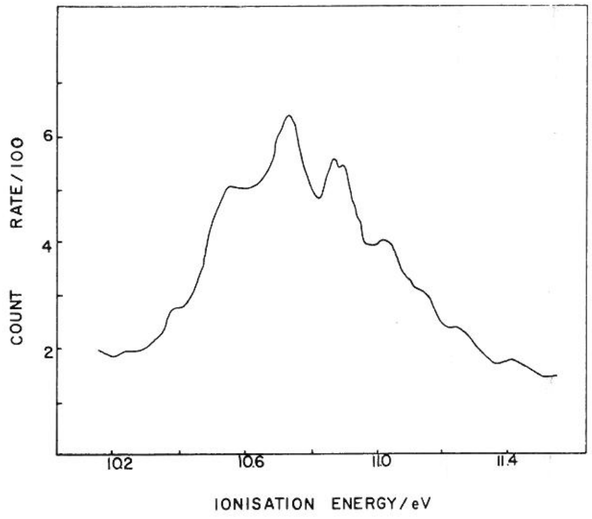

Figure 1. Photoelectron spectrum attributed to methanal azine.

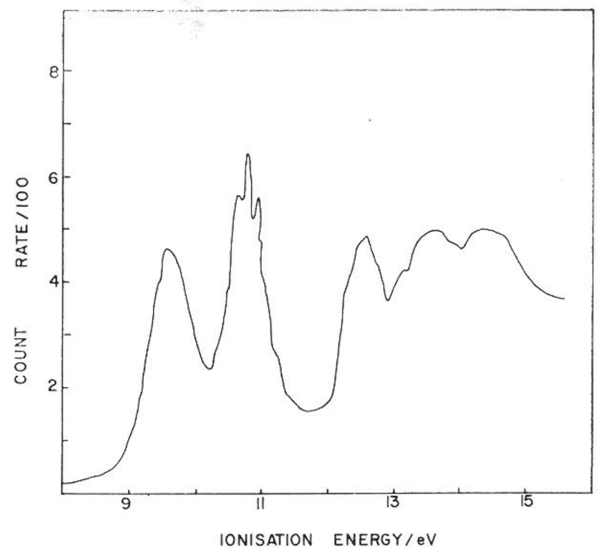

Figure 2. Second band of photoelectron spectrum of methanal azine on an expanded scale to show fine structure.

The second region of electron emission signal shows fine structure superimposed upon a continuous background. The peaks in the fine structure occur at 10.38, 10.55, 10.73, 10.89 and 11.03 ± 0.01 eV, corresponding to a vibrational progression of ~1370 cm^{-1}.

Table I.—Features of the photoelectron spectrum of methanal azine.

Adiabatic ionisation energy (eV)	Vertical ionisation energy (eV)	Description
8.9	9.55	Continuous
10.37	10.72	Vibrational structure present
12.1	12.45	Continuous
13.0	13.5	Continuous
	14.4	Continuous

Discussion

Within the approximations of the orbital concept and Koopmans theorem[4], those ionisation processes in methanal azine which are expected to require relatively small energies involve ejection of electrons from non-bonding or π-bonding orbitals. Of these two kinds of orbital, a smaller ionisation energy is expected for the highest occupied non-bonding orbital than for the highest occupied π-bonding orbital.

None of the photoelectron bands depicted in Figure 1 shows the sharp, intense, clearly structured form typical of ionisation of non-bonding electrons in small molecules[4]. But in these small molecules there may occur sufficient symmetry that the non-bonding orbital is in a separate symmetry class from other occupied orbitals. However, the maximum symmetry of *s*-transoid methanal azine, known[5] to be the dominant species, corresponds[6] to point group C_{2h}; according to this group, a clear separation between π-type orbitals (classes a_u and b_g) and the remaining occupied orbitals (classes a_g and b_u) is possible, but not between the orbitals in the latter group which might be naively described as C-N σ-bonding, C-H σ-bonding, N-N σ-bonding or N non-bonding.

Comparison of the 10.37 eV band of the photoelectron spectrum of methanal azine with the 9.09 eV band[3] of butadiene-1,3 seems pertinent. This first ionisation energy of butadiene corresponds to ejection of a π-bonding electron[3]. Connected with the electronic transition, there is vibrational progression of interval 1400 cm^{-1} associated with the symmetrical C=C stretching mode which has a value of 1643 cm^{-1} in the ground state of the neutral diene. We have attributed the progression of 1370 cm^{-1} to the symmetrical stretching mode of the azine ion (this mode appears at 1615 cm^{-1} in the neutral molecule[6]) even though the band shapes of the two transitions differ considerably. The vertical ionisation energy, 10.72 eV, corresponds well to the value of 10.7 eV predicted from π-molecular orbital computations published before the present measurements were made[2]. Thus, assignment of the 10.37 eV band to a π-ionisation process seems well founded.

As there is little experimental information in the other features which can be applied directly for assignment purposes, we have recourse to precedent and assistance from theoretical computations.

Heilbronner and coworkers[7] have examined the photoelectron spectrum of azomethane $H_3C{-}N{=}N{-}CH_3$ which also has a *trans*, planar skeleton. They assigned two bands at 8.98 and 12.3 eV to ionisation processes from n_+ and n_- non-bonding orbitals, respectively, where

$$n_+ = (n_1 + n_2)/2^{1/2},\ A_g$$

and

$$n_- = (n_1 - n_2)/2^{1/2},\ B_u;$$

n_1 and n_2 are supposed to be non-bonding lone pairs, one on each of the equivalent nitrogen atoms. Thus the splitting, $\triangle = IE(n_-) - IE(n_+)$, i.e., the difference in vertical ionisation energies of these two bands, is 3.3 ± 0.2 eV. These workers[7] obtained qualitative support for this interpretation from the results of semi-empirical molecular orbital (MINDO/1) computations.

If we assume a similar splitting between what might qualitatively be described as non-bonding orbitals in *s*-transoid methanal azine, and if we further associate the first transition at 9.55 eV (maximum) with one such ionisation from an essentially non-bonding orbital on nitrogen (alternative assignment seems scarcely possible), then we might expect the other ionisation process from a nominally non-bonding orbital, by analogy, to occur at an energy ~12.85 eV. In fact, a continuous band appears at 12.45 eV (maximum), consistent with this interpretation.

The other π-orbital ionisation energy was earlier predicted[2] to be 14.0 eV. A band ~13.5 eV is observed; whether this band, or the next at ~14.4 eV, should be associated with such a π-ionisation process is uncertain, but evidence provided by other compounds[4] generally seems to favour the former band.

We have conducted CNDO and INDO semi-empirical molecular orbital computations[8,9] in connection with the four diene-type molecules earlier examined within the π-electron approximation[2]. All computations on the *s*-transoid rotamers were done on the known average structures[5,10]. For butadiene-1,3, the first ionisation is predicted to be from a π-orbital, but the second π-ionisation comes fourth or fifth with various σ-type bonding orbitals in between. Likewise, in the other substances the second π-orbital is found at much too low an energy. For the carbonyl compounds, ethandial and propenal, all the computations agree that the first ionisation of an electron from a non-bonding orbital on oxygen takes less energy than from either π-orbital. Only within the CNDO approximation for ethandial did a π-electron ionisation energy fall between those of essentially non-bonding orbitals. For methanal azine, both CNDO and INDO methods predict that the first (lesser energy) π-ionisation transition will occur between the two non-bonding electron transitions which are split by $\triangle = 2.6$ or 3.6 eV.

The CNDO and INDO methods were also applied to the less stable rotamers of these four dienes. Molecular geometries were as previously used[2] for all but methanal azine. In general, the magnitudes of ionisation energies for the planar *s*-cisoid rotamers are similar to, but slightly larger than for, the *s*-transoid rotamers. Thus, even when ionisation from non-bonding orbitals of these dienes is considered, photoelectron spectroscopy seems unlikely to prove a useful technique for detection of the less stable rotamers in the presence of an excess of the dominant conformers. Instead, the observable effects of the presence of the former may be to increase the complexity of the observed intensity distribution, thereby hindering analysis.

Methanal azine in a *s*-cisoid structure is probably not physically possible, at least with a geometrical structure simply related to that of the *s*-transoid rotamer. The reason for this is the extremely small distance, ~110 pm, between nuclei of hydrogen attached to different carbon atoms. For comparison, the corresponding internuclear separation in butadiene-1,3 is estimated to be much larger, ~230 pm (about twice the oft-quoted intermolecular radius[11] of a hydrogen atom, ~120 pm). The corresponding distance in the *gauche* rotamer deduced from electron diffraction experiments is, in contrast, 228 pm; this magnitude is practically identical with that estimated for butadiene-1,3. Thus, we can understand that only methanal azine, of these four similar diene-type molecules, seems to adopt a non-planar structure for its less stable rotamer; in ethandial and propenal, such hydrogen repulsions do not occur. (The repulsion energy corresponding to a non-bonded separation of 230 pm between hydrogen atoms can be estimated to be ~140 J mol^{-1} by the use of Williams's potential functions[12].) For such a non-planar *gauche* rotamer, with an angle of 62° between H_2CN planes,[5] there is no longer a formal distinction between σ- and π-type orbitals. The CNDO and INDO computations indicate that the splitting between essentially non-bonding orbitals on nitrogen atoms is reduced to 0.6 or 0.3 eV. The actual splitting observed[13] for hydrazine which also has a *gauche* structure, is 0.77 eV. But the magnitudes of the ionisation energies calculated for the *gauche* rotamer of methanal azine are again similar to those calculated for the *s*-transoid rotamer, independent of the type of orbital from which ionisation might occur; therefore, the prospects of detecting the *gauche* rotamer by its photoelectron spectra are not good. There seems to be no specific evidence in our photoelectron spectra for the presence of a *gauche* rotamer.

Table II.—Comparison of observed (vertical) and calculated ionisation energies of diene-type molecules in *s*-transoid conformation. Nature of orbital is indicated by n (non-bonding), σ (other sigma-type) and π (pi-type).

Butadiene - 1,3		Methanal Azine	
Obsd.[a]	Calcd.	Obsd.	Calcd.
9.09π	9.6π	9.55n	9.4n
11.55	12.9π	10.72π	10.7π
12.35	10.8σ	12.45n	12.0n
13.7	12.4σ	13.5	14.0π
15.3	13.5σ	14.4	12.7σ
Ethandial		Propenal	
Obsd.[b]	Calcd.	Obsd.[b]	Calcd.
10.6n	9.2n	10.1n	8.8n
12.2n	12.9n	10.93π	11.0π
13.85π	12.9π	13.5π	14.0π
15.5π	15.0π	14.7	12.2σ
15.8	15.3σ	16.1	13.9σ

[a] Ref. 3
[b] Ref. 4

In Table II, we list a summary of calculated and observed ionisation energies of the *s*-transoid rotamers of all four compounds. The earlier π-orbital computations[2] gave good agreement with experiment in all cases, so these results are repeated in the table. For the so-called non-bonding and other σ-type orbitals, the computed values, treated[14] as previously, are taken from the CNDO method; agreement is fair, but would be slightly worse if INDO results were used instead*.

Our photoelectron spectrum does not seem to agree well with the predictions[15] made by both the extended Hückel method and the CNDO-CI methods of semi-empirical molecular orbital calculation. However, our spectrum is similar to, and better resolved than, spectra of homologous alkyl acyclic azines[15]. These calculations indicate a much larger dependence of first ionisation energy on dihedral angle of non-planar rotamers than ours. Moreover, as these results also indicate an increase of first ionisation energy on

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*A complete list of all calculated ionisation energies, for all rotamers, is available from the authors upon request.

deviation from planarity, detection of rotamers less stable than the centro-symmetric planar conformer still seems unlikely.

Conclusions

The photoelectron spectrum less than 15 eV of the substance methanal azine vapour has been recorded and analysed. Assignments have been based on vibrational structure or precedent, and assisted by results of molecular orbital computations. The possible complication of presence of a *gauche* rotamer has been considered, and the relation to other diene-type molecules has been discussed.

Acknowledgments

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Normal Coordinate Analysis of CF_3SeCl and CF_3SeBr

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Résumé: *Une analyse par coordonnées normales a été faite sur les spectres des chlorure et bromure de trifluorométhyl-selenyle. Par affinement de moindres carrés d'un champ de forces à 17 paramètres, les fréquences calculées différaient en moyenne de 3.1 cm⁻¹ des 21 fréquences observées. L'analyse a permis de montrer que les constantes de force étaient transferrables d'une molécule à l'autre et de confirmer les attributions faites précédemment.*

Abstract: *Normal coordinates analyses of trifluoromethylselenenyl chloride and trifluoromethylselenenyl bromide have been carried out using a 17-parameter valence force field. The calculated frequencies agree with the 21 observed frequencies with an average error of ± 3.1 cm⁻¹. This study demonstrates the transferability of force constants within the molecules and confirms the vibrational assignments proposed earlier.*

Introduction

Although trifluoromethyl derivatives of selenium were first prepared about twenty years ago, it is only recently that their ir and Raman spectra have been studied[1,2]. In order to understand the nature of the vibrations in detail, we have carried out normal coordinate analyses for the two simple derivatives, CF_3SeCl and CF_3SeBr.

Experimental

The procedures for the preparation, purification and recording of the ir and Raman spectra of CF_3SeCl and CF_3SeBr have been described earlier by Wahi *et al*[1].