Journal of Photochemistry, 17 (1981) 297–302

SPECTROSCOPY OF NON-AROMATIC SCHIFF BASES†

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Summary

The photoelectron and vapour phase UV absorption spectra of a number of non-conjugated and conjugated imines, their oximes and *O*-methyloximes were determined. The assignment of the bands of lowest frequency is discussed as well as the nature of the primary steps that may occur in the related excited states ((π,π*), (n,π*) and Rydberg). The relation to certain problems connected with the chromophore of visual pigments is stressed.

1. Non-conjugated C=N compounds

The C=N bond is no less important in nature than the C=C or C=O bonds, yet its spectral properties have received much less attention. This is probably due to the instability of the simple imines with alkyl substituents only which makes the measurement of their spectra difficult.

The originating orbital for all known bands of ethylene and simple olefins is the π orbital while for ketones and aldehydes it is the oxygen lone pair n orbital. In the C=N chromophore, which in many respects has properties intermediate between C=C and C=O, there are two originating orbitals: the nitrogen lone pair orbital and the π orbital. Their mutual separation in energy is usually less than 1 eV and it depends greatly on the alkyl groups attached to the C=N bond.

Several simple imines, oximes and *O*-methyloximes were studied in our laboratory [1 - 3]. The photoelectron spectra exhibit two bands of low energy, one at about 9.0 - 9.5 eV and one at 10.0 - 10.5 eV, which are due to ionization from the n and π levels. All available experimental and theoretical evidence leads to a lone pair assignment for the photoelectron band of lowest energy in imines. To the contrary, in oximes and *O*-methyloximes the π band seems to be the band of lower energy. Evidence for this comes from the partly resolved vibrational fine structure of the π bands and from the shift of the bands when the C=N bond is conjugated with C=C bonds. In singly conjugated *O*-methyloximes, for example, the first band is typically near 8.6 eV and the second band is near 10.0 eV. The difference (1.4 eV) is greater than that for the related non-conjugated *O*-methyloxime (about 0.9 eV). Now, if the first band was an n band and the second

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† Paper presented at the Xth International Conference on Photochemistry, Iraklion, Crete, Greece, September 6 - 12, 1981.

0047-2670/81/0000-0000/$02.50

band was a π band in the non-conjugated molecule, the two bands should come into near coincidence for the singly conjugated molecule because of the larger shift that the π level is expected to undergo. This is actually what happens in imines; the fact that the mutual distance between the two bands actually increases in oximes and in *O*-methyloximes shows that their order is π,n and not n,π as in the imines [3].

The electronic absorption spectra of a number of non-conjugated C=N compounds were measured in the vapour phase. The (n,π*), (π,π*) and lower Rydberg bands had to be located, a task made difficult by the diffuse character of the spectra. Table 1 shows the pertinent data for two molecules chosen as examples for imines and *O*-methyloximes.

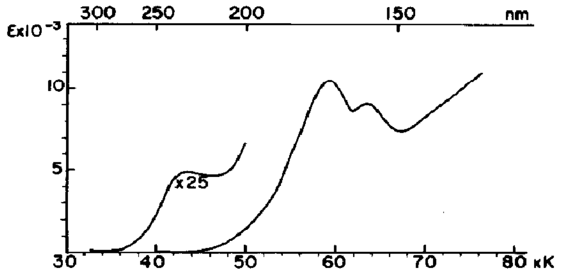
As can be seen, there are significant differences between the spectra of these molecules (Figs. 1 and 2). The intense (π,π*) band is always easy to recognize. Its frequency is lower in the *O*-methyloxime than in the imine. The analogy with ethylene suggests that in the excited state the geometry around the C=N bond is far from being coplanar. The lack of fine structure precludes any serious attempt to ascertain this but the asymmetrical shape of the band with a broad tail at its low frequency side is reminiscent of the protracted tail of the (π,π*) band of ethylene. As is expected from the known ionization potentials with reasonable term values (Table 1), in imines the lowest Rydberg band (n,3s) must lie on this low frequency wing of the (π,π*) band, contributing to its breadth. We have argued that the lowest photoelectron band of the oximes and *O*-methyloximes must relate to ionization from the π orbital, not from the n orbital. Since the (π,π*) band is at lower frequencies for the two types of molecule, the (π,3s) band is expected to be in near coincidence with the (π,π*) band. Actually, the (π,3s) band cannot be located with any degree of certainty.

TABLE 1

The lowest photoelectron and UV absorption bands of a typical non-conjugated imine and a non-conjugated *O*-methyloxime

	$C_2H_5CH{=}NC_2H_5$[a]	$(CH_3)_3CCH{=}NOCH_3$[a]
(n,π*)	43 100 (232 nm)	(46 000)
(n,3s)	(50 000)	(56 000)
(π,3s)	(58 000)	(48 700)
(π,π*)	59 500 (168 nm)	51 000 (196 nm)
Ionization potential (vertical)		
n	76 200 (9.45 eV)	81 500 (10.1 eV)
π	84 500 (10.35 eV)	74 200 (9.2 eV)
3s term value		
n	(26 200)	(25 500)
π	(26 500)	(25 500)

[a] Data are in wavenumbers unless indicated otherwise. The numbers in parentheses are estimated values.



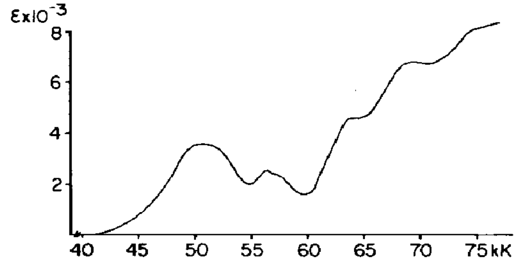


Fig. 1. The far UV absorption spectrum of $C_2H_5CH{=}NC_2H_5$ in the vapour phase (molar absorption coefficient *vs.* energy in kilokaysers) (from ref. 1).

Fig. 2. The far UV absorption spectrum of $(CH_3)_3CCH{=}NOCH_3$ in the vapour phase (molar absorption coefficient *vs.* energy in kilokaysers) (from ref. 3).

The weak (n,π*) band is readily assigned in the imine. It is not resolved for the *O*-methyloxime and must be contained in the low frequency wing of the (π,π*) band.

From a photochemical point of view the main observation is that the C=N chromophore is in certain respects intermediate between the C=C and C=O chromophores. While the spectrum of C=C is a π spectrum and the spectrum of C=O is a lone pair spectrum, in C=N derivatives we have a more complicated situation. In non-conjugated imines (Schiff bases) the (singlet–singlet) band of lowest energy is (n,π*), as in ketones or aldehydes. However, it is overlapped from the high frequency side by the broad wing of the (π,π*) band on which the (n,3s) and (π,3s) Rydberg bands are also superimposed. It should be noted in this respect that the (n,π*)–(π,π*) separation is much less in imines than in aldehydes or ketones.

For oximes and *O*-methyloximes the (n,π*) and lowest Rydberg band, (π,3s) in this case, both lie on the low frequency wing of the (π,π*) band which is at lower frequencies than in imines.

The coincidence or near coincidence of two or more bands, both Rydberg and non-Rydberg, in the spectra of these molecules makes us think that photon absorption for these molecules will result in several primary steps whose relative proportions will depend markedly on the exciting frequency. The primary steps probably involve single-bond cleavages as well as molecular elimination. In particular, imines below 43 000 cm^{-1} are expected to photolyse in the (n,π*) excited state and to behave as ketones or aldehydes, while at higher frequencies a more complicated pattern should result.

2. Conjugated C=N compounds

In the photoelectron spectra of singly conjugated imines such as *N*-ethylcrotonaldehyde imine the n and π bands are in near coincidence with the π band overtaking the n band (75 000 cm^{-1} (9.3 eV) for the π band and 77 400 cm^{-1}

(9.6 eV) for the n band), while in singly conjugated oximes and *O*-methyloximes the two bands are clearly separated with the lower π band coming first and the n band coming after. In 2-hexenal-*O*-methyloxime, for example, the first band is near 69 400 cm^{-1} (8.6 eV) and the second band is near 80 700 cm^{-1} (10.0 eV).

In the UV absorption spectrum of *N*-ethylcrotonaldehyde imine the (n,π*) band is a well-pronounced shoulder at 37 000 cm^{-1} (270 nm), a significant shift from the non-conjugated imines. The prominent first (π,π*) band has its maximum at 47 340 cm^{-1} (211 nm). With plausible term values the lowest 3s Rydberg band should coincide with the (π,π*) band and could not be identified. The strength of the first (π,π*) band indicates at least an approximately s-*trans* configuration. Several transitions must contribute to the band and shoulders observed at higher frequencies (higher Rydberg transitions and weak contributions to higher (π,π*) bands). In many respects the spectrum is similar to that of 1,3-butadiene with the (n,π*) band added to it.

In singly conjugated oximes and *O*-methyloximes the intense (π,π*) band moves to lower frequencies. In 2-hexenal-*O*-methyloxime, for example, it is centred at 44 000 cm^{-1}. The (n,π*) band which can still be distinguished as a shoulder for the imines is hidden under the (π,π*) band. With the ionization potential at 69 400 cm^{-1} (8.6 eV) and an estimated term value of 24 000 cm^{-1} the lowest Rydberg band (π,3s) should be at about 45 000 cm^{-1}, also in coincidence with the (π,π*) band. The preponderance of the (π,π*) band shows that the molecule has an approximately s-*trans* configuration.

The spectrum of a singly conjugated imine is intermediate between those of butadiene and acrolein with distinguishable (n,π*) and (π,π*) bands, while in the spectra of oximes and *O*-methyloximes the two bands coincide. The lowest Rydberg band coincides with the (π,π*) band for all three types of compound. Thus it can be expected that the photochemical behaviour of singly conjugated imines is closer to that of acrolein, and the behaviours of oximes and *O*-methyloximes are expected to be closer to that of butadiene.

The differences between imines, oximes and *O*-methyloximes become insignificant for doubly and more highly conjugated compounds. The lowest photoelectron band is always connected with the highest occupied π orbital, the n orbital becoming second or third highest. The ionization potential of heptadienal-*O*-methyloxime, for example, is 66 100 cm^{-1} (8.2 eV); the second ionization potential is at much higher energies (78 200 cm^{-1} (9.7 eV)). In the UV absorption spectrum the (π,π*) band appears at 39 000 cm^{-1} (256 nm). The (n,π*) band is hidden. The lowest Rydberg band (π,3s), with the ionization potential at 66 100 cm^{-1}, is expected to be near 42 000 cm^{-1}, at the ***high*** frequency wing of the (π,π*) band. The (π,π*) band has some partly resolved vibrational fine structure, as is often the case for conjugated polyenes. The photochemistry of C=N compounds which are doubly or more highly conjugated is expected to be similar to that of the related polyenes.

At this point we add a comment on the oxime and *O*-methyloxime ot the retinylidine Schiff base, the chromophore of visual pigments. The lowest photoelectron bands are at 58 900, 66 100 and 71 000 cm^{-1} (7.3, 8.2 and 8.8 eV). These bands must all belong to π levels since the spectrum of the aldehyde retinal itself contains the same bands. The molecules must be remarkably good electron donors.

So far we have not been able to obtain a vapour phase UV absorption spectrum of either the oxime or the *O*-methyloxime of the retinylidene Schiff base. In a 10^{-3} M solution in acetonitrile the (π,π^*) band of the *O*-methyloxime has its maximum at 27 400 cm^{-1} (365 nm). The band has a regular shape with no indication of weaker bands superimposed on its low frequency wing. According to the above discussion the (n,π^*) band must be at significantly higher frequencies. With an ionization potential at 59 000 cm^{-1} the lowest Rydberg band $(\pi,3s)$ must also be higher in energy, perhaps near 34 000 cm^{-1} (294 nm), at least in the vapour state.

3. The A_g^- bands

In 1967 Koutecky [4] drew attention to the fact that configuration interaction might push some of the (π,π^*) bands which are symmetry forbidden in the all-*trans* polyenes to frequencies lower than that of the intense first (π,π^*) band. He also pointed out that such bands might play a role in the photochemical step of vision. Later these bands received much attention both experimentally [5] and theoretically [6] (see ref. 3 for other references). In the two-photon spectrum of all-*trans* retinol (vitamin A) Birge *et al.* [7] have found a band that is 1600 cm^{-1} lower than the maximum of the intense (π,π^*) band.

Although this band is extremely weak in hydrocarbons with a centre of symmetry, there is no reason why it should be so weak in Schiff bases and other highly substituted derivatives. This is the case for the Schiff base of all-*trans* retinal and 11-*cis* retinal, among others. These molecules are perturbed by the presence of the nitrogen atom, several methyl groups, molecular associations that can affect them in condensed media, the departure from coplanarity of the π system etc. They have no centres of symmetry and, in fact, no overall symmetry whatsoever. Therefore, in our opinion the A_g^- bands should be found in these Schiff bases and their oximes and *O*-methyloximes provided that they are not overwhelmed by overlap with stronger bands.

To our knowledge two-photon spectroscopic measurements have never been attempted on Schiff bases. However, if there were any A_g^- bands in the retinylidene Schiff base at frequencies lower than the strong (π,π^*) band, they should be detected by conventional absorption spectroscopy. From the *O*-methyloxime we were able to prepare solutions with concentrations such that a band for which $\varepsilon_{\mathrm{max}} = 1$ should have been detectable [3]. None was found, however. The reason for this can only be that these bands are at higher frequencies, hidden under the envelope of much more intense bands. In a forthcoming publication an attempt will be made to show that the presence of the nitrogen atom in these molecules and, to an even greater extent, protonation actually pushes the bands to higher frequencies.

There seems to be general agreement that the photochemical state of vision is the first singlet (π,π^*) excited state. Surprises might still occur in this respect, however.

Acknowledgments

This paper is based on results obtained with A. Dargelos, P. Dupuis, J.M. Leclercq, R. Pottier, R. Roberge and D. Vocelle [1 - 3].

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