December, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 3915—3919 (1982) 3915

Photoelectron Angular Distribution Study of Some Isoxazoles Combined with Perturbation Theoretic Approach

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(Received July 15, 1982)

Photoelectron spectra of isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole were studied by the technique of photoelectron angular distribution measurements combined with a first order perturbation theoretic approach. Photoelectron spectra of oxazole, 4-methyloxazole, furan, and 2-methylfuran, which are closely related to isoxazole, were also discussed at the same time for the sake of comparison. The first three bands of the isoxazoles were assigned to the π, π, and n bands from the top, respectively, while those of the oxazoles were identified as the π, n, and π bands from the top.

Isoxazole is one of the typical five-membered heteroaromatics with two heteroatoms and important from the pharmacological standpoint also. In this paper photoelectron spectra of isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole are studied by the technique of photoelectron angular distribution measurements combined with a perturbation theoretic approach. Photoelectron spectra of oxazole, 4-methyloxazole, furan, and 2-methylfuran, which are closely related to isoxazole, are also discussed at the same time for the sake of comparison.

Baker *et al.*[1] and Palmer *et al.*[2] reported the photoelectron spectrum of isoxazole formerly and considered that the first band is a π band and that the second band group is composed of a π band and an n (nonbonding) one highly overlapping with each other. But the relative ordering of the π and n bands in the second band group is not yet established. In this paper we focus our attention especially on this complicated second band group region of isoxazole and try to establish the assignments of the lower energy photoelectron spectral bands of the isoxazoles.

Formerly an empirically parameterized method based on the first order perturbation theory was developed for photoelectron spectral band assignments and applied to azaaromatics.[3] With this technique one can easily distinguish π bands from n or σ bands by regarding aza-replacements, for example, as perturbations. The same technique is applicable to the case of alkyl substitutions also.[4] In this paper at first this type of approach will be used.

Concerning photoelectron angular distributions, differential cross section (σ_Ω) for photoelectron ejection is given by the following expression[5,6] for the case of an unpolarized light and an ensemble of randomly oriented molecules:

$$\sigma_\Omega \propto \{1+(1/4)\beta(3\sin^2\theta-2)\}, \tag{1}$$

where β is an asymmetry parameter and θ is the angle between the propagation direction of an ejected photoelectron and that of an incoming photon. The β value depends not only on the kinetic energy of the photoelectron but also on the character of the MO from which the photoelectron is ejected. Therefore, the β values can be used for photoelectron spectral band assignments as exemplified in the case of benzene,[7] pyridine,[8] aliphatic alcohols, amines, and halides.[9] In this paper the combination of the photoelectron angular distribution experiments with the perturbation theoretic approach will be demonstrated to be very powerful in solving photoelectron spectral band assignment problems.

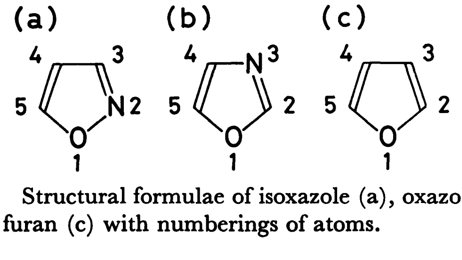

Fig. 1. Structural formulae of isoxazole (a), oxazole (b), and furan (c) with numberings of atoms.

Experimental

Materials. Pure samples of isoxazole, 5-methylisoxazole, 3,5-dimethylisoxazole, and 4-methyloxazole were kindly supplied by Dr. T. Honma of Shionogi Research Laboratories. Commercially available furan and 2-methylfuran were used without furthur purifications. Commercially available isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole were also used without furthur purifications for the photoelectron angular distribution experiments.

Measurements. The vapor phase HeI photoelectron spectra of these compounds were measured at first using the photoelectron spectrometer described formerly.[10] Xe gas was used as the internal reference standard compound for the energy scale calibrations. The HeI photoelectron angular distributions of isoxazole, 5-methylisoxazole, 3,5-dimethylisoxazole, furan, and 2-methylfuran in the vapor phases were measured using the instrument described formerly,[7] the vapor pressures of the samples being kept at 4×10^{-4} Torr (1 Torr = 133.322 Pa). The β values were obtained according to formula (1) using the photoelectron spectral intensities measured at two angles, $\theta=45°$ and $90°$.

Computational

The CNDO/S[11] calculations of furan, oxazole, and isoxazole were carried out by the FACOM 230-75

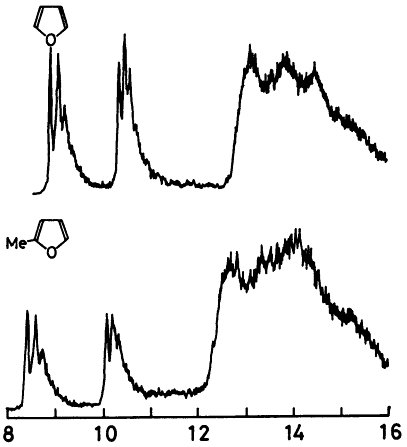

Fig. 2. Vapor phase HeI photoelectron spectra of furan and 2-methylfuran.

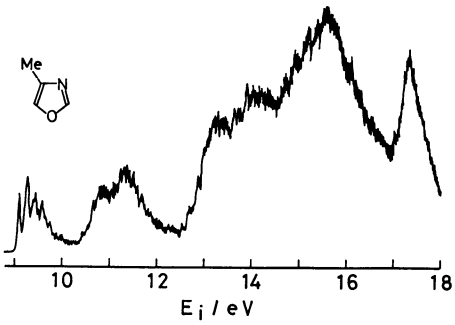

Fig. 3. Vapor phase HeI photoelectron spectrum of 4-methyloxazole.

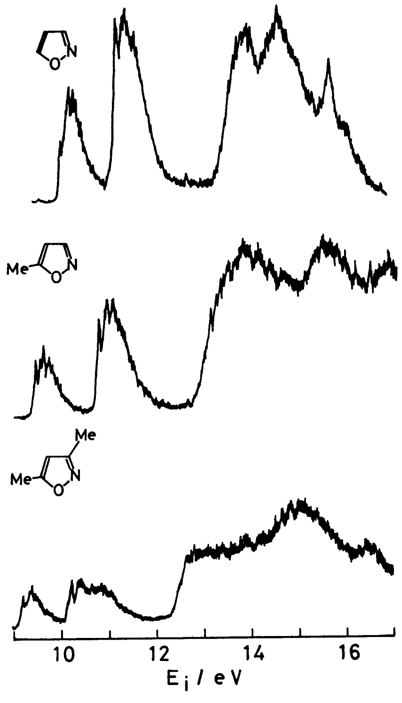

Fig. 4. Vapor phase HeI photoelectron spectra of isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole.

computer at the Institute of Physical and Chemical Research. The geometrical structural parameters of furan and isoxazole were taken from Refs. 12 and 13, respectively, and those of oxazole were assumed to be similar to those of furan.

Results and Discussion

The HeI photoelectron spectra of furan, 2-methylfuran, 4-methyloxazole, isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole are shown in Figs. 2, 3, and 4. Of these compounds the ultraviolet photoelectron spectrum of furan was reported by various authors[1,14–20] formerly, and that of isoxazole by Baker *et al.*[1] and by Palmer *et al.*[2] also. Their spectra are consistent with ours. The vertical ionization energy (E_{iv}) values of those compounds are summarized in Table 1 for the region of interest with those of oxazole.[2]

Perturbation Theoretic Approach. At first let us try to make assignments of the lower energy photoelectron spectral bands of isoxazole and its methyl derivatives from the perturbation theoretic standpoint.

According to the first order perturbation theory, E_{iv} changes (ΔE_{iv}'s) of π bands caused by substitutions (replacements) can be estimated by using the following formula:[3]

$$-\Delta E_{\mathrm{iv}j} = a + b \sum_{\mu,\nu} (C_{\mu j}^2 + m\, C_{\nu j}^2), \qquad (2)$$

where j denotes the j-th MO corresponding to a certain photoelectron spectral band in question, a is a constant introduced for statistical treatments, b is also a constant and corresponds to the HMO level one-centre Coulomb integral change of a certain atom caused by a certain substitution (replacement) at this atom, $C_{\alpha j}$ is the AO coefficient of atom α in the j-th MO, μ denotes atom μ at which a certain substitution (replacement) is introduced, ν denotes atom ν just adjacent to atom μ, and m is a kind of damping factor.

The a, b, and m values for formula (2) were taken from Ref. 3 for aza-replacements and from Ref. 21 for methyl substitutions. The $C_{\alpha j}$ values used are those obtained by the CNDO/S[11] calculations for furan, oxazole, and isoxazole. The E_{iv} values of the five-membered ring compounds estimated by this perturbation theoretic approach regarding aza-replacements or methyl substitutions as perturbations are summarized in Table 1. The reference standard compounds in this table denote the compounds, the E_{iv}'s of which are used to estimate the E_{iv}'s of the compounds in question by being corrected for the ΔE_{iv} values calculated by formula (2) with the $C_{\alpha j}$ values of those compounds.

At first in order to check the validity of the method used here, let us examine the apparent case of furan and 2-methylfuran. As is seen in Fig. 2 the first two bands of furan are rather vertical and well separated from the following bands. These bands have already been unambiguously assigned to the $a_2\pi$ and $b_1\pi$ bands from the top, respectively.[1,14–20] By introducing 2-methyl group into furan, the first two bands are slightly shifted to the lower ionization energy (E_{i}) side, but their band shapes remain still rather vertical indifferent to this substitution and these bands are well separated from the following bands. It is quite natural to assign straightforwardly the first two bands of 2-methylfuran to the

Table 1. Observed vertical ionization energy (E_{iv}) values of isoxazoles and related compounds with Π ones calculated by perturbation theoretic approach

Compound		E_{iv}/eV Band 1	2	3	R.M.S.E./eV[a]	Reference standard compound[b]
Isoxazole	Obsd	10.15	11.15[c]	11.3—11.6		
	Calcd	10.12	11.11		0.15	Furan
5-Methylisoxazole	Obsd	9.61	10.95	11.2		
	Calcd	9.68	10.95		0.16	Furan
	Calcd	9.71	10.99		0.06	Isoxazole
	Calcd	9.61	10.82		0.15	2-Methylfuran
3,5-Dimethylisoxazole	Obsd	9.34	10.35	10.81		
	Calcd	9.43	10.45		0.16	Furan
	Calcd	9.45	10.49		0.06	Isoxazole
	Calcd	9.36	10.46		0.06	5-Methylisoxazole
Oxazole	Obsd[d]	9.83	11.19	11.80		
	Calcd	9.81		11.85	0.15	Furan
4-Methyloxazole	Obsd	9.27	10.81	11.31		
	Calcd	9.39		11.45	0.16	Furan
	Calcd	9.41		11.40	0.06	Oxazole
Furan	Obsd	8.89	10.44			
2-Methylfuran	Obsd	8.38	10.15			
	Calcd	8.48	10.20		0.06	Furan

a) The root mean square error for the calculated π E_{iv}'s. b) The standard compound, the E_{iv}'s of which were used as the starting points to estimate the E_{iv}'s of the compound in question, by being corrected for the ΔE_{iv} values calculated by formula (2). c) This value is a possible candidate for the second E_{iv} of isoxazole, and 11.3 eV may be another one. d) Taken from Ref. 2.

a_2-like π and b_1-like π bands from the top, respectively. On the other hand, as is seen in Table 1, starting from the E_{iv} values of the first two bands of furan, the perturbation theoretic calculations reproduce well the observed E_{iv} values for the first two bands of 2-methylfuran, strongly supporting the above qualitative assignments.

Now let us examine the next rather slightly more complicated case of oxazole and 4-methyloxazole. As is seen in Fig. 1 of Ref. 2 and Fig. 3 both these compounds show three bands in the energy region from 9 eV to 12.5 eV separated from the following bands. In this energy region two π bands corresponding to the first two bands of furan and one n band mainly related to the nitrogen atom n orbital are expected to appear from the analogy to the case of furan and pyridine.[8,22] Concerning oxazole Palmer *et al.*[2] assigned the first and third bands to the π bands and the second band to the n band on the basis of an *ab initio* calculation and band shape considerations. Their assignment seems to be probable, because the second band is nonvertical, that is, rather broad just as in the case of the n bands of pyridine and other azaaromatics,[3,4,8,22] the first and the third bands being rather vertical as in the case of the first two π bands of the furans just we have seen above.

On the other hand, by the perturbation theoretic calculations using furan as the reference standard compound, as is seen in Table 1, the first and third bands of oxazole can be unambiguously assigned to the π bands corresponding to the first and second bands of furan, respectively, and the remaining second band is ascribed to the n band. Thus, Palmer and coworkers' assignments[2] have now been definitely substantiated.

By comparing the band shapes and the E_{iv} values of the first three bands of 4-methyloxazole with those of oxazole we may qualitatively assign the first and third bands to the π bands and the second to the n band in the case of 4-methyloxazole also. On the other hand, starting from either furan or oxazole as the reference standard compound, in the case of 4-methyloxazole also, the first three bands can be definitely assigned to the π, n, and π bands from the top, respectively, by the first order perturbation theoretic approach, supporting the above qualitative consideration. Thus, the orderings of the first three bands of the oxazoles have now been firmly established to be π, n, and π from the top.

As we have seen in the above examples, the perturbation theoretic approach seems to be very powerful to establish band assignments. Now let us move to the complicated case of the isoxazoles in question. These compounds show three photoelectron spectral band groups in the energy region from 9 eV to 12 eV. And in this energy region three bands, two of which are π bands and one of which is an n band, are expected to appear just as in the case of the oxazoles. From the relative intensity ratio of the first and second band groups of isoxazole and 5-methylisoxazole the second band groups of these compounds are naturally regarded to be composed of two bands. In the case of isoxazole Baker *et al.*[1] and Palmer *et al.*[2] formerly regarded the first band as a π band and the second band group to be composed of a π band and an n band overlapping with each other highly.

In the case of 3,5-dimethylisoxazole the first band is rather vertical and the second and third bands can be recognized separately, the second band being rather vertical with the first strong sharp peak, while the third band seems to be rather broad. From the band shape considerations we may assign the first and second bands to the π bands and the remaining third band to the n band in this case. On the other hand, according to the first order perturbation theoretic calculations using furan as the reference standard compound, the first two bands of 3,5-dimethylisoxazole can be definitely assigned to the π bands corresponding to the first two π bands of furan from the top, respectively, and the remaining third band is ascribed to the n band as is seen in Table 1, the above qualitative considerations being strongly supported.

The vertical features of the first band and the lower energy part of the second band group can be recognized in the case of either isoxazole or 5-methylisoxazole also, and it is quite reasonable to correlate the first band and the lower energy part of the second band group of either isoxazole or 5-methylisoxazole with the first two π bands of 3,5-dimethylisoxazole from the top, respectively. The higher energy part of the second band group of either isoxazole or 5-methylisoxazole is now ascribed to the n band.

On the other hand, according to the first order perturbation theoretic approach the first band of isoxazole is definitely assigned to the π band corresponding to the first band of furan and the lower energy part rather than the higher energy part of the second band group is suggested to be assigned to the second π band, if we start from the E_{iv} values of furan. This is consistent with the qualitative conclusion described above.

In the case of 5-methylisoxazole, based on the perturbation theoretic calculations, the first band and the lower energy part and higher energy part of the second band group can be assigned to the π, π, and n bands from the top, respectively, by starting from either furan or 2-methylfuran. The same assignments can be obtained by starting from the E_{iv} values of isoxazole on the assumption that the assignments in the case of isoxazole given above are correct. This fact supports the validity of the band assignments for the first three bands of isoxazole given above.

According to the first order perturbation theoretic calculations starting from either isoxazole or 5-methylisoxazole on the assumption of the validity of the band assignments given above, we can get the same band ordering for the first three bands of 3,5-dimethylisoxazole as obtained above. This fact also supports the validity of the band assignments of isoxazole and 5-methylisoxazole given above.

Thus, from the first order perturbation theoretic standpoint supported by the qualitative discussions the band orderings of the first three bands of the isoxazoles are π, π, and n from the top, while those of the oxazoles are π, n, and π from the top.

Photoelectron Angular Distributions. In order to establish the assignments of the second and third bands of the isoxazoles more firmly, the photoelectron angular distributions of isoxazole, 5-methylisoxazole, 3,5-dimethylisoxazole, furan, and 2-methylfuran were measured. The β values (see formula (1)) for these compounds are plotted in Figs. 5 and 6 with the photoelectron spectra measured at the magic angle, $\theta=54.7°$. The β values of these compounds for several E_{iv} values are summarized in Table 2. Sell and Kuppermann[19] measured the HeI photoelectron angular distributions of furan, their results being almost consistent with ours.

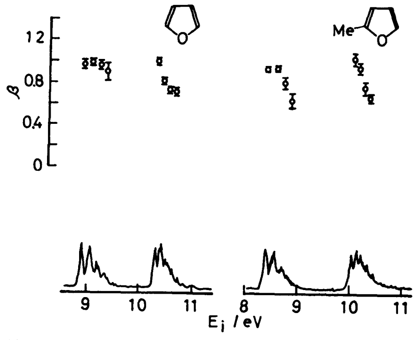

Fig. 5. HeI photoelectron angular distribution asymmetry parameter (β) values plotted with photoelectron spectra measured at $\theta=54.7°$ for furan and 2-methylfuran.

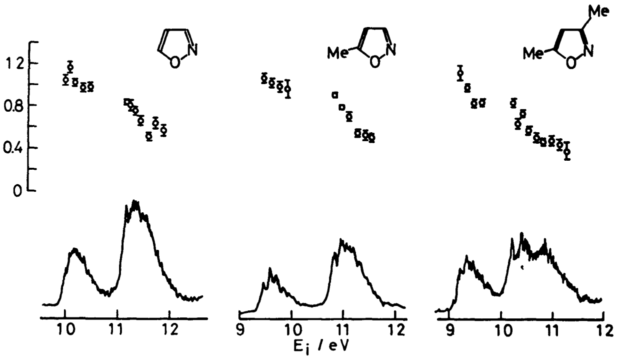

Fig. 6. HeI photoelectron angular distribution asymmetry parameter (β) values plotted with photoelectron spectra measured at $\theta=54.7°$ for isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole.

Table 2. Photoelectron angular distribution asymmetry parameter (β) values of isoxazoles and furans at some key points with ionization energy (E_{I}) values indicated

Compound	E_{I}/eV	β[a)]
Isoxazole	10.15	1.02 ± 0.03
	11.15	0.84 ± 0.02
	11.31	0.75 ± 0.04
	11.57	0.51 ± 0.04
5-Methylisoxazole	9.61	1.02 ± 0.04
	10.79	0.90 ± 0.02
	10.95	0.78 ± 0.02
	11.17	0.54 ± 0.04
3,5-Dimethylisoxazole	9.34	0.98 ± 0.04
	10.20	0.84 ± 0.04
	10.35	0.73 ± 0.04
	10.81	0.47 ± 0.03
Furan	8.89	0.97 ± 0.04
	10.44	0.82 ± 0.03
2-Methylfuran	8.38	0.93 ± 0.03
	10.15	0.94 ± 0.05

a) The root mean square errors are given.

At first let us examine the results for furan and 2-

methylfuran, the assignments of the first two bands of which are definitely the a_2(-like) π and b_1(-like) π from the top, respectively. As is seen in Fig. 5 in the case of furan and 2-methylfuran the first two π bands show large β values from 0.8 to 1 at the band maxima indifferent to the symmetries of the corresponding MOs. Keeping this point in mind let us move to the case of the isoxazoles in question.

In the case of 3,5-dimethylisoxazole, the first three bands can be well recognized separately, and the first two bands show relatively high β values from 0.7 to 1 at their band maxima, while the third band shows relatively low β value, 0.47, at the band maximum. Remembering the fact that isoxazole and furan are iso-π-electronic with each other, the first and second bands of 3,5-dimethylisoxazole may be assigned to the π bands by comparing the β values of the first three bands of this compound with those of the first two π bands of furan, the remaining third band of 3,5-dimethylisoxazole with low β value being ascribed to the n band. These assignments may be further supported by the fact that the n band of pyridine iso-π-electronic with isoxazole shows low β value around 0.2, the following two π bands showing relatively high β values.[8] Combining this result with the perturbation theoretic discussions given above, the first three bands of 3,5-dimethylisoxazole are now definitely assigned to the π, π, and n bands from the top, respectively.

Moving to the case of isoxazole and 5-methylisoxazole, the first bands of these compounds show high β values around 1.0 at the band maxima, and by comparing these values with those of the lower energy π bands of 3,5-dimethylisoxazole and the furans, it is definite that the first bands of isoxazole and 5-methylisoxazole are the π bands as assigned by the first order perturbation theoretic discussions given above. The lower energy parts of the second band groups of isoxazole and 5-methylisoxazole show high β values comparable to those of the lower energy part of the second band of 3,5-dimethylisoxazole, and the higher energy parts of the second band groups of isoxazole and 5-methylisoxazole show low β values just as the third band of 3,5-dimethylisoxazole which is definitely the n band as discussed above. From these facts we can definitely assign the lower energy parts of the second band groups of isoxazole and 5-methylisoxazole to the π bands and the higher energy parts to the n bands. These assignments are consistent with those obtained by the first order perturbation theoretic considerations.

Summing up the discussions given above the orderings of the first three bands of the isoxazoles treated here have now been firmly established to be π, π, and n from the top, and those of the oxazoles π, n, and π from the top. Combination of the photoelectron angular distribution experiments with the perturbation theoretic approach has been demonstrated to be very powerful in the photoelectron spectral band assignments.

We express our sincere thanks to Dr. T. Honma of Shionogi Research Laboratories for the pure samples.

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