Ab initio Calculations and Photoelectron Spectra of Cyclic Oxamides

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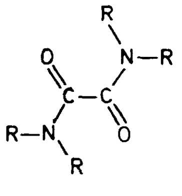
Photoelectron spectra of five-, six-, and seven-membered cyclic oxamides in which the oxamide unit is forced to adopt an *s-cis* or twisted *s-cis* conformation have been recorded. The spectra have been interpreted using *ab initio* calculations. In comparisons with acyclic *s-trans* oxamides it is found that the influence of the *s-trans–s-cis* conformational change on the ionization energies is masked by the effects of the alkyl parts of the ring systems. Ionization energies of cyclic oxamides with different ring sizes show some effects due to twisting around the inter-carbonyl bond, but also in this case the alkyl parts of the ring systems strongly influence the spectra.

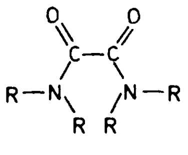
OXAMIDES and other α-dicarbonyl compounds have recently been intensively investigated by various spectroscopic methods. Photoelectron (p.e.) spectroscopy,[1-6] u.v. absorption and emission spectroscopy,[7,8] and n.m.r. spectroscopy [9] have been employed in studies on the electronic and steric interactions in this class of compounds.

Previous papers on p.e. spectra of oxamides have mainly been concerned with assignments of ionization events,[1] with the effects of *N*-alkylation on the ionization energies,[2,3] and with the energy separation of the n_+/n_- ionization processes.[4] Simple additivity rules for N-alkyl shifts have been established and have been very useful in the interpretation of p.e. spectra.[1,3]

For oxamide and its *N*-substituted derivatives, two planar conformations, *s-trans* and *s-cis*, are possible.



s - trans



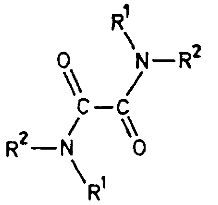
s - cis

Steric interactions may force the oxamide unit to adopt twisted conformations. Very little is known about the conformational properties of this class of compounds, but oxamide itself is *s-trans* and planar in the crystalline state.[10] *N*-Alkyl-substituted oxamides are generally also *s-trans*,[8] but may be more or less twisted around the carbonyl–carbonyl bond, depending on the degree of substitution. Tetra-alkyl-substituted oxamides are most severely twisted, with a dihedral angle close to 90°, according to n.m.r.[9,11,12] and dipole moment studies.[13] Strong dipole–dipole repulsions between the carbonyl groups and repulsive steric interactions between nitrogen substituents prevent the *s-cis* conformation from being significantly populated. The planar *s-cis* conformation may not even be a local minimum on the potential energy surface.[14]

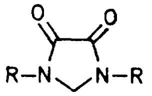
All oxamide derivatives studied so far by p.e. spectroscopy have been *s-trans* or *s-transoid* (twisted *s-trans*). The only exception is a study by McGlynn *et al.* on imidazolidine-2,4,5-trione and some of its *N*-alkyl derivatives.[3] These compounds may be considered as *s-cis* oxamide derivatives, but the p.e. spectra were more conveniently interpreted in terms of a partition into urea and *s-cis* glyoxal.

In this paper we report the p.e. spectra of some cyclic oxamides, in which the oxamide unit is forced to adopt an *s-cis-* or twisted *s-cis*-conformation by the constraints of a ring system. Comparisons with the corresponding *s-trans*-compounds are made. Compounds (I)—(VI) have been studied.

In earlier work, semiempirical CNDO/S calculations have been employed in the interpretation of p.e. spectra of oxamides.[1-3] This type of calculation is parametrized to fit electronic spectra and it has shown to be well suited to the prediction of p.e. spectra using the negative of the calculated molecular orbital (MO) energies as an approximation to the ionization potentials (Koopmans' theorem). The success of the CNDO/S method in reproducing p.e. spectra implies that the deficiencies in Koopmans' theorem, *i.e.* its neglect of electron reorganization energy in the molecular ion and of differences in correlation energies between the ground state molecule and the ion, to some extent are taken care of by the parametrization. Furthermore, this implies that

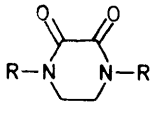


(I) $R^1 = R^2 = H$
(II) $R^1 = H, R^2 = CH_3$
(III) $R^1 = R^2 = CH_3$



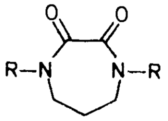
(IV)

a; R = H
b; R = CH$_3$



(V)

a; R = H
b; R = CH$_3$



(VI)

a; R = H
b; R = CH$_3$

the MO energies and the order of the MOs, as calculated by CNDO/S and similar methods, do not necessarily refer to the ground state of the molecule. It is thus to be expected that in some cases the order of the MOs in the ground state may be different from the order of the ionization events observed in the p.e. spectrum and assigned to these orbitals.[15]

In this work we have employed *ab initio* calculations to obtain MO energies. In order to calculate ionization energies for comparisons with experimental values from p.e. spectra, we have made empirical corrections for reorganization and correlation effects. This approach has been successful in earlier studies.[16,17] In this way we hope to be able to predict both the order and the energies of the MOs in the ground state *and* the order and energies of ionization events, as they show up in the p.e. spectra.

The purposes of the present work are as follows: (i) to investigate the ability of the computational approach used to support the interpretation of p.e. spectra of oxamides, (ii) to study the influence of conformations of oxamides on the ionization energies in p.e. spectra, and (iii) to evaluate the dependence of the ionization energies on the ring size of cyclic *s-cisoid* oxamides.

EXPERIMENTAL AND COMPUTATIONS

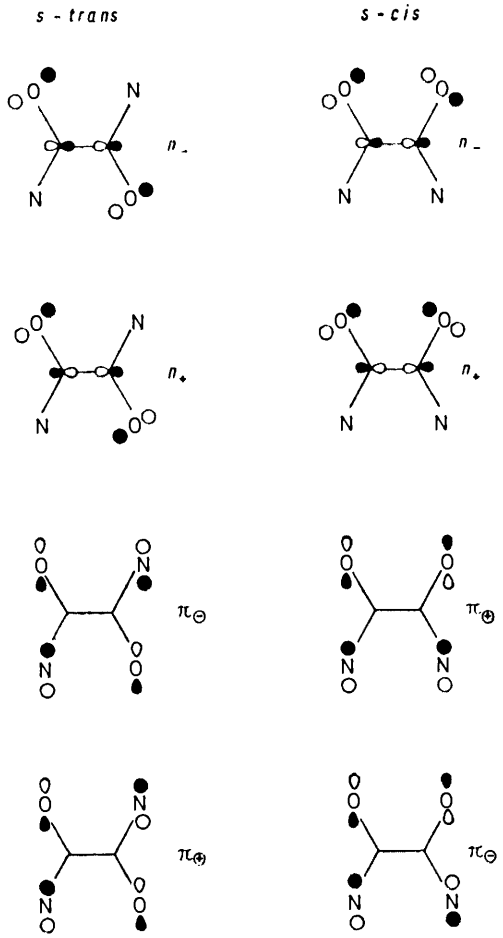
Photoelectron Spectra.—P.e. spectra were recorded on a Perkin-Elmer model PS-18 photoelectron spectrometer. The ionization energy was provided by the He^{I} (21.22 eV) resonance line. The range of temperatures used for solid samples was 53—150 °C. Spectra were calibrated with regard to energy and resolution using the $^{2}P_{3/2}$ line (12.13 eV) of Xe and the $^{2}P_{3/2}$ line (15.76 eV) of Ar. No decomposition of any molecule studied in this work was observed under the experimental conditions described above.

Synthesis.—Tetramethyloxamide (III) was prepared according to Persson and Sandström.[18] The synthesis of compounds (IVb), (Va), (Vb), and (VIb) will be described elsewhere.[14]

Calculations.—The *ab initio* calculations were carried out using the computer program MOLECULE.[19] For carbon, nitrogen, and oxygen, a Gaussian basis set of seven *s*-type and three *p*-type functions contracted to two and one, respectively, was used (a minimal basis). The basis set for hydrogen was made up from four Gaussian *s*-type functions contracted to one. Calculations on oxamide (I) were also performed with a contraction to a ' split shell ' basis with four *s*-type and two *p*-type orbitals for carbon, nitrogen, and oxygen and two *s*-type orbitals for hydrogen. Orbital exponents and contraction coefficients were those given by Clementi *et al.* (C, N, O; 7/3 basis set)[20] and Huzinaga (H).[21] In the latter case a scaling factor of 1.34 was used.

The MOs have been classified according to the notation introduced by McGlynn *et al.*[1] The MOs discussed in this work and denoted n_{+}, n_{-}, $\pi_{\oplus}$, and $\pi_{\ominus}$ are shown in the Scheme. MO energies were converted into ionization energies as described in detail below.

Geometries.—The oxamide molecule has been studied by *X*-ray diffraction,[10] but for the remaining compounds investigated in this work no experimental geometries are available. Geometries used in the calculations were constructed from those of analogous molecules. As a starting point, the *X*-ray structure of oxamide was modified in order to make the geometry more appropriate for the gas phase. Strong hydrogen bonding in the crystalline state significantly influences the geometric parameters of this molecule. The modifications made were guided by observed differences in structural parameters between *X*-ray [22] and electron diffraction [23] geometries of amides. The intercarbonyl bond length was given a value close to that of the corresponding bond length of glyoxal [24] and biacetyl [25] in



SCHEME

TABLE 1

Geometries used in the *ab initio* calculations [a]

Bond lengths (Å)		Bond angles (°)	
C_{sp^2}—C_{sp^2}	1.52	CCO	123, 126 [b]
C=O	1.22	C_{sp^2}—C_{sp^2}—N	115, 106 [b]
C_{sp^2}—N	1.36	C_{sp^2}—N—H	120
N—H	1.02	C_{sp^2}—N—C_{sp^3}	120, 112.3,[b] 126.5 [c]
N—C_{sp^3}	1.46, 1.44 [b]	H—C_{sp^3}—N	109.5
C—H	1.09	C_{sp^3}—C_{sp^3}—N	110
C_{sp^3}—C_{sp^3}	1.54		

[a] The symmetries used for the cyclic compounds were: C_{2v} for (IVa), C_2 for (Va) and (VIa), with CO—CO dihedral angles of 0, 20, and 60°, respectively. All amide units were kept planar. [b] Used for (IVa). [c] Used for (Va).

the gas phase, and bond angles were modified to values appropriate for the *s-cis*-conformation.[26]

The structural parameters for the oxamide unit thus constructed were kept as unchanged as possible in the evaluation of the geometries for the cyclic compounds. The remaining parameters for the ring systems were estimated from standard values and from analogous ring compounds. The final geometries are given in Table 1. As shown below, moderate changes of the geometric parameters have an insignificant effect on the calculated orbital energies.

RESULTS

For *s-trans*-oxamide (I), using a minimal basis, the highest occupied MO is calculated to be $\pi_\oplus$, but the three MOs $\pi_\oplus$, n_+, and $\pi_\ominus$ are almost degenerate (Table 2). The n_- orbital is significantly more stable. The MO order in *s-cis*-oxamide is calculated to the $\pi_\ominus$, n_+, $\pi_\oplus$, and n_- (Table 2), with a larger separation between $\pi_\oplus$ and $\pi_\ominus$ and a smaller separation between n_+ and n_- than was found for the *s-trans*-conformation. The dependence of the MO energies on twisting around the intercarbonyl bond is shown in Figure 1.

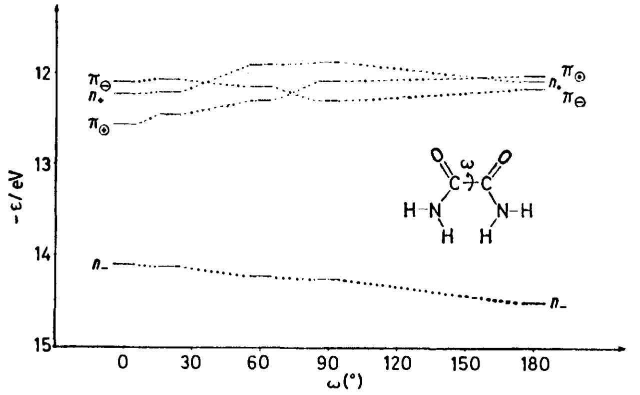


Figure 1 Dependence of orbital energies on dihedral angle for oxamide (I)

Using the more extensive 'split-shell' basis set, all four MOs increase in energy by approximately the same amount, *ca.* 1 eV (Table 2), leaving the separations between the orbitals essentially unchanged and the orbital order unaffected. The same result is observed for *s-cis* and 90° twisted oxamide (Table 2). These results justify our use of the minimal basis set for all other calculations described in this work to economize on computer time. The calculated MO energies are given in Table 2. To obtain an estimate of how possible deficiencies in the constructed geometries of the cyclic compounds (IV)—(VI) would affect the computed energies, the sensitivity of these energies to moderate changes in geometrical parameters was investigated. A 0.02 Å change in the C–C or C–N bond lengths resulted in MO energy changes of < 0.1 eV. The same result was obtained when the CCO bond angle was increased by 5° or the CCN angle decreased by the same amount. Thus, the effects of moderate geometrical changes on the computed MO energies are apparently small. Conversion of MO energies to ionization energies requires corrections for reorganization energies in the molecular ion and for differences in correlation energies between the ground and ionized states. We have used an approach based on *ab initio* calculations,[16,17] which has been successfully employed in studies on the assignments of ionization events in p.e. spectra. The differences between calculated energies for the four highest occupied orbitals in *s-trans*-oxamide (I) (Table 2) and the corresponding ionization energies as observed and assigned by McGlynn *et al.*[3] (Table 3), were formed and used as empirical corrections to (the negative of) the calculated MO energies for other oxamide derivatives. The corrections thus obtained are n_+ -2.26, n_- -2.80, $\pi_\oplus$ -0.99, and $\pi_\ominus$ -1.69 eV. As discussed by Roos *et al.*,[17] the corrections should be constant for each orbital type throughout a series of similar molecules. Since the corrections are largely determined by the gross structure of the orbitals the corrections for $\pi_\oplus$ and $\pi_\ominus$ should be inverted for *s-cis*-

Table 2

Molecular orbital energies from *ab initio* calculations (eV)

Compound	n_+	$\pi_\ominus$	$\pi_\oplus$	n_-
(I) *s-trans*	12.06	12.14	12.03	14.52
(I) *s-trans* [a]	11.18	11.13	11.06	13.52
(I) 90°	11.87	12.31	12.06	14.26
(I) 90° [a]	10.95	11.42	11.15	13.15
(I) *s-cis*	12.23	12.10	12.55	14.09
(I) *s-cis* [a]	11.36	11.20	11.57	12.85
(II) *s-trans*	12.02	11.69	11.52	14.48
(IVa)	12.02	12.49	11.73	14.69
(Va)	12.20	11.26	12.13	14.11
(VIa)	11.78	11.40	11.55	13.89

[a] 'Split-shell' basis. Otherwise a minimal basis set was used.

Table 3

Calculated and experimental ionization energies for compounds (I)—(VI)

Compound	MO	Calculated (eV)	Experimental (eV)	
(I)	n_+		9.80 [a]	
	$\pi_\ominus$		10.50	
	$\pi_\oplus$		11.04	
	n_-		11.72	
(II)	n_+		9.33 [a]	
	$\pi_\ominus$		9.62	
	$\pi_\oplus$		10.07	
	n_-		11.20	
(III) [b]	n_+	8.70	8.9—9.2	9.02 [a]
	$\pi_\oplus$	8.87		9.34
	$\pi_\ominus$	9.24		9.08
	n_-	10.38	10.5	10.49
(IVa)	n_+	9.76		
	$\pi_\oplus$	10.04		
	$\pi_\ominus$	11.50		
	n_-	11.89		
(IVb)	$\pi_\oplus$	9.16	9.3—9.5	
	n_+	9.29		
	$\pi_\ominus$	10.53	10.7	
	n_-	11.37	11.5	
(Va)	n_+	9.94	9.70	
	$\pi_\ominus$	10.27	10.20	
	$\pi_\oplus$	10.44	10.55	
	n_-	11.31	11.70	
(Vb)	$\pi_\ominus$	9.30	9.20	
	n_+	9.47	9.30	
	$\pi_\oplus$	9.56	9.60	
	n_-	10.79	10.35	
(VIa)	n_+	9.52		
	$\pi_\oplus$	9.86		
	$\pi_\ominus$	10.41		
	n_-	11.09		
(VIb)	$\pi_\oplus$	8.98	8.8—9.2	
	n_+	9.05		
	$\pi_\ominus$	9.44		
	n_-	10.57	10.5	

[a] Ref. 2. Assignments based on CNDO/S calculations.
[b] The carbonyl–carbonyl bond 60° twisted.

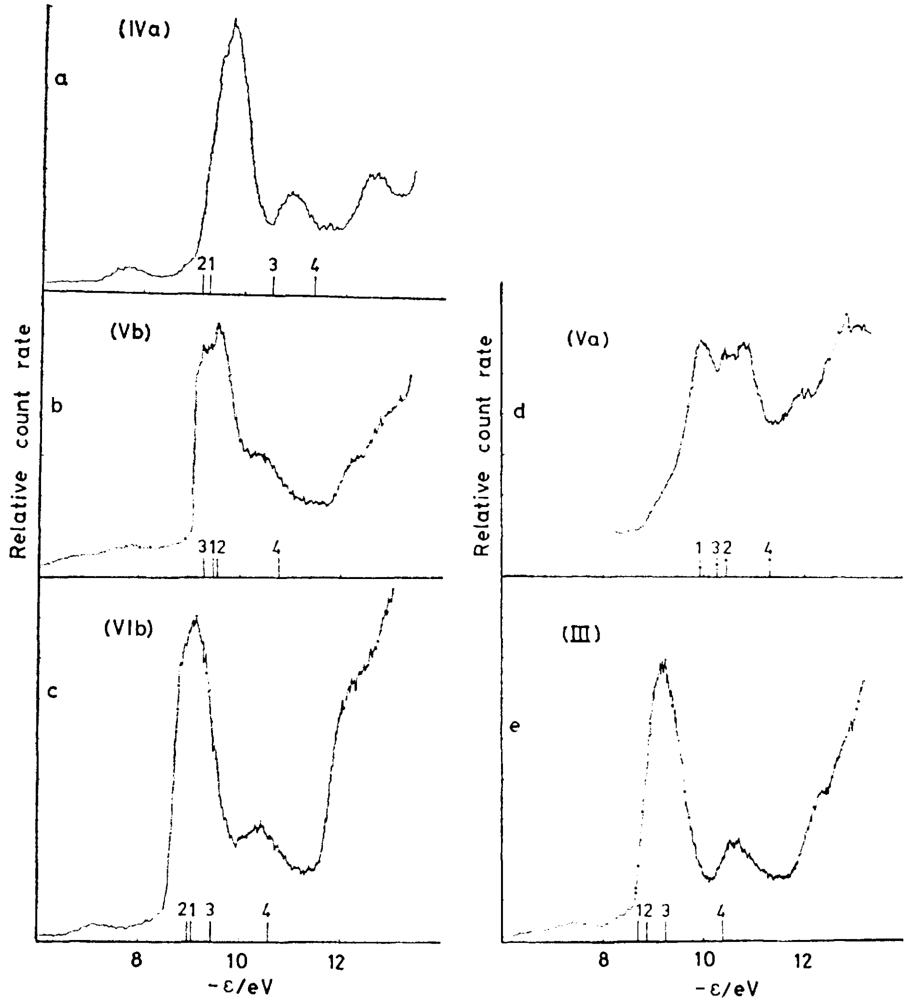


FIGURE 2 Photoelectron spectra of compounds (III), (IVb), (Va and b), and (VIa). Vertical bars indicate calculated ionization energies. The numbers above the bars indicate orbital type: 1 = n_+, 2 = $\pi_\oplus$, 3 = $\pi_\ominus$, and 4 = n_-

oxamides. Inspection of the Scheme shows that the gross structure of the $\pi_\oplus$ orbital of the *s-trans*-conformer is similar to that of the $\pi_\ominus$ orbital of the *s-cis*-conformer and *vice versa*. The approach described above is based on the assumption that variations in ionization energies in a series of similar molecules are reflected in the variations of MO energies. This justifies the use of the same notation for orbital and ionization energies.

It is interesting to note that the differences between the MO energies for *s-trans*-oxamide (Table 2), calculated by the ' split-shell ' basis set, and the corresponding experimental ionization energies (Table 3) are very similar to those obtained by Roos *et al.* in their studies on azabenzenes [17] and anhydrides,[16] using a similar basis set. This implies, as discussed by Roos *et al.*,[16] that empirical corrections obtained from studies on one class of molecules may be used for other classes as well, provided that the calculations are being done with basis sets of approximately the same quality.

All calculations in this work, except for compound (II), were done for the *N*-unsubstituted parent compounds. The MO energies were converted to ionization energies as described above. *N*-Methylation effects were taken into account using the *N*-methyl shifts determined by McGlynn *et al.* (n_+ −0.47, n_- −0.52, $\pi_\oplus$ −0.97, and $\pi_\ominus$ −0.88 eV), with $\pi_\oplus/\pi_\ominus$ inversion for *s-cis*-compounds.[3] These shifts have proved to be remarkably constant and additive for amides and oxamides.[1] Experimental and calculated ionization energies are summarized in Table 3. Experimental p.e. spectra in the 8—12 eV region are shown in Figure 2 with the calculated ionization energies and their assignments indicated by vertical bars.

The p.e. spectra of most of the compounds studied show extensively overlapped bands. The spectrum of (Va) is however quite well resolved and may be used as a test case for the approach described above. The calculated ionization energies agree very well with the experimental ones, especially for the three lowest ionization events (see Figure 2d and Table 3). *N*-Methylation shifts all ionizations towards lower energies, but the $\pi_\oplus$ and $\pi_\ominus$ bands are more sensitive to the alkylation effect than the n_+ and n_- bands.[3] This results in a strong overlap of the n_+, $\pi_\oplus$, and $\pi_\ominus$ bands in the p.e. spectra of (Vb) (Figure 2b). It is clearly a great advantage to be able to study the *N*-unsubstituted compounds of this class of molecules, since the p.e. spectra are more resolved with less *N*-substitution. However, all attempts to synthesize compounds (IVa) and (VIa) have failed so far.[14] The calculated ionization energies for these compounds, as given in Table 3, thus constitute a prediction of their p.e. spectra.

DISCUSSION

As mentioned in the introduction, the order of MO energies does not need to be the same as the order of ionization energies. For *s-trans*-oxamide (I) the MO order is $\pi_{\oplus}$, n_{+}, $\pi_{\ominus}$, and n_{-} (Table 2), while the experimental order of ionization energies is n_{+}, $\pi_{\ominus}$, $\pi_{\oplus}$, and n_{-} (Table 3). In this case, however, the three highest occupied MOs are nearly degenerate. The case of (Va) is more clear cut. For this molecule, the calculated MO order is $\pi_{\ominus}$, n_{+}, $\pi_{\oplus}$, and n_{-}, with a significant separation between $\pi_{\ominus}$ and $n_{+}/\pi_{\oplus}$. Due to differences in correction terms for orbitals of π- and σ-type (see above), the order of the $\pi_{\oplus}$ and n_{+} processes is reversed in the experimental p.e. spectra. Great caution should thus be exercised if conclusions about the order of MO levels are to be drawn from p.e. spectra. Since CNDO/S calculations reproduce p.e. spectra very well, the same caution applies to conclusions drawn from such calculations.

N-*Methyl Shifts*.—The observed *N*-methyl shifts for oxamides are close to 0.5 eV for n_{+} and n_{-} and 0.9—1.0 eV for $\pi_{\oplus}$ and $\pi_{\ominus}$.[3] This difference is expected, since the n orbitals are largely localized on oxygen, with small amplitudes on nitrogen. In contrast, the $\pi_{\oplus}/\pi_{\ominus}$ orbitals have large amplitudes on nitrogen. CNDO/S calculations on oxamides give a fair account of the *N*-methyl effect.[3] However, the *ab initio* calculations employed in the present work show almost no shift of the n orbitals when calculations on oxamide and *NN'*-dimethyloxamide are compared. The energies of the $\pi_{\oplus}/\pi_{\ominus}$ levels is, on the other hand, increased by *ca.* 0.5 eV (Table 2). These calculated *N*-methyl shifts are thus *ca.* 0.5 eV smaller than the effects observed on ionization energies in p.e. spectra. Although these differences between calculated and experimental values may to some extent be due to the limited basis set used in the calculations, they more probably imply that the effects of *N*-methyl substitution on p.e. spectra of oxamides (and other classes of compounds as well) are a composite of changes in MO energies and changes in reorganization and correlation energies.

Conformation of Oxamides and its Influence on P.e. Spectra.—The p.e. spectra of *s-trans-NN'*-dimethyloxamide (II) and its cyclic *s-cis*-analogue (Va) show significant differences (Table 3). Although the order of ionization events (n_{+}, $\pi_{\ominus}$, $\pi_{\oplus}$, and n_{-}) is the same for the two molecules, the ionization energies in the 9—12 eV region are increased by 0.4—0.6 eV on going from (II) to (Va). These differences are not those expected for a conformational effect on going from *s-trans* to *s-cis*. CNDO/S calculations indicate small conformational effects, $<$ 0.1 eV, on the n_{+} and $\pi_{\ominus}$ levels. The $\pi_{\oplus}$ and n_{-} levels are somewhat more affected, showing shifts of +0.2 and −0.3 eV respectively.[8] CNDO/2 Calculations give exactly the same results.[27] *Ab initio* calculations give somewhat larger differences (see Figure 1 and Table 2), but again the n_{+} and $\pi_{\ominus}$ MOs are less influenced by the *s-trans–s-cis* conversion than are the $\pi_{\oplus}$ and n_{-} levels. Also in this case the energy changes of the two latter MOs have different signs.

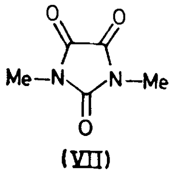
Calculations of ionization energies of *s-trans* (II) and *s-cisoid* (II) [20° twisted as in (Va)], including reorganization and correlation terms, result in the following shifts on the ionization energies on going from *s-trans* to *s-cisoid* (20°): n_{+} +0.01, $\pi_{\oplus}$ −0.27, $\pi_{\ominus}$ +0.70, n_{-} −0.4 eV. It is clear that the observed differences in the spectra of (II) and (Va) cannot solely be interpreted in terms of effects due to conformational changes. The observed shifts must be a composite of a conformational effect and an effect due to differences between two *N*-methyl groups and an ethylene bridge. This effect, however, is not to be found in the energies of the MO levels. The n_{+}/n_{-} and the $\pi_{\oplus}$ levels in (II) and (Va) have very similar energies (Table 2). The $\pi_{\ominus}$ MO lies *ca.* 0.5 eV higher in (Va) than in (II) depending on the CH_2–CH_2 antibonding character of this orbital in (Va). Instead, differences in the reorganization and correlation term necessary to convert MO energies to ionization energies must be invoked. It should be noted that the procedure used in the present work very satisfactorily reproduces the p.e. spectrum of (Va). This implies that the correction terms evaluated from p.e. spectra and *ab initio* calculations of oxamide (I) are also valid for the cyclic *s-cisoid*-oxamides, that is no extra terms due to the alkyl bridges need be included. As discussed above this is not the case for MO levels if methyl groups are included in the MO calculations. This analysis indicates a serious problem in studies of unstable or low population conformers by p.e. spectroscopy. A common technique for such studies is the preparation of model compounds in which the desired geometrical or conformational properties are introduced by rigidly fixing part of the molecule by alkyl bridges. This may lead to a complete masking of the desired effect, by the influence of the bridging alkyl part, as in the case described above. In such cases conclusions drawn from p.e. spectra may be totally misleading.

Ring Size and Ionization Energies.—Compounds (IVb)—(VIb) form a series of molecules with increasing twist around the intercarbonyl bond. Compound (IVb) is probably planar or close to planar. Models and analogous ring compounds suggest that the twisting in (Vb) and (VIb) is *ca.* 20 and 60°, respectively. As indicated by the assignments in Figure 2, the five-membered ring compound (IVb) is quite different from the other two and will therefore be dealt with separately.

The p.e. spectra of (Vb) and (VIb) are quite similar (Figures 2b and c), the main difference being a small but significant shift of the low energy band towards lower ionization energies as the ring size increases. This may be due to a corresponding increase in the intercarbonyl dihedral angle and/or to differences in the lengths of the alkyl parts of the ring systems. *Ab initio* calculations including the correction terms described above nicely reproduce the difference in p.e. spectra between (Vb) and (VIb) (Table 3) but the picture that emerges is not a simple one. The three ionization events making up the low energy band all qualitatively behave as expected for an increasing twist of the oxamide unit. According to calculations summarized in Figure 1, the energies of the n_+ and $\pi_\oplus$ levels increase on going from a 20 to a 60° twist. A small decrease in the energy of the $\pi_\ominus$ level is also expected. These changes show up somewhat enlarged in the calculations of ionization energies of (Vb) and (VIb). However, according to calculations on oxamide (Figure 1), the n_- level should exhibit a decrease in energy with increasing twist. Calculations on (Vb) and (VIb) show an increase in the energy of the n_- level. It is thus clear that differences in the inductive effects of the alkyl parts of the ring system influence the p.e. spectrum to some extent.

This may also be seen in the calculated MO energies of (Va) and (VIa) (Table 2). The differences in energies, especially for the n_+ and $\pi_\oplus$ levels, are about twice as large as the corresponding differences between 20 and 60° twisted *s-cis*-oxamide. The conclusion is that the shifts observed in the p.e. spectra of (Vb) and (VIb) are about equally due to conformational changes and to differences in alkyl inductive effects. The p.e. spectrum of tetramethyloxamide (III) shows a further shift of the low-energy band towards lower ionization energies than does (VIb). This shift is also reproduced by the calculations (Table 3), using the MO energies for 60° twisted oxamide and adding corrections for methyl groups. Since identical geometries and dihedral angles were employed in the calculations of ionization energies for (III) and (VIb), the observed shifts must be interpreted as a differential influence of the *N*-alkyl substituents.

NN′-*Imidazolidine*-4,5-*dione* (IVb).—This compound may be viewed as a model for a planar *s-cis*-oxamide unit. The geometry is quite different from that of oxamide itself (Table 1), but the main differences are to be found in the bond angles, and these differences, as shown above, are not expected to influence the p.e. spectrum to a significant degree. In contrast to the other oxamide derivatives studied in this work, the low-energy ionization band is calculated to consist of only two ionization energies, $\pi_\oplus$ and n_+, with the $\pi_\ominus$ event of considerably higher energy. This conclusion is supported by the analysis of the p.e. spectrum of *NN*′-dimethylimidazolidine-2,4,5-trione (VII) by McGlynn *et al.*[3] For this related compound, the first band in the p.e. spectrum is also due to the $\pi_\oplus$ and n_- ionization processes, with the $\pi_\ominus$ process *ca.* 0.7 eV higher in energy. Although the p.e. spectra of (IVb)—(VIb) are quite similar, the assignments of the two bands in the 8—12 eV region show important differences. The reason for the unexpectedly high ionization energy of the $\pi_\ominus$ process lies in the nodal properties of the corresponding MO. This orbital possesses a node at the methylene group making it quite insensitive to changes at this position. The ionization energy, 10.5 eV, is thus close to that observed for (VII) (10.97 eV).[3]



(VII)

Conclusions.—Ionization energies in p.e. spectra of cyclic *s-cisoid*-oxamides are remarkably well accounted for by MO energies from *ab initio* calculations, empirically corrected for reorganization and correlation effects. The influence of the alkyl parts of the cyclic ring systems necessary to force the oxamide unit into *s-cisoid*-conformations seriously masks the effects of conformational change. A qualitative picture of the degree of twist of the oxamide unit in different ring compounds may be obtained, but differential effects due to different lengths of cyclic alkyl chains prohibits a more quantitative analysis.

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