

# Ultraviolet Absorption and Photoelectron Spectra of Some Cyclic and Open-chain Mono- and Dithiooxamides

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A series of dithiooxamides with dihedral angles of ca. 90, 65 and 30° between the thioamide chromophores have been studied by ultraviolet photoelectron and absorption spectroscopy. Assignment of ionizations and absorption bands have been made on the basis of previous CNDO/S and *ab initio* calculations of orbital and transition energies in the analogous oxamide systems. The assignments in the photoelectron spectra have been corroborated by a study of some monothiooxamides.

The ultraviolet-visible absorption spectra of thio-carbonyl compounds in general and of thioamides in particular have been studied over a long period of time.<sup>1–5</sup> More recently, the absorption spectroscopic studies have been supplemented with investigations of ultraviolet photoelectron spectra.<sup>6–8</sup> One reason for this interest may be the fact that these compounds often present well resolved transitions, which appear in an easily accessible wavelength region and which are sensitive to substituents and solvents in a way which makes them suitable for testing theoretical calculations on various levels of approximation. Another reason may be found in the usefulness of thioamides as qualitative electronic models for amides. A certain parallelism can be expected between the energy levels and transitions in these two groups of chromophores, but the amide chromophore is much less accessible to studies because of the high energies and the closeness of its transitions.

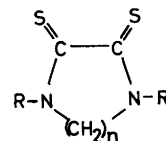
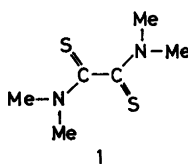
Several years ago, one of us<sup>9</sup> studied the ultraviolet–visible absorption spectra of mono- and dithiooxamides, and it was concluded that *N,N,N',N'*-tetraalkyl derivatives are so strongly twisted about the pivot bond that the thioamide

parts appear as essentially isolated chromophores. This result was later corroborated by emission spectroscopy<sup>10</sup> and by dynamic NMR spectroscopy,<sup>11</sup> and dipole moments were recorded which were in agreement with twist angles close to 90°. <sup>12</sup> *N,N,N',N'*-Trialkyl derivatives also appear twisted, whereas *N,N'*-disubstituted and less substituted compounds seem to prefer a nearly planar *s-trans* conformation, as evidenced by the low dipole moments for some representative compounds.<sup>12</sup>

The present work was undertaken to study the role of the dihedral angle about the pivot bond in determining the orbital and transition energies in dithiooxamides. *N,N,N',N'*-Tetramethyldithiooxamide (1) was chosen as a model for a system with perpendicular thioamide groups. In the cyclic compounds (2) the dihedral angle depends on the length of the bridge. According to molecular mechanics calculations,<sup>13</sup> the angle is 65° in the seven-membered ring compounds 2a and 2b, and 31° in the six-membered compound 2c.

## EXPERIMENTAL

The preparation of the compounds is described elsewhere.<sup>9,14,15</sup> The photoelectron spectra (UPS)



2a: R = Me, n = 3  
 2b: R = iPr, n = 3  
 2c: R = Me, n = 2

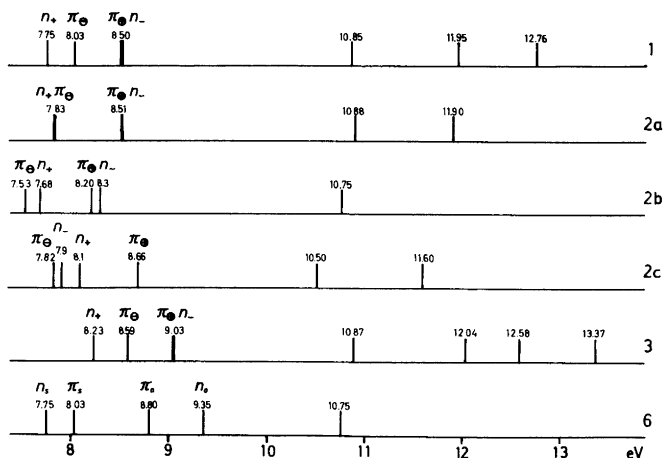


Fig. 1. Vertical ionization potentials and assignments for the dithiooxamides and monothiooxamide 6.

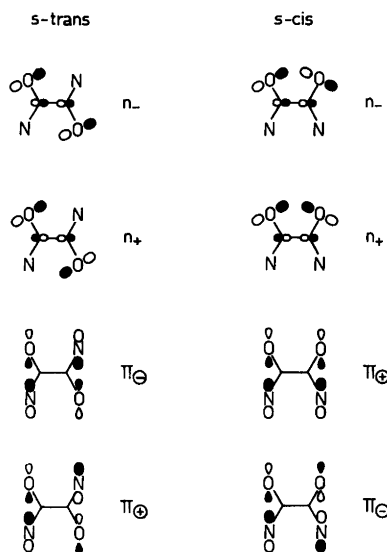
were recorded with a Perkin-Elmer Model PS-18 photoelectron spectrometer, employing the He (I) 21.22 eV resonance line for ionization. The spectra were calibrated with respect to energy and resolution with aid of the  $^2P_{3/2}$  line (12.13 eV) of Xe and the  $^2P_{3/2}$  line (15.76 eV) of Ar. No decomposition of any molecule studied in this work was observed under the experimental conditions. The vertical ionization potentials are reported in Fig. 1.

The ultraviolet spectra were recorded with Cary Model 15 and Cary Model 219 spectrometers. For identification of  $n \rightarrow \pi^*$  transitions, spectra should preferably have been recorded in a completely non-polar solvent, such as cyclohexane, and in pure ethanol. However, due to solubility problems, varying proportions of chloroform had to be employed also in the most dilute solutions (*ca.*  $10^{-5}$  M). The solvents used, and the positions and extinction coefficients of the absorption maxima are reported in Table 1. Some representative spectra are shown in Fig. 3.

## RESULTS AND DISCUSSION

The notion of a complete isolation of the thioamide chromophores in a  $90^\circ$  twisted dithiooxamide like 1 is not valid. A simple argument based on through-bond interaction, assuming mainly  $p$  character for the sulfur lone pairs ( $n$ ) shows that these may interact quite strongly by intervention of the  $\sigma$ -orbitals in the C—C bond. To a first approximation, the splitting caused by this interaction should

be independent of the dihedral angle. Larson and McGlynn<sup>16</sup> performed CNDO/S calculations with configuration interaction (CI) on oxamide for the dihedral angles  $0, 45, 90, 135$  and  $180^\circ$ , and they found a splitting of the  $n$  levels into a higher symmetric ( $n_+$ ) and a lower antisymmetric ( $n_-$ ) combination (Scheme 1), with energies rather in-



Scheme 1.

sensitive to the dihedral angle and with a splitting of *ca.* 2.3 eV. Ionizations assignable to these orbitals have been observed in the photoelectron spectra of several oxamides.<sup>17-19</sup> Two of us<sup>19</sup> have performed a photoelectron spectroscopic investigation of cyclic oxamides combined with *ab initio* calculations, and the results agree with those of McGlynn *et al.* as far as the splitting of the *n* levels is concerned.

The photoelectron spectra (UPS) of the dithiooxamides in general display a group of more or less overlapping bands in the ionization potential (IP) region 7.5 to 8.7 eV. At most three resolved bands are observed, but the intensities clearly reveal that four ionization events take place. By comparison with the analogous oxamides,<sup>16,18,19</sup> these can be ascribed to the  $n_-$ ,  $n_+$ ,  $\pi_{\oplus}$  and  $\pi_{\ominus}$  levels (Scheme 1). The splitting of the *n* levels in the oxamides is of the order of 1.0–1.7 eV.<sup>18,19</sup> The overlap between the sulfur lone pairs and the  $\sigma$ -orbital in the pivot C–C bond is smaller than the corresponding overlap in the oxygen analogues, whereas the energy gap between these orbitals is greater in the dithio analogues. Therefore the splitting of the *n* levels can be expected to be significantly smaller in the latter compounds. The higher energy of the sulfur valence orbitals compared to the oxygen orbitals contributes to raise the energies of the *n* and  $\pi$  orbitals, which have contributions from sulfur basis orbitals.

In *N,N,N',N'*-tetramethyloxamide, the ionizations are assigned, from low to high ionization potentials, to the  $n_+$ ,  $\pi_{\ominus}$ ,  $\pi_{\oplus}$ , and  $n_-$  levels. The UPS of *1* shows a sharp band at 7.75 eV, a somewhat broader one at 8.03 eV and a more intense one, evidently due to two ionization events, at 8.50 eV. Both the bandshapes and analogy with the oxamide permit the alternative assignments:  $n_+$ ,  $\pi_{\oplus}$ ,  $\pi_{\ominus}$ ,  $n_-$  and  $n_+$ ,  $\pi_{\ominus}$ ,  $\pi_{\oplus}$ ,  $n_-$  from low to high IP's. An analysis of the effect of changing the dihedral angles permits a more precise assignment. In the spectrum of *2a*, only two bands are observed below 10eV, one at 7.83 eV and the other one at 8.50 eV. The reduction of the dihedral angle by *ca.* 30° from *1* should according to the *ab initio* calculations in Ref. 19 result in a decrease in the  $n_+ - n_-$  splitting, a lowering of the  $\pi_{\oplus}$  level, and a raising of the  $\pi_{\ominus}$  level. Therefore, the band at 7.83 eV is ascribed to ionizations from the  $n_+$  and  $\pi_{\ominus}$  levels, and the one at 8.50 eV to ionizations from the  $\pi_{\oplus}$  and  $n_-$  levels. Consequently, the order of IP:s in *1* should be the same one as may be calculated for a 90° twisted *N,N,N',N'*-tetramethyloxamide from data in Ref. 19, *i.e.* with the  $\pi_{\ominus}$  level at higher energy (lower IP) than the

$\pi_{\oplus}$  level.

The notation  $\pi_{\oplus}$  and  $\pi_{\ominus}$  may seem questionable for *1*, where the two thioamide groups are nearly orthogonal, but due to different interactions with other orbitals of suitable symmetry the two orbitals remain different, and it is possible to keep track of them in the calculations over an entire 180° rotation.

The assignments for *2a* are corroborated by a study of the *N,N'*-diisopropyl analogue *2b*. The inductive electron donating (+I) effect of the *iPr* group is slightly greater than that of Me, and it has been observed both in the formamide<sup>20</sup> and thioformamide<sup>7,21</sup> series that the highest  $\pi$  level is raised more strongly than the *n* level when the +I effect of the *N* substituent is increased. In agreement with this, shifts on *N,N'*-dimethylation in oxamides of *ca.* 0.5 eV for  $n_+$  and  $n_-$  and of 0.9–1.0 eV for  $\pi_{\oplus}$  and  $\pi_{\ominus}$  have been observed.<sup>18,19</sup> In the UPS of *2b*, the exchange of Me for *iPr* results in a shift to lower IP:s of all bands under discussion. The band at 7.83 eV in the spectrum of *2a* is replaced by two at 7.53 and 7.68 eV, which are assigned to  $\pi_{\ominus}$  and  $n_+$ , respectively. The remaining broad band with a peak at 8.20 eV and a shoulder at 8.3 eV is assigned to a superposition of  $\pi_{\oplus}$  and  $n_-$ .

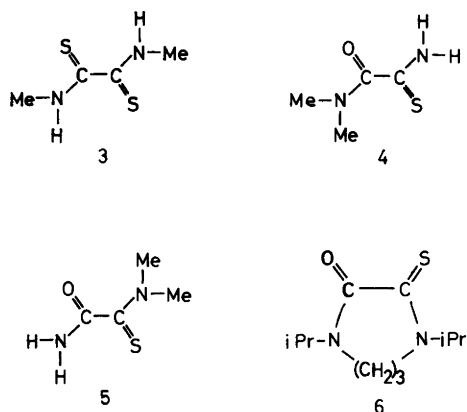
A further reduction of the dihedral angle should lead to an increase of the  $\pi_{\ominus}$  and  $n_-$  energies and a decrease of the  $\pi_{\oplus}$  and  $n_+$  energies.<sup>19</sup> This seems to be realized in the six-membered dithiooxamide *2c*. The spectrum in the 7–9 eV region is not well resolved, but it shows clear peaks at 7.82 and 8.66 eV, separated by a broad band with diffuse peaks at 7.9 and 8.1 eV. The most likely assignment is one of  $\pi_{\ominus}$ ,  $n_-$ ,  $n_+$ ,  $\pi_{\oplus}$  and  $\pi_{\ominus}$ ,  $n_+$ ,  $n_-$ ,  $\pi_{\oplus}$  from low to high IP's.

Generally, the interpretation of the observed IP:s in terms of the interactions between *n* and  $\pi$  orbitals varying with the dihedral angle is more straightforward for the dithiooxamides than for the corresponding oxamides. In the latter group, the observed deviations were explained in terms of interactions between the orbitals in the amide chromophores and those in the saturated parts of the molecules.<sup>19</sup> It is natural that these interactions should be less important in the dithiooxamides, where the energy gap between the *n* and highest  $\pi$  orbitals on one hand and the C–C  $\sigma$  orbitals on the other is *ca.* 1.5 eV greater.

The *ab initio* calculations on the oxamide system referred to above<sup>19</sup> predict a crossing over of the  $\pi_{\ominus}$  and  $\pi_{\oplus}$  levels between the dihedral angles 60°

and  $90^\circ$ , and a slight raising of the energies of both levels with increasing dihedral angle. Simultaneously, both  $n$  levels are lowered, and in *s-trans* oxamide the calculated order of the levels, from high to low energy, is  $\pi_\oplus$ ,  $n_+$ ,  $\pi_\ominus$ , and  $n_-$ . *N,N'*-Dimethyldithiooxamide (3) is probably close to the *s-trans* form. Its UPS displays sharp bands at 8.23 and 8.59 eV and a broader band, evidently due to two ionization events, at 9.03 eV. These bands appear to correspond closely to those of 1 though all bands of 3 are displaced by *ca.* 0.5 eV to higher IP:s. However, the arguments given above show that one cannot safely make the same assignment for the two compounds, *i.e.*  $n_+$ ,  $\pi_\ominus$ , and  $(\pi_\oplus + n_-)$  with increasing IP. If only the *N*-methylation shift had been operating, the increments given above should lead to the prediction 8.25 eV ( $n_+$ ), 9.00 eV ( $n_-$ ), 9.03 eV ( $\pi_\ominus$ ) and 9.50 eV ( $\pi_\oplus$ ). In the oxamide system, the calculated effect of changing the dihedral angle from  $60$  to  $180^\circ$  is to raise the  $\pi_\oplus$  level by 0.4 eV, to leave the  $\pi_\ominus$  level unchanged, and to lower the  $n_+$  level by 0.2 eV and the  $n_-$  level by 0.3 eV. If we add these effects to the *N*-methylation shifts we arrive at the assignment  $n_+$ ,  $\pi_\ominus$ ,  $(\pi_\oplus + n_-)$ , *i.e.* the same as for 1.

In monothiooxamides, the  $n$  and  $\pi$  levels have rather different energies in the two chromophores, and a much weaker interaction should be expected. In fact, the UPS of *N*<sup>o</sup>,*N*<sup>o</sup>-dimethylmonothiooxamide (4) and its *N*<sup>s</sup>,*N*<sup>s</sup> analogue (5) are surprisingly well reproduced by adding the UPS of thioformamide and *N,N*-dimethylformamide (for 4), and of *N,N*-dimethylthioformamide and formamide (for 5), respectively, (Fig. 2). The effects of coupling,



*i.e.* the deviations from the component spectra, are clearly smallest in 5, where the differences in energy are the largest. Also in the cyclic monothiooxamide 6 the ionizations at lowest energy are clearly split into one group of predominantly thioamide character (7.75 and 8.05 eV) and one of amide character (8.79 and 9.37 eV).

The ultraviolet absorption spectra cannot be profitably discussed on the basis of the energies of the ground state levels alone. However, Larson and McGlynn<sup>16</sup> have calculated the energies of the excited states of oxamide by the CNDO/S method with configuration interaction (CI) for several dihedral angles. A qualitative correspondence should be expected between the effects of the dihedral angle on the state energies for oxamides and dithiooxamides, and therefore we base our discussion upon these calculated state energies, part of which are shown in Scheme 2.

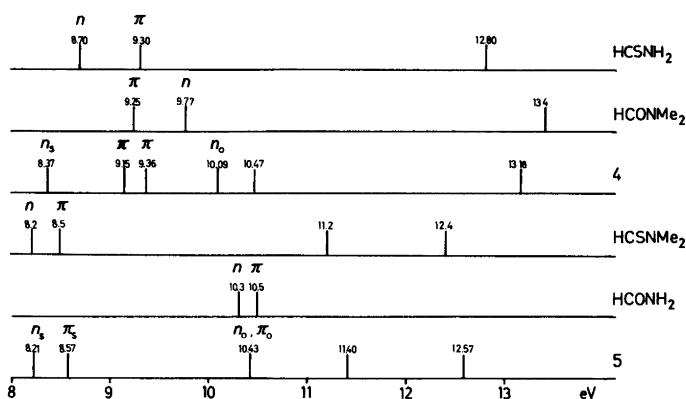
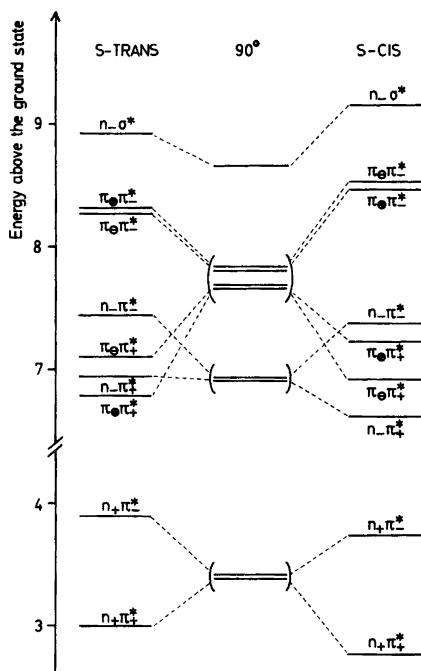


Fig. 2. Vertical ionization potentials and assignments for the monothiooxamides 4 and 5 and for the component amides and thioamides.



Scheme 2.

The CI calculation on  $90^\circ$  twisted oxamide gave two  $n\pi^*$  states, one corresponding to a transition at 179 nm with oscillator strength 0.01, and one at 364 nm with zero oscillator strength. The calculations also indicate a considerable splitting of the lowest  $\pi\pi^*$  state except for dihedral angles around  $90^\circ$ , where a splitting of only 0.2 eV ( $1600\text{ cm}^{-1}$ ) is calculated. The energies of the lowest  $\pi\pi^*$  states are calculated to be quite similar in acetamide and in a  $90^\circ$  twisted oxamide.

Even if the calculated transition energies seem rather unrealistic, the splitting pattern should be correct. We can therefore expect the following transitions on a nearly  $90^\circ$  twisted dithiooxamide like *1*: One quite weak and one somewhat stronger  $n \rightarrow \pi^*$  transition (to the  $n_+ \pi^*$  and  $n_- \pi^*$  states) and two close-lying  $\pi \rightarrow \pi^*$  transitions (to the  $\pi_0 \pi_0^*$  states, where  $\pi_0$  represents the highest bonding  $\pi$  orbital). The  $n \rightarrow \pi^*$  transitions should fall above and below 365 nm, and the  $\pi \rightarrow \pi^*$  transitions near 272 nm, these being the wavelengths of the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions in *N,N*-dimethylthioformamide<sup>3</sup> (data from non-polar solvents). We observe (Fig. 3 and Table 1) one band at *ca.* 365 nm ( $\epsilon = 530$ ), which, because of its relatively high intensity, is ascribed to the transition to the  $n_- \pi^*$  state. The transition to the  $n_+ \pi^*$  state, being of much less intensity, is probably hidden under the 365 nm band. We also find two strong bands at 276 nm and 260 nm ( $\epsilon = 17400$  and 14900 respectively). Besides, a shoulder can be discerned on the long-wavelength side of the band at 276 nm, corresponding to a band at *ca.* 295 nm with  $\epsilon$  *ca.* 6000 (the values in Table 2 are for the point of inflection on the curve). The separation between the two latter bands (0.29 eV) and their intensity relation are in reasonable agreement with those calculated for the two lowest  $\pi \rightarrow \pi^*$  transitions (separation 0.20 eV and oscillator strengths 0.05 and 0.37, respectively),<sup>16</sup> and this assignment is therefore proposed. The band at 262 nm may be due to an  $n \rightarrow \sigma^*$  transition in the thiocarbonyl groups. A band assigned to such a transition appears in the region 220–230 nm in spectra of simple thiocarbonyl compounds,<sup>22</sup> and the raising of one n level ( $n_+$ ) by the coupling should lead to a bathochromic shift of this transition. The calculations in Ref. 16 (Scheme 2) indicate that the

Table 1. Ultraviolet spectra of dithiooxamides.

Compound	Solvent <sup>a</sup>	$n \rightarrow \pi^*$		$\pi \rightarrow \pi^*$				$n \rightarrow \sigma^*$		
		$\lambda_{\max}/\text{nm}$	$\epsilon$	$\lambda_{\max}/\text{nm}$	$\epsilon$	$\lambda_{\max}/\text{nm}$	$\epsilon$	$\lambda_{\max}/\text{nm}$	$\epsilon$	
<i>1</i>	A	365	530	<i>ca.</i> 295 s <sup>b</sup>		<i>ca.</i> 9000	276	17400	260	14900
	B	345 s	500	<i>ca.</i> 295 s		<i>ca.</i> 9000	272	20500	260 s	17800
<i>2a</i>	A	392	860	306	8900	278	12700	240	10800	
	B	382	1090	306	11200	274	12400	238	11800	
<i>2c</i>	A	480 s	43	412	540	312	8400			
	B	470 s	75	400	880	316	11500			

<sup>a</sup> A = chloroform – cyclohexane 3:7 (v/v). B = chloroform – ethanol 3:7 (v/v). <sup>b</sup> Shoulder.

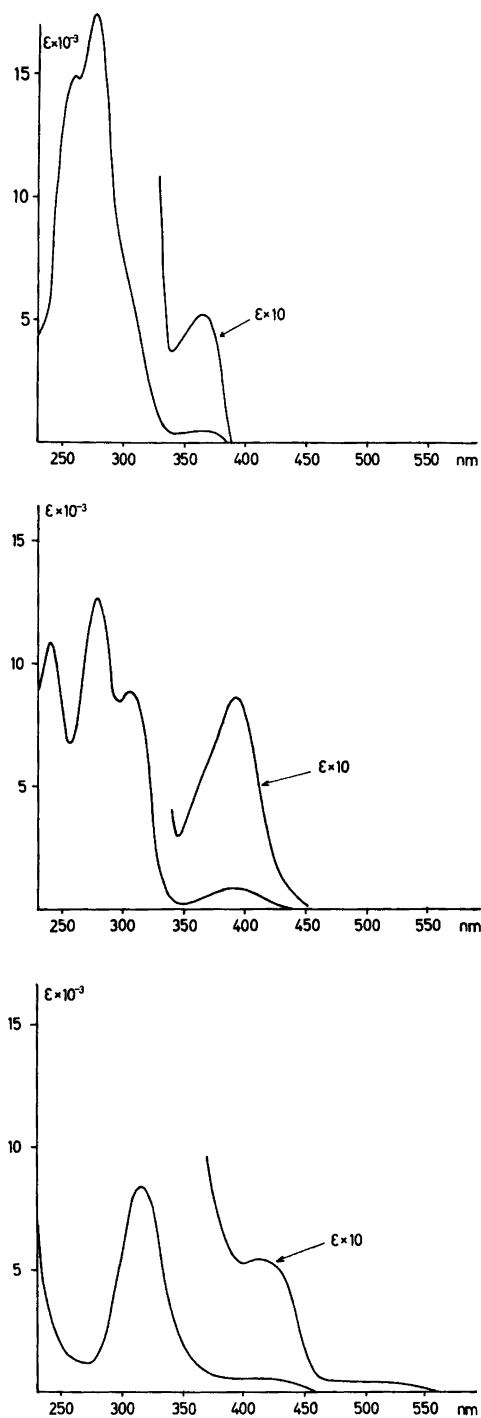


Fig. 3. UV absorption spectra in chloroform–cyclohexane (3:7 v/v) of (a) *1*, (b) *2a* and (c) *2c*.

lowest  $n\sigma^*$  state is considerably lower in the  $90^\circ$  twisted oxamide than in the *s-cis* and in particular in the *s-trans* form.

When the dihedral angle between the thioamide chromophores is reduced, as in *2a*, the splitting of the pairs of  $n\pi^*$  and  $\pi\pi^*$  states should be larger. Four distinct  $\pi \rightarrow \pi^*$  transitions should be possible, to the following states, from low to high energy:  $\pi_{\oplus}\pi^*$ ,  $\pi_{\ominus}\pi^*$ ,  $\pi_{\ominus}\pi^*$  and  $\pi_{\oplus}\pi^*$ . Similarly, transitions to the  $n_+\pi^*$ ,  $n_+\pi^*$ ,  $n_-\pi^*$  and  $n_-\pi^*$  states are possible (Scheme 2). The two  $\pi^*$  states form a close-lying pair, as do the  $\pi^*$  states.

The spectrum of *2a* displays a band at 392 nm ( $\epsilon=860$ ), most likely due to the lowest  $n_-\pi^*$  transition (or to both of them), *i.e.* corresponding to the 365 nm band in the spectrum of *1*. The two  $n_+\pi^*$  transitions, which should be considerably weaker, are probably hidden under the 392 nm band.

A band at 306 nm ( $\epsilon=8900$ ) can be ascribed to a transition to the  $\pi_{\oplus}\pi^*$  state, corresponding to the band at 295 nm in *1*. Two bands at 278 nm ( $\epsilon=12700$ ) and 240 nm ( $\epsilon=10800$ ) are tentatively assigned to one  $\pi \rightarrow \pi^*$  and one  $n \rightarrow \sigma^*$  transition, in this order. Both bands show a slightly negative solvatochromy (2.5 and 4 nm from cyclohexane to ethanol) of about the order of magnitude found for  $\pi \rightarrow \pi^*$  transitions in other thioamides,<sup>23,24</sup> whereas  $n \rightarrow \sigma^*$  transitions in simple thioamides generally are more strongly affected.<sup>24</sup>

Diminishing the dihedral angle should lead to a further lowering of the  $n_+\pi^*$ ,  $n_-\pi^*$  and  $\pi_{\oplus}\pi^*$  states. In good agreement with this, the spectrum of *2c* shows a weak band ( $\epsilon=43$ ) as a shoulder at 480 nm, a region where *2a* has no absorption. A somewhat stronger band, ascribed to the transition to the  $n_-\pi^*$  state, appears at 412 nm ( $\epsilon=540$ ), and a still stronger one ( $\epsilon=8400$ ) at 312 nm is ascribed to the transition to the  $\pi_{\oplus}\pi^*$  state. In agreement with this assignment, the two weaker bands show strong negative solvatochromy. No further bands appear above *ca.* 240 nm. The successive retreat of the  $n \rightarrow \sigma^*$  band to shorter wavelengths in the series *1*, *2a*, *2c* is entirely in agreement with the calculated dependence of the energy of the  $n_-\sigma^*$  state on the dihedral angle.<sup>16</sup>

Summing up, the effects on the UV spectra of changing the dihedral angle between the thioamide chromophores in dithiooxamides can be qualitatively explained by analogy with the corresponding effects in the oxamide system calculated by the CNDO/S-CI method.<sup>16</sup>

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