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Optical Activity of cis-Oxamide and -Dithiooxamide Chromophores

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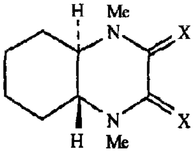
Abstract - The long-wavelength part of the CD spectrum of the dithiooxamide **2** exhibits four Cotton effects; three of them show the same signs as three lowest energy bands in the parent oxamide **1**, due to a similar nature of the corresponding electronic transitions.

Spectroscopic properties of oxamides and dithiooxamides have been recently the subject of many experimental[1-8] and theoretical studies.[2,7,8] The interaction of two amide or thioamide units causes splitting of the n, π and π* levels and leads to several absorption bands in an easily accesible region. The CD spectra can provide an additional information on electronic transitions, revealing hidden absorption bands due to positive and negative signs of the corresponding Cotton effects (CEs). The CD spectra of some N-substituted *trans*-dithiooxamides have been reported,[4,7] but there are no reports on less accessible *cis*-dithiooxamides and their parent oxamides.



1, X = O
2, X = S

In this study the electronic absorption and CD spectra of (R)-*trans*-1,4-dimethyl-2,3-dioxodecahydroquinoxaline (**1**) and its dithio analogue **2**, both molecules of C_2 symmetry, are presented. The bicyclic oxamide **1**[9a] was obtained by the condensation of (R)-*trans*-1,2-bis(methylamino)cyclohexane with diethyl oxalate following the procedure analogous to that reported by Isaksson et al.[10] Next, the oxamide **1** was converted into the deeply red dithiooxamide **2**[9b] with Lawesson's reagent.[11] The UV spectrum of **1** (Fig. 1) is similar to that reported for other oxamides[2] and shows two absorption bands: one intense at 226 nm and the second of moderate intensity appearing as a shoulder near 250 nm. Both can be assigned to the π-π* transitions according to Larson and McGlynn.[2] In the corresponding CD spectrum two CEs of the opposite signs are well defined in the range of the above transitions. CNDO/S-CI calculations for cis-oxamide predict the existence of four n-π* excited states but only one of them can be identified with difficulty as an inflection point on the UV curve;[2] the remaining are masked by much stronger π-π* bands. The CD spectrum of 1 allowes the detection of the n-π* excitation as a very weak negative CE at 308 nm.

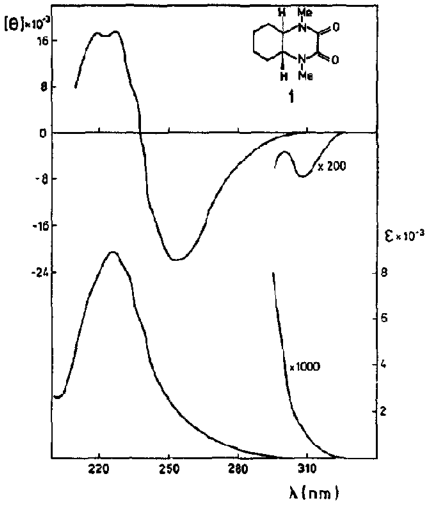


Fig. 1. UV (lower curve) and CD spectra of oxamide 1 in cyclohexane-dioxane (4:1).

The substitution of sulfur for oxygen carbonyls results in bathochromic shifts of the corresponding absorption and CD bands in the dithiooxamide 2. Moreover, they are much better resolved than the analogous transitions in the parent oxamide 1, i.e. the absorption spectrum of 2 (Fig. 2) exhibits two n-π* bands at 480 (ε 98) and 422 nm (ε 840) in cyclohexane-CH_2Cl_2, and they shift to shorter vavelengths (470 and 395 nm, respectively) in MeOH. A strong absorption at 315 (ε 11800) and a shoulder at 280 nm (ε 3700), positions of which are almost independent of solvent polarity, correspond to two π-π* transitions. The lowest energy absorption in 2 is very broad, what may indicate an additional contribution, possibly from the S-T (singlet-triplet) transition, to this band. This type of transition was observed by McGlynn and coworkers in the single crystal spectra of N,N'-Dimethyldithiooxamide.[3] A mutual correspondence between the CE signs of the second, third and fourth band in the CD spectrum of 2 and those of three lowest energy CD bands of 1 points to a similar origin of the corresponding transitions in both compounds. The long-wavelength CE of **2** appearing as a diffuse band at 503 nm can be assigned to the n-π* excitation, the counterpart of which in the spectrum of **1** is hidden under the strong π-π* band. The CD of **2** shows two additional intense CEs at 250 and 227 nm of less clear origin. They may be due to the n-σ* and/or higher energy π-π* transitions.

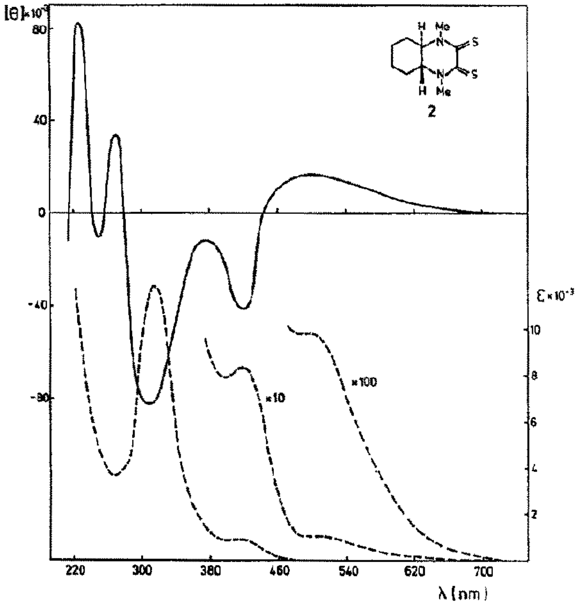


Fig. 2. UV-VIS (lower curve) and CD spectra of dithiooxamide **2** in cyclohexane-CH_2Cl_2 (3:2).

Optimization of molecular geometries by the MNDO method[12] showed that the piperazine-2,3-dione and piperazine-2,3-dithione moieties in **1** and **2**, respectively, assume a half-chair (twisted) conformation, whereas the *cis*-oxamide and -dithiooxamide units are twisted. The calculated X=C-C=X dihedral angles are of 44.8° and 49.5° for **1** and **2**, respectively; the last value is higher than that found in the crystal structure of unsubstituted piperazine-2,3-dithione (35.4°).[13] The rigid bicyclic skeleton of **1** and **2** implies the M-chirality of the chromophores, which determines the CE signs of these compounds. Based on Hug and Wagnière's rule[14] for chromophores of C_2 symmetry and the energy-level diagram for the excited states of dithiooxamides proposed by Sandström and coworkers,[6] the left-handed chirality of **2** should lead to the positive CE for the lowest energy transition n_+-π^*_+ (notation according to Larson and McGlynn[2]) and of A symmetry, the negative CE for the n_+-π^*_+ (B) and the sequence of the negative and positive CEs for the π_--π^*_+ (B) and π_+-π^*_+ (A) transitions, respectively. The observed CD spectrum of **2** shows the correspondingly-signed CD bands in the same order.

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9. (a) Oxamide **1**: m.p. 154°C; $[\alpha]^{22}_{578}$ -150.7 (*c* 2, $CHCl_3$); IR (CCl_4) ν 1680 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.33 (m, 2 H), 2.99 (s, 6 H, Me), 2.25 (m, 2H), 1.88 (m, 2 H), 1.4-1.3 (complex m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.92 (CO), 58.40, 28.56, 28.39, 23.43.
   (b) Dithiooxamide **2**: m.p. 241-243°C; $[\alpha]^{20}_{578}$ +640 (*c* 0.1, $CHCl_3$); IR (CCl_4) ν 1350, 1115 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55, (s, 6 H, Me), 3.43 (m, 2 H), 2.46 (m, 2 H), 1.95 (m, 2 H), 1.6-1.3 (complex m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.54 (CS), 61.07, 37.81, 28.94, 23.64.
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