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Original Scientific Paper

Electronic Structure and Spectra of Thiolo- and Dithiocarbamates. MO Treatment

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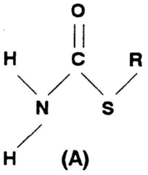
Electronic absorption spectra of some thiolo- and dithiocarbamates are reported. The observed spectra have been computer deconvoluted and accurate peak parameters have been determined. Assignment of the observed bands has been facilitated by MO computations. Comparison with the spectra of carbamates enabled prediction of the effect of replacing oxygen by sulphur on the electronic structure of carbamates.

INTRODUCTION

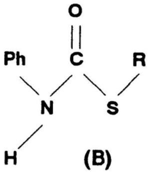
The UV spectra of sulphides have been investigated by several workers[1,2] and the topic has been reviewed.[3] However, conclusions have not been consistent.[4,5] Detailed analysis[6] of the low lying electronic transitions of the C–S–C chromophore indicated that the sulphur »4s« orbital is essential for the description of these excited states.

Analysis of the UV spectra of aliphatic dithiocarbamates[7] showed that these compounds possess three main bands in the near UV region at 350, 280 and 260 nm; their assignment was the subject of several publications.[8-12]

Thiolocarbamates and dithiocarbamates studied in the present paper are:



(A)



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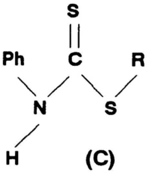

(C)

R phenyl-
p-tolyl-*p*-Cl-phenyl-

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EXPERIMENTAL

S-arylthiolocarbamates(A), *N*-phenyl-*S*-arylthiolocarbamates(B), and *N*-phenyl-*S*-aryldithiocarbamates(C) have been prepared as reported in the literature.[13-15]

All UV spectra were reported at room temperature on a Pye-Unicam SP-8800 spectrophotometer using 1.0 cm pathlength cells. Computer deconvolution of the spectra is based on both the least squares fitting procedure and differentiation.[16-18] The calculation method adopted in this work is the INDO/S-CI. The parametrization scheme used for the computation has been given previously.[19-23]

RESULTS AND DISCUSSION

(A) S-Arylthiolocarbamates

The electronic absorption spectrum of *S*-phenylthiolocarbamate in methanol is presented in Figure 1. The first absorption profile observed in the spectrum is much more intense and shows no structural features as compared to that observed in the

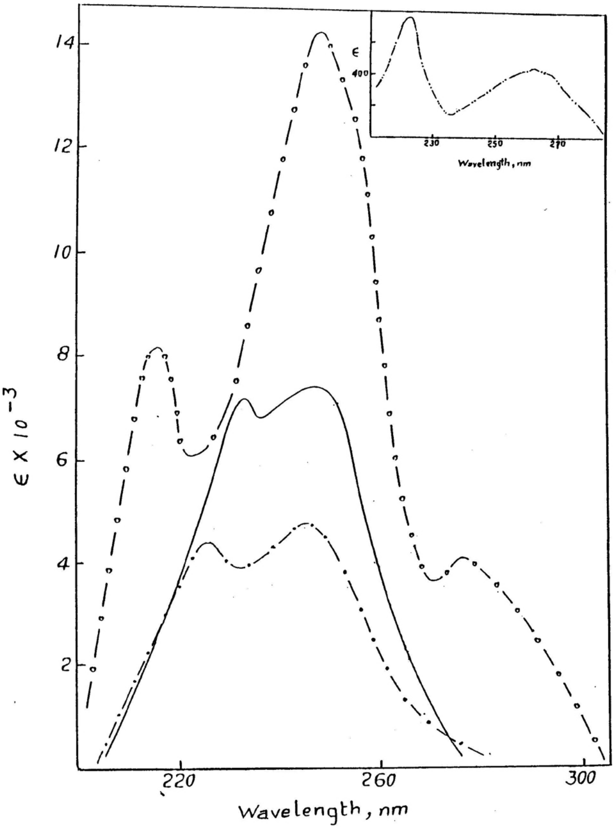

Figure 1. Electronic absorption spectra in methanol:
— • — *S*-phenylthiolocarbamate.; ——— *S*-*p*-tolylthiolocarbamate.;
— o — *S*-*p*-chlorophenylthiolocarbamate; — · · — *O*-phenylcarbamate.

spectrum of *O*-phenylcarbamate (Figure 1). Furthermore, the intensity ratio of the first to the second band profile has been reversed.

The observed spectrum of *S*-phenylthiolocarbamate has been computer deconvoluted; Figure 2. The fit to the profile is very good at the most difficult points, the peak and valley areas, yet the fit on the low energy edge is not as accurate. The general features of the low energy wing of the spectrum of *S*-phenyl derivative are very similar to those observed in the case of aromatic sulphides. MO computation of the spectrum predicted that no allowed $^1(\pi,\pi^*)$ state occurs in this region.

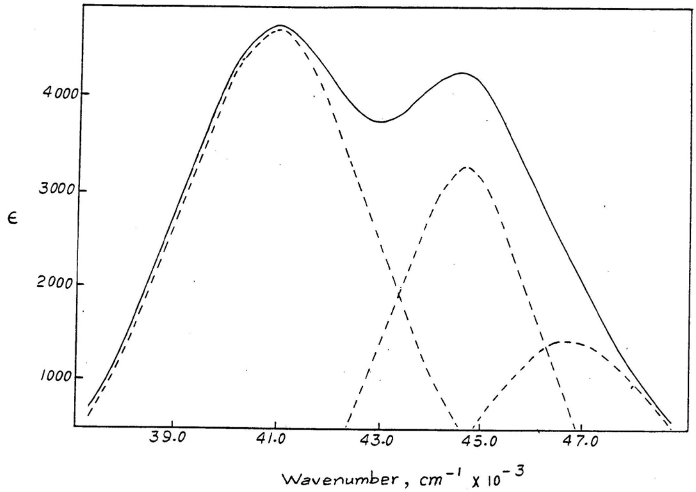

Figure 2. Computer deconvoluted spectrum of *S*-phenylthiolocarbamate. ——— overall fitted spectrum, - - - - component Gaussian bands.

The first deconvoluted band may be safely assigned as $^1(\pi,\pi^*)$ state II (Table I). Computation shows that this state seems to be localized on the Ar-S subsystem with very little contribution from a charge-transfer configuration (Ar→C). The second Gaussian resolved at 224 nm corresponds very well to the theoretically computed $^1(\pi,\pi^*)$ state III (Table I). Analysis of the configurations contributing to this state indicates a pronounced charge-transfer character. The same trend has also been observed for the third Gaussian band. However, there is a major difference in the assignment of the two states. Thus, state III is an intramolecular charge transfer involving the entire molecule, while state IV is nothing but a transition localized on the Ar-*S* moiety alone. This transition involves a considerable charge- transfer in the direction *S*→Ph; against the dipole moment vector.

The spectrum of *S*-*p*-tolylthiolocarbamate, Figure 1, is similar to that of the *S*-phenyl derivative. However, the spectrum of *S*-*p*-tolyl derivative shows a little red shift and a considerable increase in the intensity of the observed transitions as compared to that of *S*-phenyl derivative.

TABLE I

Theoretical and experimental transition energies and intensities of the observed bands in the spectra of the studied compounds

Compound		ΔE, eV		f	
		Obs.	Calc.	Obs.	Calc.
S-phenyl-thiolocarbamate	I	--	4.24	--	0.000
	II	5.05	4.90	0.090	0.019
	III	5.54	5.85	0.002	0.002
	IV	--	6.00	--	0.003
S-*p*-tolyl-thiolocarbamate	I	4.93	4.59	0.024	0.040
	II	5.34	5.50	0.008	0.149
	III	--	5.79	--	0.040
S-*p*-chlorophenyl-thiolocarbamate	I	4.43	4.24	0.053	0.090
	II	4.98	4.90	0.201	0.018
	III	6.11	6.02	0.004	0.002
N-phenyl-*S*-phenyl-thiolocarbamate	I	--	4.20	--	0.000
	II	4.71	4.86	0.311	0.576
	III	5.23	5.30	0.034	0.495
	IV	5.58	5.60	0.159	0.532
	V	5.90	5.97	0.063	0.058
N-phenyl-*S*-*p*-tolyl-thiolocarbamate	I	--	4.18	--	0.000
	II	4.80	4.85	1.282	1.057
	III	5.18	5.26	0.590	0.385
	IV	5.44	5.39	0.043	0.078
	V	5.77	5.82	0.080	0.001
N-phenyl-*S*-*p*-chlorophenyl-thiolocarbamate	I	--	4.00	--	0.000
	II	4.46	4.93	0.358	0.450
	III	5.08	5.04	0.450	0.093
	IV	5.71	5.44	0.053	0.522
	V	5.96	6.00	0.044	0.001
N-phenyl-*S*-phenyl-dithiocarbamate	I	4.44	4.31	0.033	0.000
	II	4.52	4.63	0.058	0.027
	III	5.01	4.82	0.119	0.440
	IV	5.61	5.64	0.339	0.023
N-phenyl-*S*-*p*-tolyl-dithiocarbamate	I	4.58	4.60	0.170	0.021
	II	4.96	4.80	0.058	0.503
	III	5.04	5.02	0.123	0.078
	IV	5.58	5.50	0.410	0.012
N-phenyl-*S*-*p*-chlorophenyl-dithiocarbamate	I	4.41	4.38	0.100	0.000
	II	4.59	4.67	0.007	0.540
	III	4.86	4.89	0.797	0.017
	IV	5.46	5.58	0.199	0.145

In addition, the spectrum of *S-p*-chlorophenylthiolocarbamate, Figure 1, shows a well defined band in the region 280–290 nm. This band has only been observed as an inflection in the *p*-methyl derivative. Aryl sulphides show a weak intensity, long wavelength absorption band (275–300 nm) whose intensity is very sensitive to the type of substituent in the phenyl ring and those attached to the sulphur atom.[6] Therefore, one can assume that the long wavelength absorption bands of the thiolocarbamates correspond to this sulphide absorption band and are assigned to the $^1(\pi,\pi^*)$ states. The intensities of these bands indicate that resonance interaction between the sulphur atom and the aryl moiety is maximum in the *S-p*-chlorophenyl derivative. The π-bond orders calculated for these three compounds indicate a predominant conjugative interaction between the sulphur atom and the carbonyl group (0.18) at the expense pf *S*-Ar (0.08) conjugation.

(B) *N-Phenyl-S-arylthiolocarbamates*

The electronic absorption spectrum of *N,S*-diphenylthiolocarbamate is presented in Figure 3. The sulphide absorption band in the 275–300 nm region is well resolved, in addition to the three main band systems. The theoretically computed spectrum reveals that:

(1) the long wavelength low intensity band in the 275–300 nm region may well correspond to $^1(n,\pi^*)$ state.

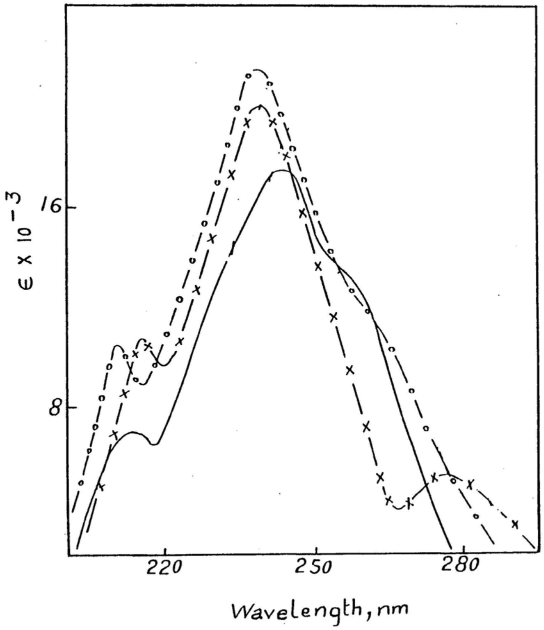

Figure 3. Electronic absorption spectra in methanol:
– o – *N*-phenyl-*S*-phenylthiolocarbamate. ——— *N*-phenyl-*S-p*-tolylthiolocarbamate.
– x – *N*-phenyl-*S-p*-chlorophenylthiolocarbamate.

(2) the first allowed $^1(\pi,\pi^*)$ state II corresponds very well to the second absorption band resolved at 258 nm. Analysis of the MO's involved in the configurations indicates that transition to this state would involve the entire molecule with a charge-transfer from both the *N*-ph and the *S*-ph moieties to the carbonyl group.

(3) the $^1(\pi,\pi^*)$ states III and IV are localized on the *N*-ph and *S*-ph subsystems, respectively, and show charge migration in the direction $X \rightarrow$ph ($X=N$ or S), that is opposite to the dipole moment vector.

The observed spectrum of *N*-phenyl-*S*-*p*-tolylthiolocarbamate (Figure 3) shows the same general features and trends observed for its parent compound, *N,S*-diphenylthiolocarbamate. On the other hand, *p*-chloro substitution has a marked effect on the general appearance of the spectrum with no dramatic effect on the assignment of the observed transitions (Figure 3). The fits to the observed profiles are excellent. The first $^1(\pi,\pi^*)$ state I (Table I) indicated that it involves pronounced charge transfer in the direction of the dipole moment vector. Assignments of all other observed transitions are essentially the same as that for the parent compound.

(C) N-Phenyl-S-aryldithiocarbamates

The electronic absorption spectra of *N,S*-diphenyl, *N*-phenyl-*S*-*p*-tolyl- and *N*-phenyl-*S*-*p*-chlorophenyldithiocarbamates are given in Figure 4. The spectra of the three compounds show striking similarities, indicating that substitution of the *S*-phenyl ring with electron-releasing or withdrawing substituents has no effect on the observed band positions. The intensity of the short wavelength band (≈220 nm) is most affected by *S*-phenyl substitution. The spectra of the studied dithiocarbamates are completely different from those of the corresponding carbamates. Replacement of oxygen by sulphur introduces major electronic changes that lead to increased delocalization and interaction between the different subsystems of the molecule.

The spectra of the dithiocarbamates show n-π^* transition in the 300–320 nm region, as predicted by the results of MO computations. The enhanced intensities of the observed $^1(n,\pi^*)$ transitions may be attributed to the combined effect of (i) the considerable overlap with the allowed $^1(\pi,\pi^*)$ states which permits a transfer of intensity to the weaker band and (ii) by analogy to thioamides,[24] anticipated large geometry changes between the $^1(n,\pi^*)$ state and the ground state would enhance the vibronic allowedness of the $^1(n,\pi^*)$ state. The second absorption band system observed in the spectra of the dithiocarbamates at 270–280 nm is also observed in the spectra of aliphatic dithiocarbamates. Thus, substitution of the *S*-phenyl ring has no effect on the position of this band.

In contrast to the behaviour of the second absorption band, the position of the third absorption band (240–255 nm) in the spectra of the compounds is sensitive to *S*-phenyl substitution. MO computation predict two allowed $^1(\pi,\pi^*)$ states in this region in the case of the *p*-tolyl derivative. The first is localized on the *N*-phenylcarbamate subsystem with a net CT in the direction of the dipole moment vector. The second state is localized on the *S*-phenylcarbamate subsystem and exhibits a small net CT opposite to the dipole moment vector. This state shows a much greater degree of delocalization in the case of the *S*-*p*-chlorophenyl derivative. The remaining absorption band observed in the 230–210 nm region may be assigned to the $^1(\pi,\pi^*)$ state IV (cf. Table I).

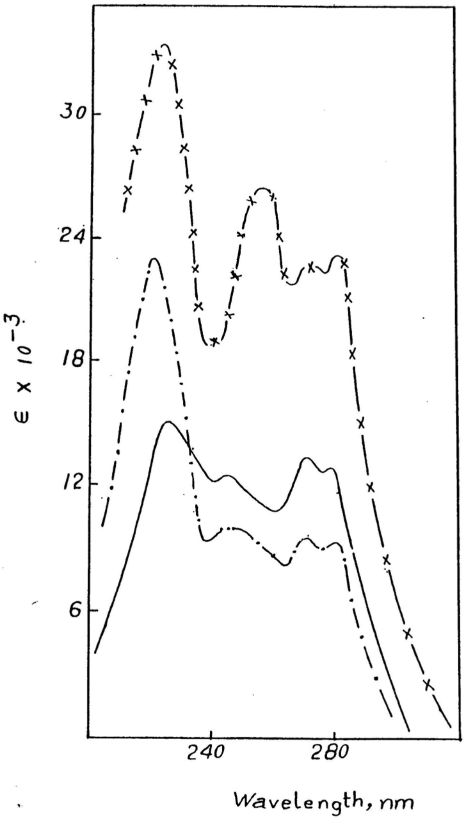

Figure 4. Electronic absorption spectra in methanol:
–• – *N*-phenyl-*S*-phenyldithiocarbamate. ——— *N*-phenyl-*S*-*p*-tolyldithiocarbamate.
– x – *N*-phenyl-*S*-*p*-chlorophenyldithiocarbamate.

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SAŽETAK

Elektronska struktura i spektri tiolo- i ditiokarbamata. MO- obrada

M. M. Hamed, A. G. El-Kourashy, H. Moustafa i R. Hilal

Opaženim spektrima tiolo- i ditiokarbamata kompjutorski su određeni maksimumi i točni oblici. Obilježavanje određenih vrpci izvršeno je uz pomoć MO-izračunavanja. Usporedbom sa spektrima karbamata predviđen je utjecaj zamjene atoma kisika s atomom sumpora na elektronsku strukturu karbamata.