Spectrochimica Acta, Vol. 35A, pp. 509 to 512
0584-8539/79/0501-0509$02.00/0

The electronic spectrum of the dimer of thiocarbonyl chloride

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(*Received* 12 *May* 1978)

Abstract—The electronic spectrum of the dimer of thiocarbonyl chloride has been measured and interpreted in terms of D_{2h} symmetry and with the aid of computer resolution and of CNDO molecular orbital calculations. Evidence is presented for sulphur–sulphur interactions.

INTRODUCTION

The dimer of thiocarbonyl chloride has the structure [1–5] shown in Fig. 1.

Evidence for this comes from the study of the i.r. and Raman spectra of the molecule [3–6] and from crystallographic work [6]. This study of the electronic spectrum of the molecule extends the work of Barrett and Hitch [7] who discussed the spectra of molecules containing two sulphur atoms which are not formally bonded to each other.

EXPERIMENTAL

Materials. Thiocarbonyl Chloride was obtained from the Aldrich Chemical Co. Inc., hexane from B.D.H. Ltd., and diethyl ether and ethanol from May and Baker Ltd.

The hexane was of spectroscopic grade and was used without any further purification and the other solvents were dried and distilled before use. Thiocarbonyl chloride was distilled before use and its purity was confirmed by G.L.C.

Preparation of the thiocarbonyl chloride dimer. Thiocarbonyl chloride dimer was prepared by irradiating the monomer in a fused silica flask with the full radiation from a medium pressure mercury vapour discharge lamp. After a period of irradiation the dimer was obtained as a cream coloured solid which crystallised out from the remaining monomer. The dimer was purified by vacuum sublimation using a cold finger to collect the sublimed product. White needle shaped crystals were obtained which had a melting point of 114°C.

Spectra. A Cary Model 16 Spectrophotometer, flushed out with dry nitrogen, was used to measure the spectra. The cells were of spectrosil grade fused silica of 1 mm optical path length.

RESULTS

Spectra

The recorded spectra were subjected to computer resolution into the smallest number of bands whose mathematical form was given by the equation

$$\varepsilon_\nu = \varepsilon_{\nu_{\max}} \exp\left[-c|\nu - \nu_{\max}|^n\right]$$

where ε_ν represents the molar absorption coefficient at any frequency, ν, $\varepsilon_{\nu_{\max}}$ being its maximum value and c and n being constants characteristic of any one band.

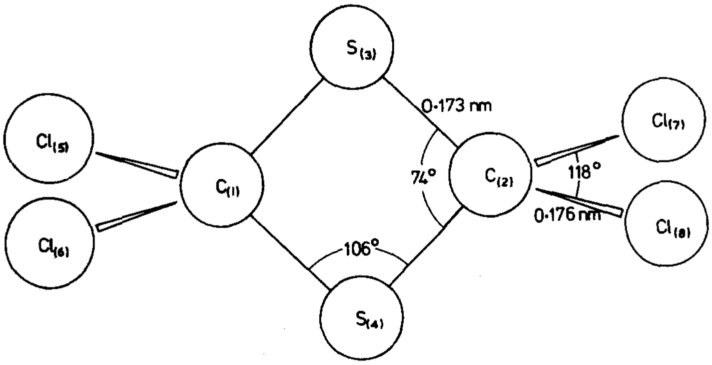


Fig. 1. The CNDO optimised structure and geometry of $C_2S_2Cl_4$.

The computer program [8], used for the resolution process, optimised the values of $\varepsilon_{\nu_{\max}}$, c, $\nu_{\max}$ and n for each band found, the $\nu_{\max}$ being expressed eventually as $\lambda_{\max}$, the wavelength of maximum absorption. The observed spectrum of the thiocarbonyl chloride dimer in ethanol solution and the computer-resolved bands are shown in Fig. 2.

The values of $\varepsilon_{\nu_{\max}}$, c, $\lambda_{\max}$ and n are listed in Table 1. In hexane solution the computer resolution produced two bands with peaks at 235 and 221 nm with ε values of 1000 and 1380 M^{-1} cm^{-1} respectively. In ether solution the corresponding bands appeared at 234 and 218 nm with ε values of 2800 and 3320 M^{-1} cm^{-1} respectively.

Molecular orbital calculations

A CNDO program [9] was used to calculate the molecular orbitals of the thiocarbonyl chloride dimer. For the purposes of the calculation the carbon atoms

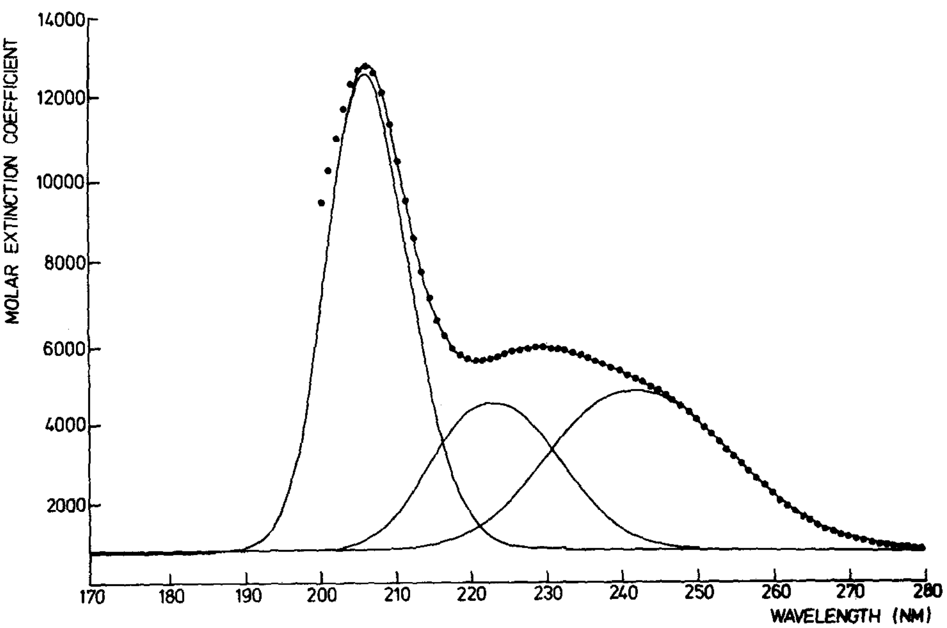


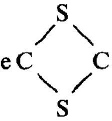
Fig. 2. The observed (dotted line) and computer-resolved (full line) spectrum of $C_2S_2Cl_4$ in ethanol solution.

Table 1. Characteristics of the observed and resolved spectra of thiocarbonyl chloride dimer in ethanol solution

Observed Spectrum		Resolved Spectrum			
λ_{max}(nm)	$\varepsilon(M^{-1}cm^{-1})$	λ_{max}(nm)	$\varepsilon(M^{-1}cm^{-1})$	c	n
246sh	4640	242	4750	14.94	2.15
230	5840	223	4440	25.76	2.24
207	12860	207	12630	27.65	1.93

were placed along the z axis and the sulphur atoms along the y axis as in Fig. 1. Optimisations of the CSC and SCS bond angles and the C—S bond length were carried out with respect to the minimisation of the total energy of the molecule. The optimum values for the CSC and SCS angles were 106° and 74° respectively and the optimum C—S bond length was found to be 0.173 nm.

The molecular orbital calculations show that there are four orbitals which are most probably concerned with the transitions in the observable region of the spectrum of the dimer. The group atomic orbitals which are used in the construction of the molecular orbitals are defined in Table 2 and their contributions to the molecular orbitals are shown in Table 3.

The $3p_x$ orbitals of the sulphur atoms interact in a π manner and such interaction is expressed in orbitals b_{3u} (sulphur—sulphur bonding) and b_{1g} (sulphur—sulphur antibonding), these being the highest energy filled levels. The molecular orbital calculations show that the most probable lowest energy vacant orbital has a_g symmetry (σ^*) and is C—S, C—Cl antibonding and C—C, S—S bonding. The third highest energy filled orbital is of b_{2u} symmetry and is bonding with respect to the  ring and is C—Cl antibonding.

DISCUSSION

The i.r. and Raman spectroscopy of the thiocarbonyl chloride dimer show that it has a centre of symmetry and that the molecule most probably belongs to the D_{2h} point group [4, 6].

The long-wavelength transitions of the monomer are $^1n_S \rightarrow {}^3\pi^*$, $^1\pi \rightarrow {}^1\pi^*$ and $^1n_S \rightarrow {}^1\pi^*$ [10] which indicate that the long-wavelength transitions of the dimer should originate in orbitals mainly localised on the sulphur atoms. The CNDO calculations are consistent with such a conclusion and show that there are three transitions which may occur in the accessible u.v. region. These are $b_{3u} \rightarrow a_g$ $(A_g \rightarrow B_{3u})$, $b_{1g} \rightarrow a_g$ $(A_g \rightarrow B_{1g})$ and $b_{2u} \rightarrow a_g$ $(A_g \rightarrow B_{2u})$ in order of increasing energy.

The $b_{3u} \rightarrow a_g$ transition is allowed by D_{2h} symmetry and would, therefore, be expected to be intense. The $b_{1g} \rightarrow a_g$ transition is forbidden by D_{2h} symmetry but involvement of the sulphur d orbitals can cause the

Table 2. Group atomic orbitals of the thiocarbonyl chloride dimer

Group Atomic Orbital	Contributions from Atomic Orbitals (coefficients omitted)	Symmetry (D_{2h})
G_1	$C_1(s) + C_2(s)$	a_g
G_2	$C_1(p_x) + C_2(p_x)$	b_{3u}
G_3	$C_1(p_y) + C_2(p_y)$	b_{2u}
G_4	$S_3(s) - S_4(s)$	b_{2u}
G_5	$S_3(p_x) + S_4(p_x)$	b_{3u}
G_6	$S_3(p_x) - S_4(p_x)$	b_{1g}
G_7	$S_3(p_y) - S_4(p_y)$	a_g
G_8	$S_3(p_y) + S_4(p_y)$	b_{2u}
G_9	$Cl_5(p_x) - Cl_6(p_x) + Cl_7(p_x) - Cl_8(p_x)$	a_g
G_{10}	$Cl_5(p_x) + Cl_6(p_x) + Cl_7(p_x) + Cl_8(p_x)$	b_{3u}
G_{11}	$Cl_5(p_y) + Cl_6(p_y) + Cl_7(p_y) + Cl_8(p_y)$	b_{2u}
G_{12}	$Cl_5(p_y) - Cl_6(p_y) + Cl_7(p_y) - Cl_8(p_y)$	b_{1g}
G_{13}	$Cl_5(p_z) + Cl_6(p_z) - Cl_7(p_z) - Cl_8(p_z)$	a_g
G_{14}	$Cl_5(p_z) - Cl_6(p_z) - Cl_7(p_z) + Cl_8(p_z)$	b_{3u}
G_{15}	$S_3(d_{z^2}) - S_4(d_{z^2})$	b_{2u}
G_{16}	$S_3(d_{xy}) + S_4(d_{xy})$	b_{1g}
G_{17}	$S_3(d_{z^2}) + S_4(d_{z^2})$	a_g

Subcripts on atomic symbols refer to atomic positions as shown in Fig 1.

Table 3. Major group atomic orbital contributions to the molecular orbitals of the thiocarbonyl chloride dimer

Group Atomic Orbital	Molecular Orbital				
	Symmetry	b_{2u}	b_{1g}	b_{3u}	a_g
	Energy (Hartrees)	-0.4593	-0.4587	-0.4400	-0.0193
G_1					0.3233
G_2				0.2046	
G_3		0.3819			
G_4		-0.1324			
G_5				-0.5387	
G_6			0.6673		
G_7					0.2058
G_8		-0.2478			
G_9					0.2701
G_{10}				-0.2198	
G_{11}		-0.3008			
G_{12}			-0.1302		
G_{13}					-0.1733
G_{14}				0.1804	
G_{15}		0.2505			
G_{16}			0.1288		
G_{17}					0.3107

transition to be locally allowed [10] and, in consequence, more intense than is normal for a symmetry forbidden transition.

The previous two transitions could be those observed in hexane solution (dielectric constant = 1.89) at 221 and 235 nm, which in ether solution (dielectric constant = 4.3) remain virtually unaltered at 218 and 234 nm while in ethanol solution (dielectric constant = 24.3) they appear at 223 and 242 nm with the appearance of a larger absorption band at 207 nm. It would seem that for transitions of an $n \rightarrow \sigma^*$ type the solvents are not exerting their usual influence. The third band observed in ethanol solution at 207 nm may be the $b_{2u} \rightarrow a_g$ transition which is orbitally allowed. A possible explanation of the spectra in hexane and ethanol solutions is the solvent stabilisation of the excited states in addition to the stabilisation of the non-bonding electron pairs in the ground state. This is shown diagrammatically in Fig 3.

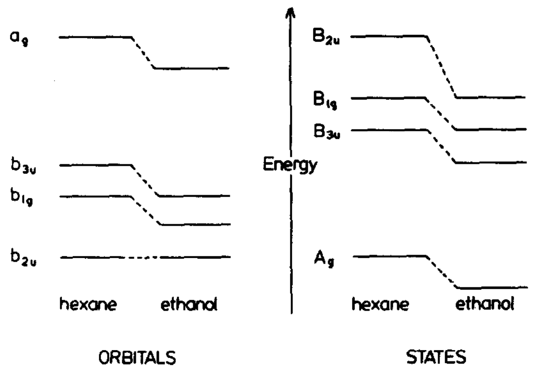


Fig. 3. The relative energies of the orbitals and electronic states of $C_2S_2Cl_4$ in hexane and ethanol solutions.

The b_{3u} and b_{1g} orbitals have large contributions from the sulphur $3p_x$ orbitals and since these orbitals may interact with a polar solvent it would be expected that their energies would be lowered by such a solvent. The b_{2u} orbital is unaffected by solvation and therefore the $b_{2u} \rightarrow a_g$ transition moves to lower energy as solvent polarity increases because as a result of the stabilisation of the excited state. In the case of the $b_{1g} \rightarrow a_g$ and $b_{3u} \rightarrow a_g$ transitions the stabilisation of the excited states is offset by a very similar stabilisation of the non-bonding electrons of the sulphur atoms from which the b_{1g} and b_{3u} orbitals are mainly composed.

The molecular orbital calculations indicate that the b_{3u} orbital is higher in energy than the b_{1g} orbital. This conclusion appears to fit in with the assignment of the long-wavelength absorption as being $b_{3u} \rightarrow a_g$, the reason for the ordering of energies of the two orbitals being suggested by the calculations. The interaction between group orbitals G_6 and G_{12} in the b_{1g} molecular orbital is S—Cl bonding, whereas the interaction between group orbitals G_2 and G_5 in the b_{3u} molecular orbital is C—S antibonding. These two major interactions provide the reason for the b_{3u} (S—S bonding) orbital being higher in energy than the b_{1g} (S—S antibonding) orbital.

Acknowledgements—We thank HELEN LEGGE for computing assistance, RICHARD LIPSCOMBE for technical assistance and S.R.C. for financial assistance.

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