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Theoretical Calculation of the Rotational Barrier, Valence Force Constants and Experimental Electronic Spectrum of Chlorocarbonylsulphenyl Chloride (ClC(O)SCl)

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The rotational barrier around the C—S bond in chlorocarbonylsulphenyl chloride (ClC(O)SCl) is investigated using the INDO, PCILO and GAUSSIAN-70 techniques. The results confirm the existence of planar *cis* and *trans* conformers with a higher stability of the latter, as suggested by previous vibrational results. The origin of the rotational barrier is due to an increase of electronic delocalization as demonstrated by INDO and PCILO calculations.

The optimized geometrical parameters obtained by means of the *ab-initio* method with an STO-3G basis set are reported for the different conformers.

Valence force constants have been calculated and the values obtained compare fairly well with the results from a previous normal coordinate calculation.

The experimental electronic spectrum, maximum molar absorptivities, oscillator strengths and a tentative assignment of its electronic bands, are reported.

INTRODUCTION

The IR and Raman spectra of gaseous and liquid chlorocarbonylsulphenyl chloride (ClC(O)SCl)¹, as well as its electron diffraction study² suggest the existence of a stable *trans* planar conformer as the most stable one. Previous experimental and theoretical studies performed on its homolog FC(O)SCl³ show that it exists as a conformational mixture, as indicated by the existence of two CO stretching bands with a temperature dependence of their relative intensities.

In order to explain the different behaviour and properties of the compounds, a theoretical treatment was performed by means of semiempirical and *ab-initio* quantum chemistry techniques. The barrier to rotation about the C—S bond was calculated using INDO, PCILO and *ab-initio* methods.⁴⁻⁶ Valence force constants were estimated from the INDO data by a simple method derived from a point charge model for the chemical bond.⁷ The

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present results are compared with numerical values obtained previously by a normal coordinate analysis.¹

The experimental electronic spectrum of ClC(O)SCl is reported and the bands tentatively assigned.

EXPERIMENTAL

The sample of ClC(O)SCl was prepared as published.¹ Electronic spectra were run with a Shimadzu UV-300 Spectrophotometer. Gas phase spectra were measured in a 10 cm quartz gas cell.

COMPUTATIONAL PROCEDURE

Molecular wave functions of the different conformers were calculated using the INDO method employing the original parametrization given by Pople *et al.*⁴. The PCILO method was also used⁵, as well as the GAUSSIAN-70 package with an STO-3G basis set.⁶

The planar *trans* conformation (regarding the halogen atoms) was suggested to be the most stable one by analogy with FC(O)SCl³ as well as by the observed band envelopes in the IR spectrum in the gas phase, the polarization of some bands in the Raman spectrum in the liquid phase¹ and by electron diffraction measurements.²

The molecular parameters were taken from³ (in Å or angular degrees) C=O: 1.183; C—Cl: 1.749; C—S: 1.791; S—Cl: 2.01; SCO: 126.9; SCCl: 106.0; CSCl: 100.6. The geometries conformations of the three principal conformers are depicted in Figure 1. The geometric parameters of the conformers were optimized by minimizing the total energy with respect to the geometry variables defining the structure. This was done by interpolation between energies calculated for a number of specific geometries around the minimum (local) energy. With the optimized structural parameters, density and overlap matrices, total and bond energies for the three conformers were determined.

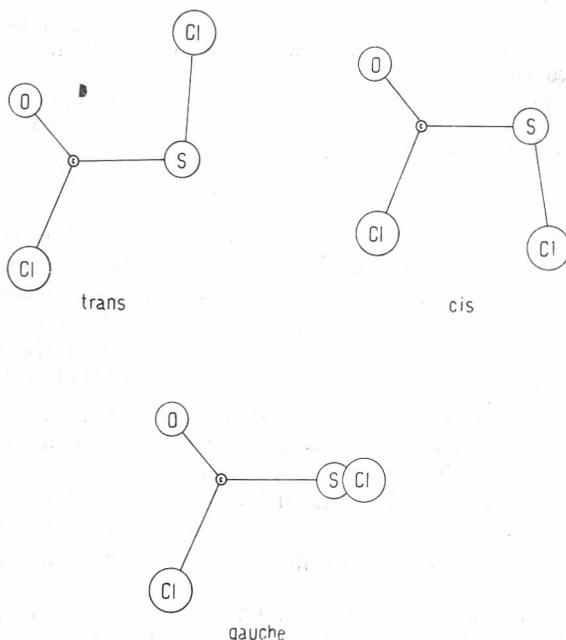


Figure 1. Geometries of the conformers of chlorocarbonylsulphenyl chloride.

RESULTS AND DISCUSSION

The conformational energies involved in the rotation of the S—Cl group around the C—S bond were calculated for different values of the azimuthal angle Θ formed by the C—S bond and the ClC(O)S(xz) plane. The results obtained by the INDO method confirm that for $\text{CSCl} = 104^\circ$ the cis and the trans conformers have the lowest energy and that the trans configuration is 145.9 kJ/mol more stable than the cis one, while the height of the rotational barrier is 10.9 kJ/mol. The PCILO and GAUSSIAN-70 methods predict that the trans conformer is 1.9 and 13.4 kJ/mol more stable than the cis one and that the corresponding heights of the rotational barrier are 36.4 and 35.2 kJ/mol, respectively. The experimental² and the optimized geometrical parameters obtained by means of the ab-initio technique are summarized in Table I for the different conformers.

TABLE I

*Experimental and Optimized Bond Angles and Bond Lengths for the Different Conformers of ClC(O)SCL, Obtained by Means of the Ab-initio Technique (GAUSSIAN-70 with STO-3G Basis Sets**

	Experimental [#]	TRANS	GAUCHE	CIS
C—Cl	1.749	1.83	1.83	1.82
C—S	1.791	1.80	1.83	1.81
S—Cl	2.01	2.08	2.09	2.07
C=O	1.183	1.21	1.21	1.20
ClCS	106.0	109.4	114.9	115.3
CSCl	100.6	100.4	97.6	104.5
OCS	126.9	128.5	125.3	122.8

* In Å or angular degrees for bond lengths or angles, respectively.

[#] From ref. 2.

We studied the orbital symmetries of the frontier orbitals and their associated eigenvalues for ClC(O)SCL in order to correlate the results obtained from different methods. It was found that they may be correlated without any inversion of the order of their eigenvalues. The HOMO is localized on the S—Cl bond and it has σ symmetry. The results indicate, at least qualitatively, that the existence of the trans conformer is favoured over the cis and gauche configuration. The INDO calculation shows from the molecular orbital analysis that the lone pairs of the sulphur and chlorine atoms are more localized in the gauche form than in the planar configuration. Thus, it can be postulated that the origin of the barrier is in the decrease of the delocalization for the gauche conformer. Consequently, the major relative stability of the planar conformers should be explained by their highest delocalization. Also, the changes in charge density caused by a trans-gauche rotation show that in the gauche form the carbonyl oxygen and carbon atoms lose negative and positive charges, respectively, while the C—S bond index in the planar configuration is higher than in the gauche configuration, showing an increase of delocalization.

If we divide the total energy variation obtained by means of the PCILO method in to its components: the zeroth order energy (ΔE^0) and the corresponding corrections of the second and third order ($\Delta(E^2 + E^3)$), the term

of higher weight could be determined and the rotational barrier origin derived. ΔE^0 and $\Delta(E^2 + E^3)$ could be considered as measures of the energy variation due to the repulsion between non-bonded atoms and the electronic delocalization, respectively. Figure 2 depicts the results of this analysis for the trans conformer. As can be seen, the second and third order energy corrections are the major contributors to the total energy and the origin of the rotational barrier is in the variation of the electronic delocalization.

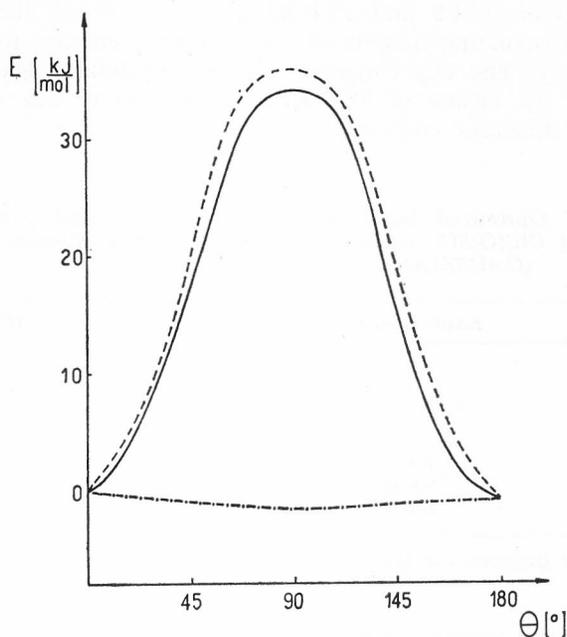


Figure 2. Decomposition of the variation of the total energy obtained by the PCILO method for trans ClC(O)SCl: ΔE^T (—) total energy variation, ΔE^0 (---): zeroth order energy, $\Delta(E^2 + E^3)$ (-·-·-): the second and third order corrections to the energy.

The valence force constants were estimated from the expression:⁷

$$f_{AB} = \left(\frac{Z_A - 2}{Z_A} \right) \left(\frac{2Z_A - Q_A}{R^3} \right) (8B_{AB} - q_B)$$

where Z_A : charge of atom A as used in the INDO approximation, q_B : net charge on atom B, Q_A : gross charge on atom A, R: bond distance, B_{AB} : bond index calculated from the Wiberg bond index.⁸ For single bonds $B_{AB} = W_{AB}$, for double bonds $B_{AB} = W_{AB}^\sigma + 2^{-1/2} W_{AB}^\pi$ and for the triple bonds $B_{AB} = W_{AB}^\sigma + (2/3) 2^{1/2} W_{AB}^\pi$. The factor $(Z_A - 2)/Z_A$, the so called atomic dipole contribution, occurs only when atom A possesses lone pairs, as in P, N, halogens, etc. Our results are listed in Table II together with those obtained previously with a normal coordinate analysis.¹ The comparison of internal force constants shows that the values obtained are reasonable. As an additional

TABLE II
*INDO and Stepwise Coupling Force Constants for ClC(O)SCl**

	$f_{C=O}$	f_{C-S}	f_{Cl-S}	f_{Cl-C}	Reference
INDO	13.60	3.10	2.90	2.52	this work
Becher-Mattes	12.60	3.18	3.21	3.17	[1]

* Units are mdyn \AA^{-1} .

check of the computational results, the S—Cl force constant for the SCl_2 molecule was also obtained using the same procedure. The value compared fairly well with the result obtained by means of normal coordinate analysis [3.32 mdyn \AA^{-1} against 2.77 mdyn \AA^{-1}].⁹

TABLE III
Experimental Electronic Spectrum of Chlorocarbonylsulphenyl Chloride: Transition Energies, Maximum Molar Absorptivities (ϵ) Oscillator Strengths (f) and Tentative Assignments

Transition energy (nm)	$\epsilon_{293^\circ\text{C}}$	f_{exp}	assignment
220	4300	0.151	$\pi^* \leftarrow \pi$
300	120	0.00362	$\pi^* \leftarrow n$

The experimental electronic spectrum of ClC(O)SCl is reported in Figure 3 and its bands at 220 and 300 nm are assigned to the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transition, respectively. Tentatively, we can correlate the $\pi^* \leftarrow n$ transition

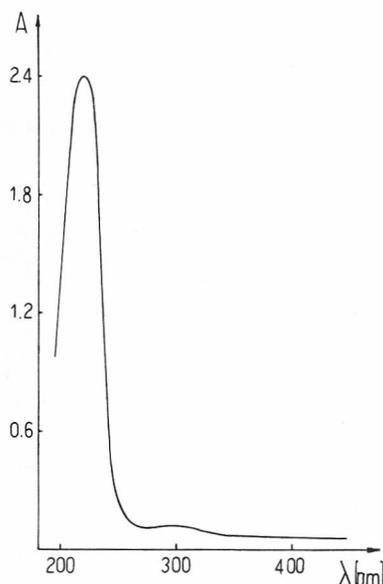


Figure 3. Electronic spectrum of chlorocarbonylsulphenyl chloride. Optical path 10 cm. Pressure 30 torr.

with the excitation of a single electron from the HOMO, localized on the sulphur lone pair, to the LUMO + 1 localized on the C=O bond.

In Table III the maximum molar absorptivities and the oscillator strengths of the electronic bands of ClC(O)SCl are reported, as well as tentative assignments.

CONCLUSIONS

It has been found that *trans* ClC(O)SCl is 1.9 or 13.4 kJ/mol more stable than the *cis* conformer and the height of the rotational barrier is 36.4 or 35.2 kJ/mol, as calculated by the PCILO and ab-initio methods, respectively. The INDO method also predicts that the *trans* conformer is the most stable, although its results are far apart from those obtained by the other two methods.

The origin of the rotational barrier is due to electronic delocalization, as demonstrated by INDO and PCILO calculations.

The ab-initio technique yielded a geometry which agreed with experimental results² and can be considered as reliable since as we go from the *cis* to *trans* conformer the CScI and ClCS angles decrease as expected due to the repulsion between the lone pairs of both Cl atoms.

The values found for the semiempirical valence force constants compare favourably with the results from a previous normal coordinate calculation.

The bands found in the electronic spectrum of ClC(O)SCl are possibly due to $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions.

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SAŽETAK

Teorijski račun rotacijske barijere i valentnih konstanti sila te eksperimentalni elektronski spektar klorokarbonilsulfanil klorida (CIC(O)SCI)

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Barijera za rotaciju oko veze C—S u klorokarbonilsulfanil-kloridu (CIC(O)SCI) istraživana je s pomoću INDO, PCILO i GAUSSIAN-70 računara. Rezultati potvrđuju postojanje planarnih *cis*- i *trans*-konformera te veću stabilnost *trans*-konformera, u skladu s prijašnjim rezultatima vibracijske analize. INDO i PCILO računi pokazuju da rotacijska barijera nastaje uslijed pojačane delokalizacije elektrona.

Optimizirani geometrijski parametri na temelju računa *ab initio* s baznim skupom STO-3G navedeni su za različite konformere.

Izračunane valentne konstante sila slične su rezultatima prijašnje analize normalnih koordinata.

Također su prikazani eksperimentalni elektronski spektar, maksimalne molarne apsorbancije, oscilatorske jakosti, kao i tentativna asignacija elektronskih vrpca.

Uz maksimalne molarne apsorbancije i oscilatorske jakosti, prikazan je i eksperimentalni elektronski spektar te tentativna asignacija elektronskih vrpca.