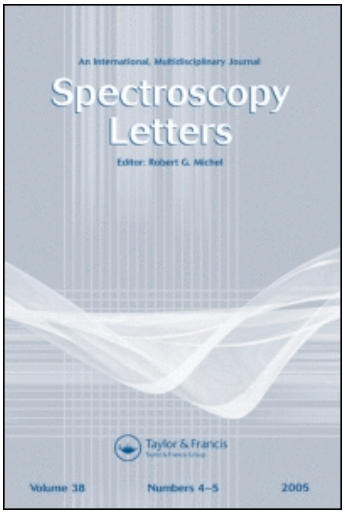

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S-O Valence Force Constants of Sulfoxides by Quantum chemical Methods

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S-O VALENCE FORCE CONSTANTS OF SULFOXIDES BY QUANTUM CHEMICAL METHODS

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Key words: force constants, sulfoxide compounds, MNDO, PM3 and CNDO calculations.

ABSTRACT. S-O stretching force constants in a series of symmetrical sulfoxide compounds were calculated from quantum chemical methods. Molecular geometries were obtained from experimental data and from MNDO and PM3 calculations. S-O bond potential energy curves were constructed around the zero-point energy and the MNDO force constants calculated in the armonic approximation were compared to force constants calculated in a point-charge bond model in the CNDO approximation. The present force constants range between 5 and 12 mdyn/Å.

INTRODUCTION

During the last time we have been developing a program of research in the Sulfur chemistry (1-3). We have mainly been interested in to analyse the role of the sulfur d orbitals in the nature of the valence bond force constants, because these multiple bonded S-O systems offer the possibility of additional bonding effects by means of the d(π)sulfur - p(π)oxygen overlap.

On the other hand, it is well known that the normal coordinate treatments (NCT) show a broad dispersion range of force constants and the power of NCT calculations is usually limited by the accuracy of the assignement of the spectral bands, as well as, the quality of the solutions of the self-consistent potential field of the NCT (4). Therefore, these chemical quantum methods (QCM)

qualify as useful tools in the estimation of force constants and the assignment of spectral bands.

In this work, a study of S-O valence bond force constants for a series of symmetric sulfoxide compounds of C_s symmetry was carried out from an electronic structural point of view. Two theoretical approachs were considered:

a. S-O force constants calculations from MNDO potential curves, by means of a complete MNDO molecular geometry optimization.

b. S-O valence force constants by the method developed by Kosmus in the framework of the CNDO molecular orbital scheme.

QUANTUM CHEMICAL METHODS

Kosmus' Method

In a previous works we have discussed the point-charge model of the bond developed by Kosmus (5), where the electronic contributions to the force constants can be estimated. The valence force constant f(SO) of a S-O bond according to Kosmus'work (6) is given by equation/1/:

$$f(SO) = [Z(O)-2][2Z(O)-Q(O)][\ 8B(SO)-q(S)]/Z(O)\ R^3 \qquad /1/$$

where Z(O) is the charge on O used in the CNDO calculation, Q(O) is the gross charge on O, q(S) is the net charge on the sulfur atom, R is the S-O bonding length and B(SO) is the bond index calculated from the Wiberg bond index (W). B(SO) for single bond is equal to W(SO), whereas for double and triple bonds Kosmus introduce the sigma (σ) and (π) contributions according to:

$$B(SO) = W\sigma(SO) + (1/2)\sqrt{2}\ W\pi \qquad /2/$$

and

$$B(SO) = W\sigma(SO) + (2/3)\sqrt{2}\ W\pi \qquad /3/$$

respectively.

Computational Methods

An Apollo 10000 computer, using precise option, was used for MNDO and PM3 calculations (7). The geometrical parameters such as bond lengths and bond angles were optimized in the MNDO and PM3 approachs, and compared to experimental data reported for these sulfoxide compounds.

The MNDO S-O potential curves were obtained under total geometry relaxation and they were fitted by means of a polynomial function in the range of mean amplitude of vibration on the fundamental level. f(SO) force constants in this MNDO framework were obtained in the armonic approximation.

TABLE I

MNDO and PM3 Molecular geometries of X_2SO symmetric sulfoxide compounds

X	Method	R(SO),A	R(S-X),A	< O-S-X	< X-S-X
O^{2-}	MNDO	1.563		109.6	
	PM3	1.640			
	exp. (4)	1.530			
Cl	MNDO	1.468	2.037	106.6	104.3
	PM3	1.478	2.080	101.7	97.6
	exp. (4)	1.45	2.07	107.5	97.4
$(CH_2)_3$	MNDO	1.509	1.802	109.5	78.7
	PM3	1.543	1.852	107.0	77.0
	exp.(10)	1.475	1.836	113.4	75.7
CH_3	MNDO	1.520	1.779	106.1	103.5
	PM3	1.557	1.818	104.5	99.3
	exp. (4)	1.477	1.76-1.81	106.7	96.4
CF_3	MNDO	1.480	1.926	104.7	106.1
	PM3	1.483	1.996	104.2	92.2
	exp.(11)	1.469	1.885	104.5	94.2
$(CH_2O)_2$	MNDO	1.483	1.650	103.8	92.9
	PM3	1.476	1.716	102.9	90.9
F	MNDO	1.480	1.607	102.8	97.2
	PM3	1.467	1.574	101.0	93.9
	exp. (4)	1.413	1.59	106.8	92.8

A CNDO/3R computational program (8) for IBM 4381 computer was employed in the Kosmus valence force constant determinations. This program allows to explicitly include the d-orbitals for sulfur atom.

RESULTS AND DISCUSSION

In Table I we show the molecular geometry optimization obtained for these symmetric sulfoxide compounds. In general we found a good agreement between MNDO and PM3 theoretical approachs, and both calculations are concordant with experimental data. In a recent paper, Buemi (9) has found similar results for PM3 calculations in thiophene derivatives. Particularly we have observed that the halogen substituents on the sulfur atom induce a shortening of the S-O bond length, while the SO_3^{2-} system presents the longer S-O bond.

TABLE II

S-O stretching force constants (mdyn/Å) for X_2SO symmetric sulfoxide compounds and S-O stretching wave number (WN, cm-1)

X	f_{MNDO}	f_I(PM3)	f_I(exp)	f_{SO}	WN(cm-1)
O^{2-} (a)	7.53	4.60	5.66	5.68	950 (4)
Cl (b)	11.56	8.59	9.30	7.74	1229 (4)
$(CH_2)_3$ (c)	9.79	7.27	8.32	8.94	1192(13)
CH_3 (d)	9.08	6.76	7.84	9.37	1109 (4)
CF_3 (e)	11.08	8.38	8.62	9.51	1242(11)
$(CH_2O)_2$(f)	11.07	8.63	- -	9.71	1220(14)
F (g)	11.11	8.96	10.02	10.78	1308 (4)

The S-O stretching force constants determined by means of the MNDO potential curves (f_{MNDO}) and by the Kosmus' model for PM3 (f_I(PM3)) and experimental geometries (f_I(exp)) are depicted in Table II. All these data are dependent of the substituent nature and they are in the range of 4.5 to 11.6 mdyn/Å.

The S-O stretching force constants calculated from the PM3 potential curves are systematically smaller than the MNDO results, and these values are found between 3.5 and 4.5 mdyn/Å. Other molecular systems present the same abnormal low values for the PM3 method (12).

In the same Table II, we present the S-O stretching force constants calculated in the pseudo-diatomic bond model (f(SO)). These f(SO) constants were determined through the experimental wavenumber data corresponding to the S-O stretching mode.

The first thing that call our attention is the good linear correlation observed for the S-O stretching wavenumber versus the calculated force constants root square ($f^{\frac{1}{2}}$) for two different quantum chemical methods. Figure 1 presents these correlations, where we have included two sets of geometries in the Kosmus'model: the PM3 theoretical values and the experimental data. This homogeneous linear trend permit us to define a substituent effect on the S-O bond nature, where the halogen substituent are predominant. On the other hand, the

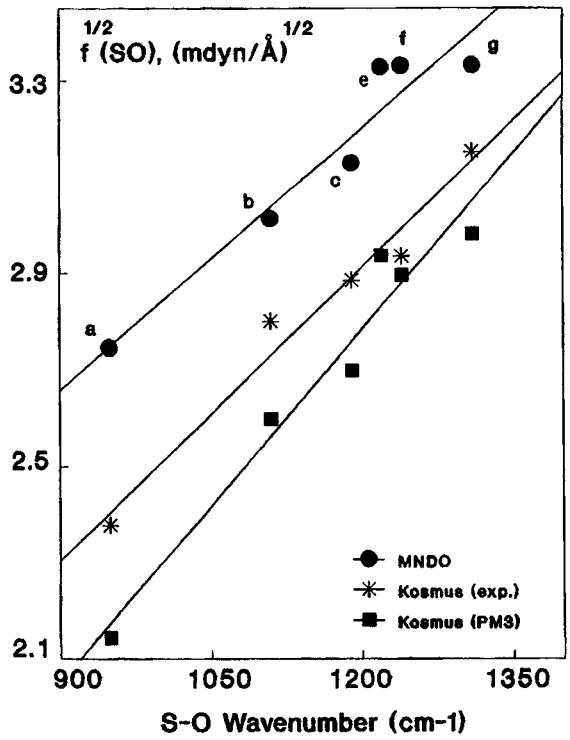

FIGURE 1.

S-O Stretching wavenumber versus theoretical force constants root square of symmetric sulfoxide compounds (see Table II).

force constant values in these two theoretical approachs range in 4 mdyn/Å between the minimum and maximum data, being slightly highest the MNDO results.

Assuming a diatomic model for the S-O bond system, we have calculated these force constants using the S-O stretching wavenumber data. In Figure 2 we present a correlation between the MNDO and Kosmus force constants and those obtained from the pseudodiatomic model. Again we can observe a good linear behavior, which well compares with the Kosmus' approach, but, this diatomic simplified model does not take into account the sulfur-substituent interactions which must exist mainly to the π-molecular orbital level. By following, an average effect on the S-O bond we are measuring by this model. However, the electronic interactions

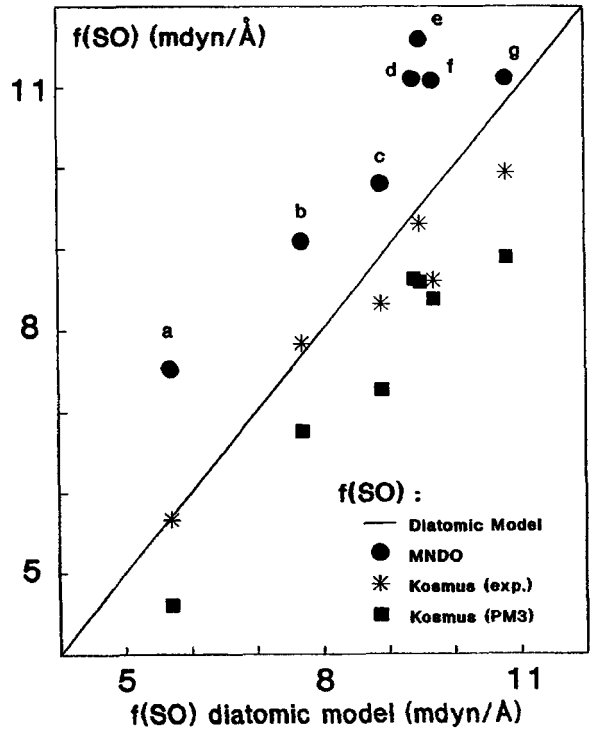

FIGURE 2.

MNDO and Kosmus force constants versus diatomic force constants of symmetric sulfoxide compounds (see Table II).

TABLE III

Density matrix elements and Wiberg bond index of the S-O bond for symmetric sulfoxide compounds

X	p_x-p_y	d_{xy}-p_y	p_z-p_z	d_{yz}-p_z	Wσ	Wπ
O^{2-}	0.224	0.537	0.287	0.480	0.984	0.677
Cl	0.334	0.673	0.429	0.658	0.985	1.210
$(CH_2)_3$	0.256	0.653	0.368	0.651	1.023	1.075
CH_3	0.288	0.644	0.322	0.631	1.020	1.008
CF_3	0.284	0.684	0.369	0.675	1.018	1.163
$(CH_2O)_2$	0.355	0.663	0.494	0.623	1.003	1.221
F	0.407	0.655	0.504	0.613	1.004	1.276

present in the S-O bond can be attainable from the CNDO molecular orbital calculations in the Kosmus' approach, such as we appreciate in the Table III, where the subtituent effect on the S-O bond (y-axis) is evidenced by means of the changes on the d(sulfur)-p(oxygen) coefficients of the density matrix, as well as, in the Wiberg bond index. Since, from this Table III we can observe that the electronic density around the S-O bond follows a cylindrical symmetry, we have preferred to calculate the Kosmus' force constants according to equation /3/.

Some scarce f(SO) values determined from NCT show a broad dispersion range. For example, Urey-Bradley-Simanouti force fields has been used in the force constants study of SOF_2 and $SOCl_2$ systems (15). These reported data have shown a good agreement with those obtained in the present work (11.2 and 9.78, respectively). However the authors conclude that the UBS field is not satisfactory enough for these compounds (15), because the force constants are dependent of substituent potential field matrix elements. In spite of our interest is not neccesarily the absolute determination of these force constant values, in general we have observed a good agreement between these QCM and other NCT studies for other compounds (1,16,17). Therefore we want particularly to call attention to the adventages of using these semiempirical QCM because permit to analyse the long distance effect of the substituents on the valence force constants, without introduce scaling factor.

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REFERENCES

1. R.G.E. Morales, F. Parrini and C. Hernández, **Sulfur Letters**, 12, 113 (1991).
2. J.S. Gómez-Jeria, R.G.E. Morales and L.M. Reyes, **The Astrophys.J.**, 302, 488 (1986).
3. R.G.E. Morales and V. Vargas, "Proc. First National Symposium of Spectroscopy and Molecular Structure", September 26 and 27, pages 10,11,13 (1991).
4. R.J. Gillespie and E.A. Robinson, **Canadian J. Chem.**, 41, 2074 (1963.
5. V. Vargas and R.G.E. Morales, **Spectrosc.Int.J.**, 7, 295 (1989).
6. W. Kosmus, **Z.Naturforsch.**, 33a, 1056 (1978).
7. J.J.P. Stewart, **J.Comp.Chem.**,10, 221 (1989).
8. J.A. Pople and D.L. Beveridge, "Approximate Molecular Orbital Theory", McGraw Hill, N.Y. (1970).
9. G. Buemi, **Gazzetta Chim.Italiana**, 121, 1 (1991).
10. J.W. Bevan, A.C. Legon and D.J Millen, **Proc.R.Soc.Lond.**, A354, 491 (1977).
11. H.A. Carter, C.S. Wang and J.M. Shreeve, **Spectrochim.Acta**, 29A, 1479 (1973).
12. V. Vargas and R.G.E. Morales, **Acta Sud Am.Quím.**, (in press).
13. M. Tamres and S. Searles, **J.Am.Chem.Soc.**, 81, 2100 (1958).

14. D.E. Rogers and G. Nickless, "Organic Sulphur Chemistry", Elsevier Pub.Co., p. 170 (1968).
15. D.A. Long and R.T Bailey, **Trans.Faraday Soc.**, **59**, 792 (1963).
16. V. Vargas, E. Clavijo and R.G.E. Morales, **Z.Naturforsch.**, **40a**, 927 (1985).
17. R.G.E. Morales, F. Parrini and C. Hernández, **Acta Sud Am.Quím.**, 8, 45 (1988).

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