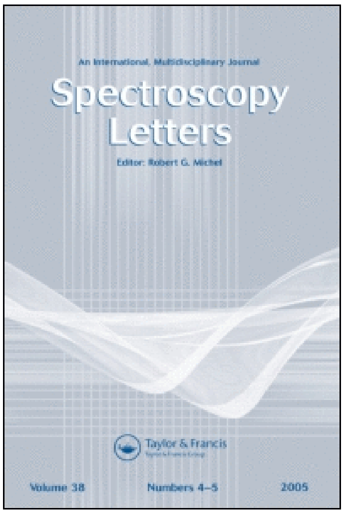

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Molecular Vibrational Constants and Chemical Bonding in Five-Membered Heteratomic Compounds

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To cite this Article Campos-vallette, M. M. and Clavijo, R. E.(1985) 'Molecular Vibrational Constants and Chemical Bonding in Five-Membered Heteratomic Compounds', Spectroscopy Letters, 18: 10, 759 — 766
To link to this Article: DOI: 10.1080/00387018508062308
URL: http://dx.doi.org/10.1080/00387018508062308

SPECTROSCOPY LETTERS, 18(10), 759-766 (1985)

MOLECULAR VIBRATIONAL CONSTANTS AND CHEMICAL BONDING IN FIVE-MEMBERED HETERATOMIC COMPOUNDS

Keywords : Molecular vibrations, Force constants, Mean Amplitudes, Chemical bond, Reactivity, Furan, Thiophene, Selenophene and Tellurophene.

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ABSTRACT

By means of the force field and mean amplitudes of vibration of furan, thiophene, selenophene and tellurophene molecules, we have concluded that the ground-state aromaticity order in the series is thiophene > tellurophene > selenophene > furan. The reactivity of these molecules to the electrophilic substitution follows the order furan > selenophene $\sim$ tellurophene > thiophene.

INTRODUCTION

One of the most simple criteria for the detection of a chemical bond is the observation of a vibrational frequency. Chemical bonds with a large force constant value, characterized by a relatively high vibrational frequency and a small amplitude of vibration,

0038-7010/85/1810-0759$3.50/0

can be regarded as rigid, chemical bonds. If the chemical bonds are associated with the lowest force constant values, corresponding to the largest mean amplitudes, they will have the greatest reactivity[1]. The pure covalent bonds are highly directional, or rigid, in comparison to polar or ionic bonds which become more flexible with increasing ionicity.

In this letter we discuss, for the first time, the characteristics of the chemical bonds in furan, thiophene, selenophene and tellurophene in terms of their fundamental frequencies, force constants and mean amplitudes of vibration.

FORCE CONSTANTS AND MEAN AMPLITUDES OF VIBRATION

The fundamental frequencies of furan, thiophene, selenophene and tellurophene and their totally deuteroderivatives were selected from vibrational spectra previously reported[2-5]. In order to carry out a normal coordinate analysis we have used the iterative consistency method[6]. The reliability of the force constant results given by this method has been tested in series of simple polyatomic molecules[7]. The diagonal values of the F° matrix for furan, which are necessary to initiate the iterative calculations, were obtained from the equation $F^{\circ}_{ii} = \Lambda_i/G_{ii}$ where $\Lambda_i = (\omega_i/1303.16)^2$, ω_i is the i^{th} experimental frequency and G the Wilson matrix. The geometrical parameters for the four molecules here considered were taken from the literature[8,9]. The final F matrix for furan, obtained after 15 iterative steps[10], was transferred to thiophene[11] and to selenophene and tellurophene[12] to start the calculation of their force field. The modifications of F° for these molecules appear principally in the coordinate which involves the S, Se and Te atoms. The final F matrices were obtained after 15 iterative steps. Force constants of the stretching modes and the calculated frequencies are shown in Table 1. The theoretical assignment was carried out by using the normal vibration modes form matrix (L) and the Potential Energy Distribution (P.E.D.).

The proposed assignment for furan and thiophene was discussed previously[10,11]. The force fields for selenophene and tellurophene[12] explain quite well their spectra and the assignment is in good concordance with reported data[5].

The force fields developed were used to calculate the mean amplitudes of vibration for different types of bonded and nonbonded interatomic distances of the molecules here considered. These values were obtained according to well-established methods[13,14]. The results for the principal interactions are displayed in Table 2 along the interatomic distances.

The calculated mean amplitudes of vibration agree well with available experimental and other theoretical data[14-16]. The present computation confirms the characteristic values for the C-C and C-H mean amplitudes as Cyvin et al.[17] pointed out.

The complete theoretical assignment of the calculated frequencies and the mean amplitudes at 298°K for furan, thiophene, selenophene and tellurophene and their totally and partially deuteroderivatives are available upon request to our Laboratory.

VIBRATING CHEMICAL BOND AND CHEMICAL REACTIVITY

The drastic drop in frequency of the symmetric and antisymmetric C-X stretching, Table 1, can be understood on the basis of the

TABLE 1.

Force Constants f (mdyn.Å^{-1}) and Calculated Frequencies (cm^{-1}).

	Furan		Thiophene		Selenophene		Tellurophene	
f(C-X)[a]	6.53		5.46		4.71		3.47	
f(C=C)	8.30		7.62		7.98		7.83	
f(C-C)	5.95		5.97		6.07		5.68	
$f(C-H)_\alpha$	5.36		5.23		5.13		5.06	
$f(C-H)_\beta$	5.29		5.24		5.13		5.07	
ν(C-X)	1043[b]	999[c]	879	838	820	759	797	688
ν(C=C)	1557	1493	1516	1406	1515	1423	1514	1434
ν(C-C)	1388		1365		1343		1318	
$\nu(C-H)_\alpha$	3173	3162	3127	3135	3110	3059	3087	3030
$\nu(C-H)_\beta$	3146	3130	3094	3083	3063	3105	3044	3083

[a] X = O,S,Se,Te

[b] Symmetry type A_1

[c] Symmetry type B_1

geometric and mass effects which influence these modes in the same sense. The vibrational coupling of the C-X stretching with the skeletal deformation modes is low and practically the same in the series. Therefore, the trend obtained in the force constants, f, and mean amplitudes, ℓ, is the expected one. From the f and ℓ values in Table 1 and 2 we could infer that the C-O bond will be highly directional and more rigid than the C-Te bond. The values f = 6.53 mdyn.Å^{-1} and ℓ = 0.0432 Å for the C-O bond in furan will

TABLE 2.

Mean Amplitudes of Vibration ℓ(Å) at 298°K and Some Interatomic Distances r_e(Å)

	Furan	Thiophene	Selenophene	Tellurophene
$\ell(C-X)^a$	0.0432	0.0457	0.0462	0.0478
$\ell(C=C)$	0.0489	0.0451	0.0442	0.0426
$\ell(C-C)$	0.0479	0.0470	0.0465	0.0462
$\ell(C-H)_\alpha$	0.0761	0.0765	0.0765	0.0765
$\ell(C-H)_\beta$	0.0761	0.0765	0.0765	0.0765
$r_e(C-X)$	1.362	1.714	1.863	2.055
$r_e(C=C)$	1.361	1.370	1.370	1.375
$r_e(C-C)$	1.431	1.423	1.423	1.423
$r_e(C-H)_\alpha$	1.075	1.078	1.078	1.078
$r_e(C-H)_\beta$	1.077	1.081	1.081	1.081

[a] X = O,S,Se,Te.

be consistent with a bond of character intermediate between C-C and C=C only if the C-C bonds are treated as pseudodiatomic : a single C-C bond with f $\simeq$ 4.5 mdyn.Å^{-1} and $\ell \simeq$ 0.050 Å and a double C=C bond with f close to 11 mdyn.Å^{-1} and $\ell \simeq$ 0.013 Å. Thus, the adquired covalency degree of the C-X bond will decrease in the series when passing from O to Te.

The force contant of the symmetric stretching of the double bonds increases in the order thiophene, tellurophene, selenophene and furan (Table 1). The increase in frequency of the corresponding mode may be caused by the change in the same order, towards a situation of lower aromaticity, following a greater localization of the double bonds. Thus, thiophen will be more aromatic than furan and both less aromatic than benzene in which f(C-C) $\simeq$ 7 mdyn.$\mathring{A}^{-1}$. This result agrees well with experimental reported data[18].

The vibrational characteristics of the C-C bonds in the series are less sensitive to the heteroatom substitution as in shown in Table 1 and 2. The stretching C-C, highly coupled to the ring modes, undergo slightly lowering in frequency.

It is well known that furan, thiophene, selenophene and tellurophene tend to react by substitution rather than addition. If the electrophilic substitution preferentially takes place through a loose vibration (low force constant value) we could predict, directly from the mean amplitudes of vibration, the order of reactivity of these molecules. Unfortunatly there is no appreciable differences between the calculated force constants and mean amplitudes of vibration for the C-H bonds in the series. Tables 1 and 2. Therefore, no information about the sequence of relative reactivities towards electrophilic substitution can be reached. However, the P.E.D. shows a vibrational coupling between the C-H stretching in α and β positions ($\nu(C\text{-}H)_\alpha$ and $\nu(C\text{-}H)_\beta$) for each molecule: while in furan $\nu(C\text{-}H)_\alpha$ and $\nu(C\text{-}H)_\beta$ for both the A_1 and B_1 modes are pure, in thiophene is practically impossible to distinguish them. The increase in vibrational coupling degree between $\nu(C\text{-}H)_\alpha$ and $\nu(C\text{-}H)_\beta$ follows the order: furan $<$ selenophene $\sim$ tellurophene $<$ thiophene. This result coincides with the observed order of ground-state aromaticities, which is, at the same time, the reverse of the observed reactivity order in the electrophilic substitution[19,20]. Thus, we expect the C-H bonds in furan to be selective to the electrophilic substitution, as is found to be the case[21].

In tellurophene the C-H bonds in α and β positions will be equally reactive to the electrophilic substitution[22].

ACKNOWLEDGEMENTS

We are grateful for the financial support from the Departamento de Investigación y Bibliotecas of the University of Chile.

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Received: 05/14/85
Accepted: 06/20/85