Semiempirical Calculations of Valence Force Constants in C_2X_4, C_3X_4 and C_4X_4 Compounds

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Valence force constants were calculated for C_2X_4, C_3X_4 and C_4X_4 ($X = H$, F, Cl, Br) with a point charge model using CNDO data. The magnitude of the valence force constants is discussed in terms of the polarization of the static electron distribution.

Introduction

Within the π-systems of organic compounds the cumulens $X_2-(C=C)_n-X_2$ are interesting concerning the nature of the $C-C$ bond and the influence of the substituents X to the π-system. As a model for the chemical bond we have taken the valence force constants for a measure of the "strenght" of a bond. This relation is very reasonable for a comparison of bond strenght within a certain type of bond or group of compounds. But this model has also some disadvantages. The force constants are not constants of motion, they are strongly dependent on the force field used for calculation. But nevertheless, the valence force constants representing the stiffness of a bond are widely used to discuss bond properties in a very useful picture.

As recently shown [1] valence force constants can be estimated from CNDO data by a simple method derived from a point charge model for the chemical bond. The valence force constant f_{AB} of a bond $A-B$ is given by

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

Z_A: charge of atom A as used in the CNDO approximanie, Q_A: gross charge on atom A, q_B net charge of atom B, R: bond distance, B_{AB}: bond index, calculated from the Wiberg bond index W_{AB} [2] for single bonds $B_{AB} = W_{AB}$, for double bonds $B_{AB} = W_{AB} + 1/2\sqrt{2}\,W_{AB}$, for triple bonds $B_{AB} = W_{AB} + 2/3\sqrt{2}\,W_{AB}$.

The factor $(Z_A - 2)/Z_A$, the so called atomic dipol force contribution occures only when atom A possesses lone pairs such as N, P, halogens, etc. For hydrogen $Z_H = 2$ must be used. This formula allows to discuss contributions of electrons in bonds and electrons on atoms to the force constants. If the trends of the vibrational forces and the ones estimated by this formula are the same, we can conclude that the CNDO data is proper to describe the structure of these compounds.

Whereas a lot of data is known for the simplest system ethene only little work has been done for C_3X_4 and C_4X_4. For this reason the vibrational force constants for these latter compounds were calculated by one of us [3]. A general problem is the comparison of the experimental force constants and the ones derived by quantum chemical methods. The values from spectroscopic measurements are based on the motion of atoms, if they are not end atoms, the masses of neighbouring atoms play an important role on the description of the motion of non terminal bonds. In our case the mass of the substituent X increases drastically from hydrogen to bromine. Regarding the $C-C$ vibration of the hydrocarbons, the hydrogen atoms are mostly moved along with the end of chain carbon atom due to the little inertia effect. The heavier the outer atoms the more static becomes their behavior on a displacement of the carbon atom.

Two extreme points of view have to be taken into account: Firstly, the $-CX_2$ group as a rigid system.

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This assumption is justified for substituents with small masses and becomes worse for heavier atoms.

Secondly, the four substituents are fixed. This assumption plays a more important role for the description of motions of compounds with heavier substituents. Within the spring model of the force constant, four fixed peripheral atoms hinder the motion of central ones. This influence depends also on the magnitude of the C – X stretching force constant, the real behaviour lies always between these two extremes. Thus the force field described by the symmetric coordinates is somehow insufficient.

Beside the problem of the description of motion of atoms there is the difficulty of correct assignment of the vibrational frequencies and accuracy of measurement. Various methods of calculation as well as the use of additional spectroscopic data, for example isotopic shifts, coriolis coupling show variable effects on the values of socalled experimental force constants. This ambiguity is drastically shown by ethene in Table 1, the mostly calculated molecule within these series.

Table 1. CNDO and experimental valence force constants (mdyn/A).

Compound	f_{C-C}		f_{C-X}		Lit.
	this work	experimental	this work	experimental	
C_2H_4	10.06	9.57	5.30	5.08	[6]
		11.341		5.58	[7]
		9.519		5.528	[8]
		9.395		5.60	[9]
		10.634		5.25	[10]
		9.305		5.17	[11]
		8.91		5.56	[12]
C_2F_4	10.27	10.256	7.02	6.57	[7]
C_2Cl_4	10.12	9.591	3.16	3.23	[7]
C_2Br_4	10.02	8.156	2.48	2.49	[7]
C_3H_4	10.14	9.75	5.40	5.09	[3]
C_3F_4	11.68	10.28	6.58	6.31	[3]
C_3Cl_4	11.15	9.33	3.08	3.39	[3]
C_3Br_4	10.92		2.41		
C_4H_4	9.90	9.11	5.27	5.01	[3]
	11.17	11.25			
C_4F_4	10.40	9.58	6.72	6.26	[3]
	11.37	11.63			
C_4Cl_4	10.31	8.62	3.09	3.47	[3]
	10.95	9.34			
C_4Br_4	10.21		2.38		
	10.91				

Details of Computation

For all computations the standard CNDO method of Pople [4] was used. For the halogens Cl and Br we omitted the d-functions. Thus more reasonable results for the valence state – 1 are obtained. For all calculations experimental geometries were used, if they were not available we assumed standard bond length and angles.

The symmetry force constants given by literature were transformed to inner force constants by the usual *U*-matrix method.

Results and Discussion

Tables 2 and 3 show the bond indices and atomic net charges obtained by CNDO calculations. Table 1 compares the calculated force constants with the spectroscopic ones given by literature.

As discussed before the comparison of the absolute values must be made with some precaution. But nevertheless the overall results are quite encouraging. The range of the calculated constants is congruent with the experimental values. It can be seen obviously that the trends within the series of compounds to be studied are the same in the calculated as well as in the experimental force constants. Thus our CNDO calculation can give some insight into the electron distributions and σ and π polarities of bonds. Due to the orthogonality constraint of the minimal basis set used in the CNDO method we are able to separate the σ and π contributions of the C – C bonds. By the definition of the Wiberg bond index, we have a pure covalent bond if W_{AB} equals 1, and a partial polarized bond if W_{AB} is less than 1. So we have two important figures to characterize a bond: on one hand there is the bond index which represents the occupation of the covalent part of a bond, on the other the atomic net charges which show the polarities within the whole molecule.

The most surprising fact by analyzing the C – C bond by this manner is that the covalency of the σ-part is neither affected by the number of cummulated π bonds nor by the substituent X. In all the studied compounds it is nearly a perfect full covalent single bond. Regarding the π bond indices we see, with the same substituent X, a decrease from $C_2 > C_3 > C_4$. (The only one exception C_2F_4 may be due to the shorter C – C bond distance, which is not quite evident.) This is a surprising fact because

Table 2. Bond distances and bond indices.

	$R_{\mathrm{C1\,C2}}$	$W^{\sigma}_{\mathrm{C1\,C2}}$	$W^{\pi}_{\mathrm{C1\,C2}}$	$R_{\mathrm{C2\,C3}}$	$W^{\sigma}_{\mathrm{C2\,C3}}$	$W^{\pi}_{\mathrm{C2\,C3}}$	R_{CX}	W_{CX}
C_2H_4	1.339	1.002	1.058				1.085	0.965
C_2F_4	1.313	0.977	0.870				1.313	0.978
C_2Cl_4	1.333	0.987	0.989				1.72	0.957
C_2Br_4	1.335	0.996	0.977				1.875	0.966
C_3H_4	1.308	0.997	0.986				1.080	0.947
C_3F_4	1.302	0.987	0.894				1.323	0.964
C_3Cl_4	1.300	0.990	0.956				1.72	0.941
C_3Br_4	1.300	0.993	0.953				1.88	0.949
C_4H_4	1.32	0.998	0.935	1.28	0.995	0.981	1.083	0.948
C_4F_4	1.32	0.986	0.812	1.28	0.995	1.047	1.32	0.965
C_4Cl_4	1.32	0.990	0.910	1.28	0.993	0.942	1.72	0.943
C_4Br_4	1.32	0.994	0.905	1.28	0.993	0.943	1.89	0.952

Table 3. Atomic net charges.

	q_{X}	q_{C1}	q_{C2}
C_2H_4	+ 0.014	− 0.028	
C_2F_4	− 0.159	+ 0.317	
C_2Cl_4	− 0.073	+ 0.146	
C_2Br_4	− 0.053	+ 0.106	
C_3H_4	+ 0.039	− 0.115	+ 0.073
C_3F_4	− 0.182	+ 0.499	− 0.270
C_3Cl_4	− 0.087	+ 0.214	− 0.077
C_3Br_4	− 0.056	+ 0.136	− 0.048
C_4H_4	+ 0.023	− 0.045	− 0.001
C_4F_4	− 0.174	+ 0.401	− 0.053
C_4Cl_4	− 0.086	+ 0.183	− 0.010
C_4Br_4	− 0.056	+ 0.136	− 0.024

usually a shorter C – C bond distance (as in C_3X_4) leads to a stronger π overlapping. But the variation of these values is not so drastic that it should have a noticable effect on the C – C force constants. In fact the order of f_{CC} is $C_3 > C_4 \approx C_2$. Thus it is obvious that including only bond orders for the interpretation of force constants is not satisfying enough. We have also taken into account the influence of the polarity of the covalent bonds described by the atomic charges. Bader et al. [5] showed how the static electron distribution can give evidence on the relaxation process during displacement of nuclei from equilibrium. As we use only CNDO data we cannot follow this concept in a sophisticated but only in a crude manner. The relaxation of electron density due to polarisation opposes the movement of nuclei which causes a higher force constant. During elongation the charge density from non bonding regions flows back to the bonding region, shortening leads to the opposite effect. Thus we can explain the much higher value of f_{CF} of the fluorine bonds. The halogen polarisation is even transferred into the C = C-skeleton and shows therefore decreasing $C_1 - C_2$ force-constants from C_nF_4 to C_nBr_4.

In C_4X_4 compounds there are two middle C atoms to equalize this effect whereas in the propadienes there is only one C atom for both CX_2-groups. As shown by Table 1 the force constants are indeed higher for the propadienes than for the other two series.

Comparing the C = C force constants of the hydrogen compounds with the halocompounds it is striking that the values of the C_nH_4 series are lower than the others. As discussed in the introduction the constants calculated by the point charge model do not take into account the mass effect of the peripheral atoms. So it is useful to compare primarily the hydrogen and fluorine compounds because in these cases the masses are most similar. In spite of the large bond indices in the C_nH_4 series the negative atomic net charges of the C-atoms cause a smaller attraction of the carbon nuclei to the electrons between them. On the other hand the deshielding of the carbon atom induced by the electronegativity of the fluorine results in a largening of f_{CC}. Within the series C_nH_4 both carbon atoms show negative net charges in C_2H_4 and C_4H_4 which is responsible for the lower value of f_{CC} in contrast with C_3H_4.

Concluding from the foregoing discussions we see that semiempirical methods can give some helpful insight into the electronic contributions to the force constants.

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