Analysis of the H-bridge in Carboxyllic Acids in Terms of Stabilization Energy Derived from Bond Lengths. Non-Hammett Properties of p-Substituted Benzoic Acids in the Crystalline State

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Harmonic oscillator stabilization energy (HOSE) is defined as the negative value of deformation energy necessary to transform a molecule from its natural geometry to its Kekule structure with purely single and double bonds. It was found that HOSE-values for dimers of carboxylic acids with centrosymmetric hydrogen bonds are well related (correlation coeff. $r = 0.972$) to the $R_{O...O}$ distances for 19 species for which measurements were carried out in both the crystalline and gaseous states. Stability of many other π-systems, e. g. aromatic and unsaturated hydrocarbons, polymethine systems (e. g. cyanine dyes), EDA-complexes, quinoid systems, etc. are successfully described in terms of HOSE-values.

Owing to H-bond formation the carboxylic acids are known to form dimers in the crystalline state. Recently this property has been widely studied by various theoretical approaches[1-3]. The aim of this paper is to present an empirical and simple way of describing the H-bond strength in terms of stabilization energy derived from the experimentally accessible bond lengths.

THE MODEL

Let us consider the energy of deformation necessary to transform molecules of a π-electron compound, say benzene, into its Kekule structure with CC-bond lengths such as in acyclic polyene (1)

$$\tag{1}$$
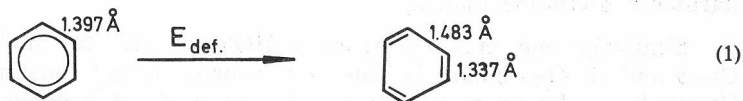
For C=C we adopt 1.337 Å and for C—C 1.483 Å, the bond lengths being determined by electron diffraction for butadiene-1,3[4]. This choice is in line with a modern definition of resonance energy[5,6]. The energy of deformation may be approximately estimated by means of applying a simple harmonic oscillator model which results in the following formula:

$$E_{def} = -\frac{1}{2} \sum_{r=1}^{n} (R_r - R_0)^2 \, k_r \tag{2}$$

where $R_0 = 1.337$ Å for n_2 shortest CC-bonds which are shortened in the course of deformation process, and $R_0 = 1.483$ Å for n_1 longest CC-bonds which are lengthened during the deformation. n_1 and n_2 are the numbers of single and double bonds in the Kekule structure of the molecule in question. Obviously $n_1 + n_2 = n$. In a more convenient way one may rewrite (2) as follows:

$$E_{def} = -\frac{1}{2} [\sum_{r=1}^{n_1} (R_r' - 1.483)^2 k_r' + \sum_{r=1}^{n_2} (R_r'' - 1.337)^2 k_r''] \tag{3}$$

where R_r' and R_r'' stand for CC-bonds which are lengthened and shortened, respectively, whereas k_r' and k_r'' are the appropriate force constants for those bonds. These force constants k_r' and k_r'' are calculated from the empirical equation based upon the linear proportionality k_r against R_r as given by eq. (4):

$$k_r = a + b\,k_r \tag{4}$$

The constants $a = 44.39 \cdot 10^{-5}$ dyn cm^{-1} and $b = -26.02 \cdot 10^3$ dyn cm^{-2} were calculated by using the following data: $R_{C=C} = 1.337$ Å and $R_{C-C} = 1.533$ Å, the CC-bond lengths in ethene and ethane, respectively, estimated by use of electron diffraction technique[7], $k_{C=C} = 9.6 \cdot 10^{-5}$ dyn cm^{-1} and $k_{C-C} = 4.5 \cdot 10^{-5}$ dyn cm^{-1} taken from the literature[8] for purely double and single CC-bonds. Incorporating a and b into eq. (3) one obtains eq. (5) in which E_{def} taken with the negative sign is called the stabilization energy denoted by the abbreviation HOSE (harmonic oscillator stabilization energy):

$$HOSE = 301.15\,(44.39 - 26.02\,R_r) [\sum_{r=1}^{n_1} (R_r' - 1.483)^2 + \sum_{r=1}^{n_2} (R_r'' - 1.337)^2] \tag{5}$$

where factor 301.15 allows to use R in Å whereas HOSE-values are given in kJ/mol. Stabilization energy defined in eq. (5) is that energy by which the real molecule is more stable than its reference structure with localized bonds (Kekule structure). In the case of benzene one obtains:

$$HOSE = 301.15\,(44.39 - 26.02 \cdot 1.397) + 3\,(1.397 - 1.337)^2 +$$
$$+ 3\,(1.397 - 1.483)^2 = 79.9 \text{ kJ/mol}$$

Thus a mole of benzene is by 79.9 kJ/mol more stable than a mole of its Kekule structure, provided the deformation energy may be described by use of simple harmonic oscillator model.

Similarly one may construct a HOSE model for molecules containing C=O and C—O— bonds. In this case in order to get constants a and b of eq. (4) we have chosen as purely double and single CO bonds those in formaldehyde and methanol, for which the electron diffraction measurements of bond lengths yield 1.209 Å[7] and 1.428 Å[9], respectively. The appropriate force constants for C=O and C—O— are 12.6 and 5.4 $\cdot 10^{-5}$ dyn cm^{-1}[8]. Using these data the a and b constants of eq. (4) for CO bonds are 52.35 $\cdot 10^{-5}$ dyn cm^{-1} and $-32.88 \cdot 10^3$ dyn cm^{-2}, respectively. Hence, the final HOSE formula for systems with CO-bonds, is as follows:
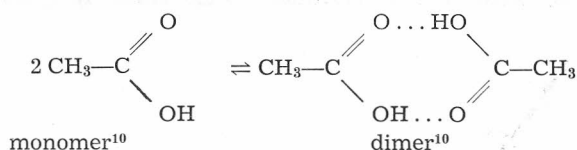
$$HOSE = 301.15\,(52.35 - 32.88\,R_{CO}) \sum_{r=1}^{n_1} (R_{CO}' - 1.428)^2 + \sum_{r=1}^{n_2} (R_{CO}'' - 1.16)^2 \tag{6}$$

In this equation C=O was taken from CO_2 [8] as a double bond. This was not used for the determination of constants of eq. (4) for CO bond since there are two force constants for $v_{C=O}$ vibration in a CO_2 molecule and it was difficult to choose the proper one. Nevertheless, C=O bond lengths in a CO_2 molecule are not influenced by resonance effect and hence they may be chosen safely for reference bond length in eq. (6). It is immediately apparent that most C=O bonds in organic systems are influenced by resonance or hyperconjugation since usually the short CO bands are as long as 1.20 Å, and this means that the HOSE-values for such bonds are about 6 kJ. If the system in question consists of both the CO and CC bonds in order to calculate the HOSE for it one must combine eqs. (5) and (6).

<div align="center">APPLICATIONS</div>

Hydrogen bond in carboxyllic acids

As a result of H-bond formation carboxyllic acids exist in the crystalline state as dimers with lengthened C=O and shortened C—O— bonds. This property can also be observed in the gaseous state. Thus for the acetic acid one may write formally the following equilibrium:
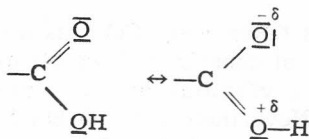
$$2\ CH_3—C\overset{\displaystyle O}{\underset{\displaystyle OH}{<}} \rightleftharpoons CH_3—C\overset{\displaystyle O\ldots HO}{\underset{\displaystyle OH\ldots O}{<}}C—CH_3$$

<div align="center">monomer[10] dimer[10]</div>

If one writes down the HOSE formula in such a way as to be able to calculate the stabilization energy of the π-electron system due to the H-bridge formation and calculated only from the changes in the π-electron structure reflected in bond lengths, the obtained value is considerable and close to the range of values characteristic of the H-bond energies[28].

<div align="center">TABLE I</div>

<div align="center">*Stabilization Energy of Carboxyllic Groups due to Hydrogen Bond Formation in Carboxyllic Acids*</div>

Acid		CO-bond lengths in Å		HOSE'/kJ
		monomer	dimer	
HCOOH[22]	$R_{C=O}$	1.217	1.220	7.8
	R_{C-O-}	1.361	1.323	
CH₃COOH[10]	$R_{C=O}$	1.214	1.231	6.7
	R_{C-O-}	1.364	1.334	
C₂H₅COOH[26]	$R_{C=O}$	1.211	1.232	10.7
	R_{C-O-}	1.367	1.329	

It is, however, obvious, that the resonance effect observed in carboxyllic groups is also due to the intra-molecular interactions, chiefly described by means of the following scheme:

$$-C\begin{matrix} \overline{\underline{O}} \\ \\ \underline{O}H \end{matrix} \quad \leftrightarrow \quad -C\begin{matrix} \overset{-\delta}{\overline{\underline{O}}!} \\ \\ \underset{+\delta}{\underline{O}}-H \end{matrix}$$

This effect results in the lengthening of C=O bonds and in shortening of C—O— bonds and is taken into account in the formula for HOSE, eq. (4). In other words in the case of dimers this formula takes into account both the effects, i. e.: H-bond formation and intra-molecular resonance in carboxyllic group. When the HOSE-values are calculated by means of eq. (6) for 19 carboxyllic acids whose measurements were carried out in crystalline or gaseous state, the results obtained are given in Table II. When the HOSE-values are plotted against the O . . . O distance in dimers, which is known as an approximate measure of H-bond strength, the linear relationship is obtained as below

$$HOSE = -1440 \; R_{O...O} + 3972$$

with correlation coefficient $r = 0.972$ for 19 experimental points. This plot is shown in Figure 1. In chossing the experimental data used for calculating HOSE-values those with (i) low residual index value $R \leqslant 0.07$ and (ii) low
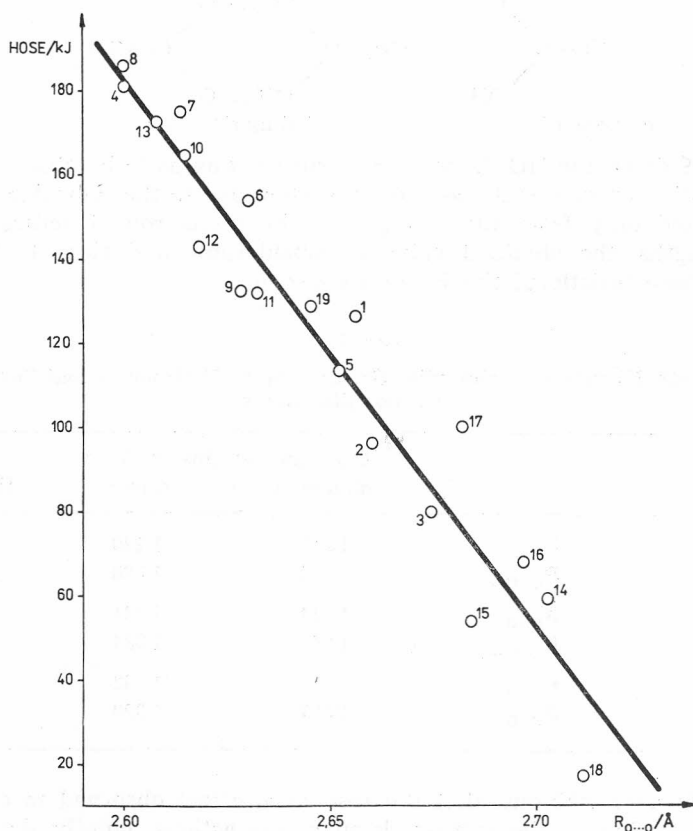

Figure 1. Plot of HOSE-values for H-bridge of 19 carboxyllic acids against $R_{O...O}$-distance.

TABLE II

HOSE- and $R_{0...0}$ *Values for Several Well Determined Carboxyllic Acids*

Acid	$\dfrac{\text{HOSE}}{\text{kJ}}$	$R_{0...0}/\text{Å}$
1) 2,4-dinitrobenzoic[11]	156.8	2.656
2) *p*-nitrobenzoic[12]	130.1	2.660
3) *p*-nitrobenzoic[13]	124.2	2.674
4) *p-n*-buthoxybenzoic (A)[14]	229.0	2.600
5) *p-n*-buthoxybenzoic (B)[14]	148.7	2.652
6) cinnamic[20]	202.3	2.630
7) *p*-methoxy-cinnamic[20]	226.9	2.614
8) 2'-iodobiphenyl-4-carboxyllic[15]	229.7	2.600
9) 3,4,5-trimethyl-benzoic[16]	176.1	2.628
10) *p*-chloro-benzoic[17]	209.9	2.615
11) *p*-methoxy-benzoic[18]	177.2	2.632
12) *p*-fluoro-benzoic[19]	186.9	2.618
13) terephthalic[21]	222.3	2.608
14) formic[22]	85.3	2.703
15) acetic[23,10]	81.2	2.684
16) chloroacetic α-form[24]	81.0	2.697
17) chloroacetic β-form[25]	120.7	2.682
18) propionic[26]	88.1	2.711
19) β-(*p*-chlorophenyl)-propionic[27]	148.4	2.645

standard deviation values for bond lengths were taken into account. The linear dependence shown in Figure 1 is observed for centrasymmetric H-bridge systems. For non-centrosymmetric hydrogen bonds the above mentioned relationship is distinctly worse.

In the case of *p*-substituted benzoic acids two interesting cases have been noticed. First, we have taken into account two X-ray measurements for *p*-nitrobenzoic acid[12,13] carried out with approximately similar accuracy but differing considerably from each other. However, both points fulfil reasonably well the above presented relationship: in Figure 1 these points are assigned 2 and 3. Another problem, still more interesting, is that for *p-n*-buthoxy-benzoic acid[14] there are two dimers in the assymetric unit differing strongly from each other. One of them (A) contains a very strong H-bond, whereas the other one (B) possesses a rather weak H-bond. The difference in HOSE-values for both the carboxyllic systems in these two dimers is as high as 80.3 kJ, whereas for their benzene ring it is as low as 2.6 kJ! This difference seems to be due to the different, non-equivalent arrangement of molecules of *p-n*-buthoxy-benzoic acid A and B in the crystal lattice. This difference in intermolecular interactions is somewhat similar to the differences of physico-chemical properties of the given compound in two different solvents: just the case of the influence of the environment on the propety of the given molecule. The above mentioned finding is very significant: one may conclude that the exocyclic parts of the aromatic system are influenced very strongly by the crystal lattice forces whereas the latters influence upon the structure

of the ring itself is very weak. The above conclusion is in line with the statement made by Kitaygorodzky[29] that intermolecular interactions in molecular crystals are too weak to affect considerably the geometry of the rigid parts of aromatic systems. On the other hand it seems to be clear now why Domenicano et al.[30] have found a fair linear relationship between the valence angle at the substituent in substituted benzenes and the substituent constants σ_I. Since Hammett himself had chosen the acidity of carboxyllic groups in substituted benzoic acids as a measure of the substituent effect, we have tried to check this postulate in the crystalline state. Plotting σ_p vs $R_{O...O}$ for several substituted benzoic acids we have obtained the graph shown in Figure 2. It is immediately clear that in the crystalline state the substituent effect
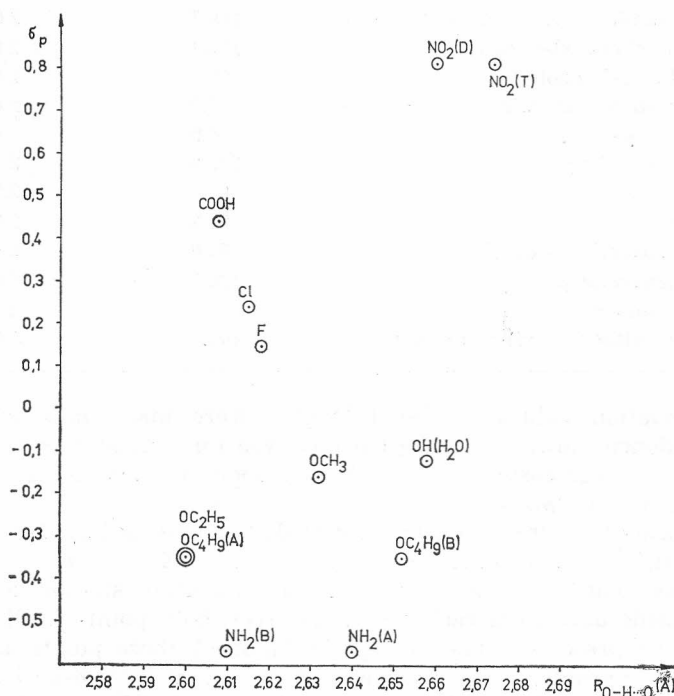

Figure 2. Plot of substituent constants for para position against $R_{O...O}$-distance. Points are assigned by symbols of the functional groups. For nitro-group D and T stand for Domenicano[12] and Tavale[13] measurements. A and B for p-amino and p-n-buthoxy derivative stand for differentiating nonequivalent dimers in the crystal lattice of these compounds.

on the properties of the carboxyllic group is not expressed in any regular way in comparison with σ_p. It is disturbed by some other effects influencing the carboxyllic group much stronger. It may be taken for granted that the above mentioned effect is due to the crystal forces which influence exocyclic substituents very strongly. The best and direct evidence for this is the existence of dimers of the same compound but which are completely non-equivalent in the same crystal lattice as it is in the case of p-amino- and p-n-buthoxy-benzoic acids as it shown in Figure 2.

STABILITY OF OTHER SYSTEMS IN TERMS OF HOSE-VALUES

There are many possibilities in applying the HOSE-values for the sake of discussing stability of various π-electron systems on the basis of X-ray or other diffraction data. Some of them are mentioned here to show the range of possible applications of the HOSE-model.

Table III shows HOSE-values for several more familiar π-electron systems. The highest HOSE per bond value (abbraviated by HOSE/b) is that for benzene, 13.3 kJ, i. e. for the most aromatic system, whereas the lowest one is that for butadiene-1,3, the reference molecule for the calculation of HOSE. In between there are other values for other systems. Let us consider 6,6'-dimethylofulvene with HOSE/b = 0.2 kJ. Pentafulvene has 5 π-electrons in the ring and according to the Hückel $4N + 2$ rule, it shows a tendency to possess 6 π-electrons. Therefore, when one methyl group is replaced by the $N(CH_3)_2$ group the HOSE/b value increases considerably up to 5.0 kJ. This is in line with the Hückel rule: the $N(CH_3)_2$ group is a strong π-donor and hence an increase of stability can be observed. Another example is annulene-18 which obeys the Hückel rule with $N = 4$ and due to its 18 π-electrons is supposed to be aromatic. It is in line with both the experimental resonance energy which is as high as 420 kJ[39] and the HOSE/b which is 9.1 kJ, i. e. in the range for aromatic systems.

Similarly as far as the cyanine dyes are concerned their HOSE/b values 8.1 kJ and 11.9 kJ indicate their high stability in agreement with chemical experience[35].

Finally, it is worth mentioning that substituted benzenes possess lower HOSE/b values than their parent molecule. For p-substituted nitrobenzenes (compounds 11—13 in Table III) the HOSE/b is contained in the range 10.2—12.9

TABLE III

HOSE-values for Several π-electron Systems

Compound	HOSE kJ	HOSE/b kJ
1) benzene[4]	79.9	13.3
2) anthracene[31]	103.3	6.5
3) phenanthrene[32]	99.9	6.2
4) pyrene[33]	132.8	7.0
5) triphenylene[34]	195.9	9.3
6) butadiene-1,3[4]	0.0	0.0
7) 6,6'-dimethyl-pentafulvene[35]	1.1	0.2
8) 6-N,N-dimethy-aminepentafulvene[35]	24.7	5.0
9) annulene-18[36]	164.0	9.1
10) cyanine dyes[35]		
(a) $[N(CH_3)_2(CH)_5N(CH_3)_2]^+ \cdot ClO_4^-$	32.4	8.1
(b) $[Nph_2(CH)_5Nph_2]^+ \cdot Br^-$	47.7	11.9
11) p-nitrobenzoic acid[12]	77.2	12.9
12) p-acetylnitrobenzene[37]	70.1	11.7
13) p-nitrotoluene[38]	61.4	10.2

ph stands for phenyl

kJ with the lowest value for p-nitrotoluene in which the through resonance effect is present. It is expressed by a decrease of HOSE/b value due to the partly quinoid structure of the π-electron system:

$$CH_3-\langle\bigcirc\rangle-NO_2 \quad \longrightarrow \quad CH_3\overset{+}{=}\langle\quad\rangle\overset{-}{=}NO_2$$

Another group of problems which may be tackled by use of the HOSE model is the EDA-complex formation. Let us consider EDA-complexes between tetracyanoquinodimethane (TCNQ) as an acceptor with various donors. As a result of the complex formation the intermolecular resonance effect occurs[40] causing changes in the geometry of its components due to the changes in π-electron delocalization ni both the π-electron donor and the acceptor. In Table IV there are shown several examples for which HOSE/b values vary to a considerable degree. The highest value is for the TCNQ · TMPD complex, 9.1 kJ, whereas for the complex with another stoichiometry, i. e. (TCNQ)$_2$TMPD the HOSE/b value drops down to 4.8 kJ. It is an obvious consequence of the weaker interaction between TCNQ and the π-donor, owing to a lower number of π-donor molecules per one TCNQ molecule.

The HOSE/b value for TCNQ is 2.2 kJ and it reflects the low stability of this system in agreement with chemical experience.

TCNQ-molecules may also form salts in which they exist as radical anions, TCNQ$^-$. In such cases a considerable increase of stability of TCNQ due to addition of 1 electron is also observed. In Table IV there are gathered HOSE and HOSE/b values for a few systems like (TCNQ$^-$, M$^+$). It is immediately apparent that HOSE/b values are rather high. The higher they are the more bulky the cation in the ion pair is. The highest HOSE value is then for [H$_2$N(CH$_2$)$_4$]$^+$·TCNQ$^-$ system, whereas the lowest one is for the ion pair with Na$^+$ as a counter ion.

Recently Kulpe and Dähne[41] have reported on an interesting effect of polymethine coupling. When p-benzoquinone is substituted in 2 and 5 positions

TABLE IV

HOSE-values for TCNQ, its Radical Anions and EDA-Complexes

Molecule[a]	HOSE/kJ	$\dfrac{\text{HOSE/b}}{\text{kJ}}$
TCNQ (CN)$_2$C$=$C$_6$H$_4=$C(CN)$_2$	17.5	2.2
TCNQ·TTF[b]	43.5	5.4
TCNQ·TMPD[c]	72.7	9.1
(TCNQ)$_2$·TMPD	38.6	4.8
TCNQ·Durol	20.2	2.5
(TCNQ$^-$, Na$^+$)	59.9	7.5
(TCNQ$^-$, Rb$^+$)	69.9	8.7
[TCNQ$^-$, H$_2$N$^+$(CH$_2$)$_4$O]	91.9	11.5

[a] All bond lengths applied in calculations taken from ref.[35]. X-ray diffraction data only. Only quinoid CC-bonds were taken into calculations.
[b] TTF = 2,2'-bis-1,3-dithiole,
[c] TMPD = N,N,N',N'-tetramethyl-paraphenylenediamine.

by a strong electron donoring group, say $N(CH_3)_2$ group, the reorganization of π-electron system occurs resulting in: equalization of C_2C_3 and C_3C_4 bond length, a slight lengthening of CO bonds and a very considerable lengthening of C_4C_5 bond length. The molecule is centrosymmetric. The observed changes in bond lengths are the result of the intramolecular charge transfer, and due to the bond length equalization (except C_1C_2 and C_4C_5 bonds) the overall effect being an increase of stability of these systems in comparison with the parent quinone. In fact, the calculated HOSE values for such systems are considerably high as shown in Table V.

TABLE V

HOSE-values for Substituted p-Benzoquinones

Compound[a]	HOSE/kJ[b]	$\dfrac{HOSE/b}{kJ}$
p-benzoquinone	27.1	3.4
3,6-dichloro-2,5-diamino-benzoquinone	73.5	9.2
3,6-dichloro-2,5-bis(monoethylamino)- -p-benzoquinone	71.3	8.9

[a] All bond lengths taken into calculations taken from ref.[41] [b] In calculation of HOSE for quinones one has to apply the quinoid Kekule structure i. e. two C=C, four C—C, and two C=O bonds.

In conclusion it seems that the above simple model of calculating stabilization energy of the π-electron systems may serve as an approximate, qualitative and convenient way of describing the stability of these systems.

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SAŽETAK

Analiza vodikovih mostova u karbonskim kiselinama pomoću stabilizacijske energije izvedene na temelju duljina veza. Ne-Hammettska svojstva *p*-supstituiranih benzojevih kiselina u kristalnom stanju

T. M. Krygowski i T. Więckowski

Harmonijsko-oscilatorska stabilizacijska energija (HOSE) definirana je kao deformacijska energija potrebita da se konjugirana molekula prevede iz svoje prirodne geometrije u (Kekuleóvu) strukturu s izmjeničnim pravim jednostrukim i dvostrukim vezama. Nađena je relacija između vrijednosti indeksa HOSE za dimere karbonskih kiselina sa središnje simetričnim vodikovim vezama i udaljenosti $R_{O...O}$ kod 19 specija za koje su mjerenja provedena u kristalnom i plinskom stanju. Također je pomoću indeksa HOSE uspješno opisana stabilnost mnogih drugih π-elektronskih sustava, kao npr. aromatičkih i nezasićenih ugljikovodika, polimetinskih boja, kvinoidnih specija, itd.

SVEUČILIŠTE U VARŠAVI
ODJEL ZA KEMIJU
POLJSKA