

CNDO/2 calculation of intramolecular hydrogen bond in 2-hydroxybenzenethiol, 1,2-benzenediol, and 1,2,3-benzenetriol

M. REMKO*

*Polymer Institute, Slovak Academy of Sciences,
809 34 Bratislava*

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The CNDO/2 method has been used for the study of hydrogen bond in 2-hydroxybenzenethiol, 1,2-benzenediol, and 1,2,3-benzenetriol. The results of the theoretical study of the strength of intramolecular hydrogen bond in compounds studied are in accordance with experimental data. Besides, the anions of 2-hydroxybenzenethiol and 1,2-benzenediol have been studied.

Был применен метод CNDO/2 для изучения водородной связи в 2-гидроксибензолтиоле, 1,2-бензолдиоле и 1,2,3-бензолтриоле. Результаты теоретического изучения согласуются с экспериментальными данными о силе внутримолекулярной водородной связи изучаемых соединений. Изучались также анионы 2-гидроксибензолтиола и 1,2-бензолдиола.

Recently, the semiempirical "all valence" SCF MO CNDO/2 method [1–3] was frequently used in the study of hydrogen bond [4, 5] and it yielded valuable information on the properties of systems with hydrogen bonds. For strong hydrogen bonds the method gives higher values than the experimental ones whereas for weak hydrogen bonds the calculations are in a good agreement with experiment [4]. Consequently, the weak hydrogen bonds may be calculated by the CNDO/2 method even for such systems where at present the *ab initio* calculations are very sophisticated.

In this paper, the CNDO/2 method was used for calculation of intramolecular hydrogen bond in several *X-ortho*-substituted phenols ($X = \text{OH}, \text{SH}$). From the spectroscopic measurements [6–9] it follows, that in these compounds only weak intramolecular hydrogen bonds not leading to the stable conformers are formed. These conformers cannot be, of course, isolated but they are sufficiently stable in order to affect the properties, especially the chemical reactivity, of the corresponding compounds.

Method of calculation

Electron structure and energy of the investigated systems were calculated by means of the CNDO/2 method [1–3] with original parameters. The calculated energy of hy-

* *Present address:* Pulp and Paper Research Institute, 890 20 Bratislava.

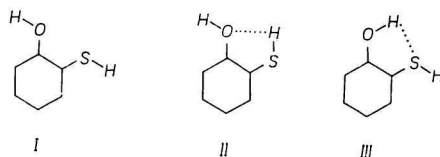
drogen bond E_{HB} was postulated as the difference between the total energy of conformer with a *trans* orientation of X—H group (X = O, S) and the total energy of conformer with an intramolecular hydrogen bond (with *cis* orientation), *i.e.*

$$E_{\text{HB}} = E_{\text{trans}} - E_{\text{cis}}. \quad (1)$$

The calculation was carried out on a CDC 3300 computer with a standard programme from QCPE 141. For theoretical calculations the experimental geometry [10] was used.

Results and discussion

In Table 1 the energies of hydrogen bonds for different conformers of 2-hydroxybenzenethiol (Scheme 1) are presented. In this case, the most stable is the conformer *III* with hydrogen bond of the type O—H···S, the energy of which is much



Scheme 1

higher than that of hydrogen bond of S—H···O type in the conformer *II*. This corresponds to the observation that the O—H groups form stronger hydrogen bonds as compared with the S—H groups [11, 12].

The values of hydrogen bond energy calculated by the CNDO/2 method for different conformers of 1,2-benzenediol and 1,2,3-benzenetriol (Scheme 2) are presented in Table 2. From Tables 1 and 2 it follows that the most stable is the conformer *III* with sulfur as proton acceptor. Energy of the corresponding hydrogen bond is higher than that in the conformer *V* with oxygen as proton acceptor. A similar tendency in the strength of hydrogen bond in five-membered rings of the studied compounds, was also observed experimentally [6, 13, 14].

Table 1

Calculated energies of different conformers of 2-hydroxybenzenethiol

Conformer	$E_{\text{elec.}}$ a.u.	E_{total} a.u.	E_{HB} kcal mol ⁻¹
<i>I</i>	-251.7710	-76.4808	0
<i>II</i>	-252.3550	-76.4814	0.4
<i>III</i>	-252.2985	-76.4854	2.9

Table 2

Calculated energies of different conformers of 1,2-benzenediol and 1,2,3-benzenetriol

Conformer	$E_{\text{elec.}}$ a.u.	E_{total} a.u.	E_{HB} kcal mol ⁻¹
IV	-265.0845	-84.0199	0
V	-265.6472	-84.0221	1.4
VI	-330.7592	-102.4890	1.8
VII	-330.1091	-102.4860	0

Table 3

CNDO/2 charges in hydrogen-bonded (X—H · Y) systems

Conformer ^a	Charges				
	O	H	S	H	O
I	-0.236	+0.137	-0.062	-0.016	—
II	-0.134	—	-0.064	-0.003	—
III	-0.237	+0.145	-0.086	—	—
IV	-0.228	+0.129	—	+0.135	-0.240
V	-0.237	+0.141	—	—	-0.249
VI	-0.237	+0.144	—	+0.143	-0.235
VII	-0.228	—	—	+0.133	-0.228
VIII	-0.232	+0.081	-0.691	—	—
IX	-0.290	+0.154	-0.704	—	—
X	-0.579	—	-0.154	-0.075	—
XI	-0.598	—	-0.220	-0.004	—
XII	-0.236	+0.064	—	—	-0.595
XIII	-0.281	+0.120	—	—	-0.603

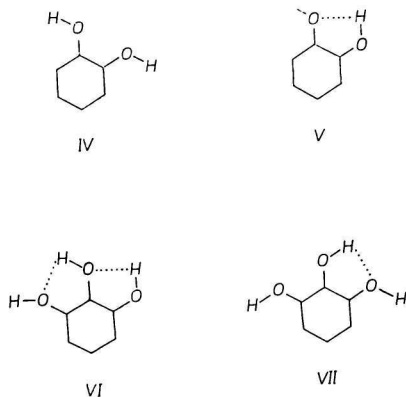
a) Conformers are numbered according to the Schemes 1—3.

Table 4

Calculated energies for different conformers of anions of 2-hydroxybenzenethiol and 1,2-benzenediol

Conformer	$E_{\text{elec.}}$ a.u.	E_{total} a.u.	E_{HB} kcal mol ⁻¹
VIII	-243.6858	-75.7541	0
IX	-244.1760	-75.7655	7.1
X	-242.2003	-75.6314	0
XI	-242.7228	-75.6303	-0.7
XII	-255.7771	-82.1587	0
XIII	-256.2887	-83.1655	4.3

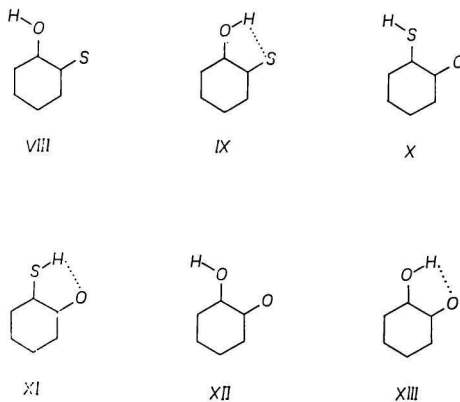
Energy of one hydrogen bond in 1,2,3-benzenetriol is higher than that in 1,2-benzenediol. Then the total energy of hydrogen bond in 1,2,3-benzenetriol is given by the sum $(E_{\text{total}}^{\text{IV}} - E_{\text{total}}^{\text{V}}) + (E_{\text{total}}^{\text{VII}} - E_{\text{total}}^{\text{VI}})$ and represents $3.2 \text{ kcal mol}^{-1}$.



Scheme 2

Total charges of atoms bonded by hydrogen bond of the studied conformers are presented in Table 3. Similarly as in systems with intermolecular hydrogen bond [5], the total charge of atoms involved in hydrogen bond changes also in the investigated conformers. Generally, the electron charge on electronegative atoms O and S increases while the charge on hydrogen bonded by a hydrogen bond decreases. At the same time, in a hydrogen bond of the type $\text{S}-\text{H} \cdots \text{O}$ as well as in the corresponding anion $\text{S}-\text{H} \cdots \text{O}^-$, hydrogen has a negative total charge.

In comparison to six-membered rings (e.g. salicylaldehyde where a change of both σ and π electron distributions occurs as a consequence of the formation of hydrogen bond [15]) in the studied five-membered rings mainly the σ electron distri-



Scheme 3

bution changes and the π electron distribution remains unchanged. The increase of the total charge on oxygen or sulfur atoms is mainly due to a shift of the σ charge from hydrogen in corresponding hydrogen bond.

The total energies of anions of different conformers of 2-hydroxybenzenethiol and 1,2-benzenediol (Scheme 3) are given in Table 4. For anions with a hydrogen bond of the type $\text{O}-\text{H}\cdots\text{S}^-$ and $\text{O}-\text{H}\cdots\text{O}^-$ the energy of hydrogen bond is substantially increased. On the other hand, the unstability of the conformer with hydrogen bond $\text{S}-\text{H}\cdots\text{O}^-$ is somewhat surprising.

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