A QUANTUM-CHEMICAL STUDY OF PHENOL SELF-ASSOCIATION OF OPEN AND CYCLIC DIMERS AND TRIMERS

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Itermolecular hydrogen bond in the open/linear and cyclic/closed dimers and trimers of phenol has been studied by means of the quantum-chemical PCILO method. Our calculations have shown that the open/linear associate is more stable in the case of the dimers. On the contrary, the cyclic/closed associate is more stable in the case of the trimers.Positive cooperativity has been observed by formation of both the open/linear and cyclic/closed trimers.

Due to its polar hydroxyl group, phenol can form hydrogen bonds and act as both a proton-donor and a proton acceptor. The aromatic ring of phenol can also form hydrogen bonds of X-H ... π type with suitable proton donors. Phenol and its derivatives form strong hydrogen bonds with various proton acceptors which were studied intensively both experimentally[1-4] and theoretically[5-22]. Numerous experimental studies[1,2,13-30] showed that in non-polar solvents phenol undergoes self-association forming gradually dimers, trimers, and higher *n*-mers. According to experimental investigations[13,19,31] within limited extent of phenol concentrations the dimerization mainly represents a self-association reaction. With increasing phenol concentration the number of trimers and higher *n*-mers also increases[23,27,27]. The only discrepancies exist in the question whether the lower *n*-mers (dimers, trimers, tetramers) are cyclic or linear. The quantum-chemical CNDO/2 calculations[32] of the open and cyclic phenol dimers showed that the open dimers are more stable than the cyclic ones.

The aim of the present communication is a quantum-chemical study of the open and cyclic dimers and trimers of phenol and determination of relative stability of the individual phenol *n*-mers.

CALCULATION METHOD

The calculations were carried out by means of the original PCILO method[33]. Geometry of the complexes studied was optimized with respect to the $R_{O \cdots O}$ distance (Fig. 1). The cyclic dimers and trimers were considered in the calculations as planar with C_s symmetry. Due to the stereochemistry reasons in the case of the open-chain dimers and trimers, the calculations were carried out with the non-planar structures in which the proton-donor OH groups were oriented in the direction of lone electron pairs of oxygen atom. In the case of the cyclic dimer the φ angle (Fig. 1) was kept at the value of 60° (ref.[10]). The O—H groups of the cyclic trimer were considered to form regular hexamers. The hydrogen-bond energy was defined as the difference between the total energy of the isolated monomers and that of the model complex:

$$E_{HB} = E_{(R_\infty)} - E_{(R_{min})} \,. \qquad (1)$$

The calculations were carried out with the use of experimental geometry of phenol[34] using a Siemens 4004/151 computer (The Computer Centre of Comenius University) and the QCPE No 220 program[35].

RESULTS AND DISCUSSION

Table I gives the results of our PCILO calculations of the equilibrium geometries, hydrogen bond energies, and average hydrogen bond energies of the phenol complexes studied. In the case of the dimers the open/linear structures were found to be the most stable with the energy of 15·11 kJ/mol. The interaction energy of two hydrogen bonds of the cyclic dimers has only the value of 8·04 kJ/mol. Similarly, quantum-chemical calculations showed that the open complexes are more stable than the cyclic complexes in the cases of dimers of water[36], methanol[37,38], and phenol[32], as well as of the system phenol–methanol[10].

Josefiak and Schneider[29] studied self-association of phenol in CCl_4 with the use of high-pressure near infrared spectroscopy. Their measurements showed that the presumption of the monomer–dimer equilibrium represents a good first approximation in dilute solutions. The open dimers were found to be more stable then the cyclic ones.

As to the phenol trimers, our calculations showed that the cyclic trimer with three hydrogen bonds is more stable than the open trimer. However, the average hydrogen-bond energy E_d (Table I) is higher in the case of the open dimers and trimers. On going from the dimers to trimers the value of average hydrogen-bond energy increases, hence positive cooperativity is observed. The average hydrogen-bond energy increases considerably on going from the cyclic dimer to trimer. This increase is predominantly due to the topological effect. From the quantum-chemical studies[39] it is well known that the hydrogen bond complexes tend to maintain linear X—H···Y

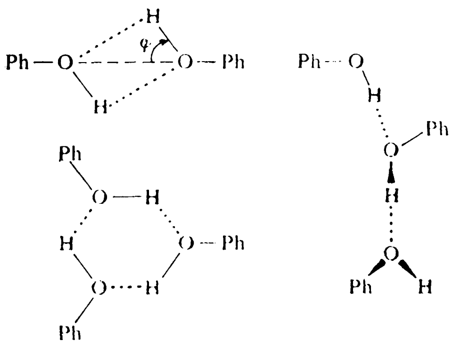


Fig. 1

Model of the hydrogen bond in the studied dimers and trimers of phenol

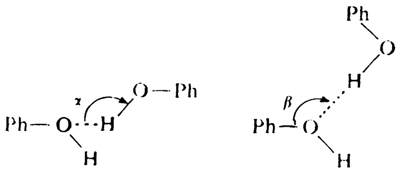
TABLE I

The PCILO equilibrium geometries, interaction energies, and average hydrogen-bond energies of the open and cyclic dimers and trimers of phenol[a]

System	$R_{O\cdots O}$, nm	E_{HB}, kJ/mol	E_d, kJ/mol
dimer open/linear	0·271	15·11	15·11
cyclic/closed	0·225	8·04	4·02
trimer open/linear	0·266	31·14	15·57
cyclic/closed	0·271	41·27	13·75

[a] The average hydrogen-bond energy was calculated from the relation E_D = (energy of monomers − energy of complex)/h, where h means the number of hydrogen bonds.

hydrogen bond to reach the maximum electrostatic stabilization which is the most important component of the hydrogen bond energy. Similarly, experimental studies showed that deformation of linearity at hydrogen atom (Fig. 2(*a*)) results in considerable reduction in the bond energy. On the contrary, the deviation from linearity at the proton-acceptor atom (Fig. 2(*b*)) reduces the hydrogen bond energy to a substantially lesser extent[40]. With respect to these known facts we also carried out the PCILO calculations with the open/linear planar phenol dimer in which the both phenol molecules occupy the same plane and have the C_s symmetry. The C—O···H—O angle was taken equal to 120° (ref.[10]). Hence, in this dimer the linearity of the O···H—O bond is maintained at the hydrogen atom, and the dimer represents (together with the previous open dimer) the case (*b*), Fig. 2, of the angle deformation of hydrogen bond. The hydrogen bond energy of this dimer only increases by 18% (E_{HB} = 18·54 kJ/mol, $R_{O\cdots O}$ = 0·266 nm) when changing the β angle from 109° to 120°. The calculations of these two open-chain phenol dimers also showed that there exists no distinct preference of formation of the hydrogen bond in the direction of the lone



(*a*) (*b*)

FIG. 2

The angle deformations of hydrogen bond

electron pairs. On the contrary, a somewhat more stable open planar dimer was calculated in which the proton-donor OH group was oriented out of the direction of the lone electron pairs. A similar trend was also observed experimentally in hydrogen-bonded crystals[40,41] with the use of neutron diffraction.

The cyclic dimers and trimers of phenol represent, on the contrary, an angle deformation of the hydrogen bond at the hydrogen atom (Fig. 2(*a*)). On going from the dimer to trimer, the average hydrogen bond energy increased by as much as 340% when the α angle was changed from 95° (cyclic dimer) to 120° (trimer).

In accordance with experimental facts our calculations showed considerable changes of the hydrogen bond energy accompaniyng the angle deformation of the hydrogen bond at hydrogen atom, whereas, on the contrary, the angle deformation at the proton-acceptor oxygen atom has an only small effect on the value of the energy of the cyclic trimers as compared with the cyclic dimer. Hence the considerable increase in the average hydrogen bond energy of phenol is due especially to the angle deformation at the hydrogen-bond hydrogen atom. A much smaller effect of this H deformation can be presumed in the case of the higher cyclic *n*-mers of phenol where the changes in the α angle are smaller. Such a trend was really observed in the case of analogous self-association of methanol[38].

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