A PCILO study of the hydrogen bond of linear ethers and crown ethers with phenol

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The PCILO method was used for calculation of interaction energies of phenol with linear and crown ethers. The geometry of all interacting molecules was at first completely optimized.

The linear ethers represented systems of the structure R—(CH$_2$—CH$_2$—O)$_x$—R with the number of oxygen atoms $x = 1, 2, 3, 4, 6$ and R = = —CH$_3$, —CH$_2$—CH$_3$. 1,4-Dioxan, 12-crown-4, and 18-crown-6 were calculated as cyclic ethers.

Association energies were shown to be almost independent of the number of oxygen atoms in an ether molecule. This holds for both linear and cyclic ethers. Differences in association energies of linear and cyclic ethers are small (to 2 kJ mol^{-1}).

As a whole, the hydrogen bond between associates may be considered as weak; it follows from the value of the energy (about -20 kJ mol^{-1}) and from the —O—O— distance, which is only little smaller than a sum of van der Waals radii of oxygen atoms.

Для расчета энергий взаимодействия фенола с линейными и краун-эфирами был использован метод PCILO. Геометрия взаимодействующих молекул была предварительно полностью оптимизирована.

Линейные эфиры были представлены системами строения R—(CH$_2$—CH$_2$—O)$_x$—R с числом кислородных атомов $x = 1, 2, 3, 4, 6$ и R = —CH$_3$, —CH$_2$—CH$_3$. В качестве циклических эфиров рассчитывались 1,4-диоксан, 12-краун-4 и 18-краун-6.

Показано, что значения энергий ассоциации почти не зависят от числа атомов кислорода в молекуле эфира. Это относится как к линейным, так и к циклическим эфирам. Разница величин энергии ассоциации для линейных и циклических эфиров невелика (не более 2 кДж моль$^{-1}$).

В целом, водородная связь между ассоциатами довольно слаба, что следует как из значения ее энергии (около -20 кДж моль$^{-1}$), так и из расстояния —O—O—, которое лишь немного меньше, чем сумма Ван-дер-Ваальсовых радиусов атомов кислорода.

The suitability of the PCILO (Perturbative Configuration Interaction using Localized Orbitals) method for quantum chemical calculations of the hydrogen bond energy of the complexes $O\!-\!H\ldots O<$, $O\!-\!H\ldots O=$, $N\!-\!H\ldots N\leqslant$, $N\!-\!H\ldots O<$, etc. was demonstrated by Hobza and Zahradník [1]. A comparison of the results from the PCILO and CNDO/2 or ab initio methods for various types of complexes showed that the PCILO method yields in most cases more correct values for interaction energies with respect to the experimentally found values [2, 3]. The PCILO method is suitable for interaction energy calculations between nonpolar, polar or charged systems [4, 5]. The PCILO method has some drawbacks, such as overestimation of the delocalization energy and, on the other hand, underestimation of the interbond correlation energy. As the authors [1, 6] have reported, it should be mentioned that the reliability of the results of interaction energies calculated by the PCILO method is the best if none of the interacting systems contains double bonds. The reliability of the results worsens if one molecule contains conjugated π-system; in the interaction of the two π-systems the PCILO method fails in many cases. In spite of this it is necessary to emphasize that in the study of hydrogen bonds the PCILO method has been successful because it is a combination of the CNDO/2 parametrization and the perturbation theory. This improves the reliability and accelerates calculations of the interaction energies of the systems provided by this method if compared with the CNDO/2 method.

Although hydrogen bond has been the subject of extensive experimental and theoretical studies, there are many unsolved problems, especially in the region of associations conditioned by certain configuration and conformational arrangements of functional groups or associating molecules. This type of associations is especially characteristic of biosystems. Crown ethers and their linear analogues α-methyl ω-methoxy polyoxyethylenes belong to molecules, the association abilities of which significantly depend on conformation.

Since crown ethers are soluble in both polar and nonpolar solvents, they are able to transfer complexed ions through the interface from polar to the nonpolar phase. They are therefore often used as catalysts in organic synthesis. Even in the study of associations of ions with crown ethers (with different ring size), correlation was found between the ring size and ionic radius of the atom [7]. Various crown ethers show selectivity with respect to some ions and other bind much weaker ions. For instance, 18-crown-6 binds preferentially K^+ (Ref. [8]).

The authors [9] presented a survey of the results on the complexation of crown ethers and other heterocyclic rings with neutral molecules. The goal of these papers was on the one hand the study of associations, and on the other hand, practical aims, such as immobilization of volatile or gaseous poisonous or other toxic substances and their release from the complex [10]. Complexation

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of 18-crown-6 with dimethyl sulfoxide was proposed as a method for isolation of 18-crown-6 from a mixture of compounds after reaction [11].

The experimental results obtained by IR and NMR [12, 13] method indicate that crown ethers alter conformational structure as a result of complexation [14].

The aim of this paper is to examine the ability of cyclic and linear ethers to form hydrogen bonds with proton donor. Phenol was chosen as proton donor because of its chemical simplicity. To be able to evaluate the whole process of the interaction of phenol with the given ethers, a theoretical study in at least two steps is necessary. The first step is the investigation of the most stable conformer for individual ethers but also for phenol. The second step is the study of the complex-forming ability of ethers resulting from the hydrogen bond formation. The ability of the complexation of crown ethers with their linear analogues is evaluated simultaneously.

Semiempirical quantum chemical PCILO method based on the perturbation theory has been described in detail earlier [15, 16]. The corresponding energy is determined by the standard Rayleigh—Schrödinger perturbation theory, restricted up to the third order. An actual version of the PCILO method used for the calculation of the hydrogen bond energy of the systems ether—phenol has been described elsewhere [17].

Calculations and molecules studied

The geometry for a phenol molecule was taken from [4], where by the PCILO method the most stable form of the benzene ring was calculated. It is a ring with double bond length of 138 pm and the length of a single C—C bond 142 pm. The C—H bond is 108 pm long.

In the following step, conformational studies were done for linear ethers. The calculation confirmed that the most stable form of the O—C—C—O segment is the *gauche* form. The optimization of the geometry of five linear ethers with the number of oxygen atoms in chain = 1, 2, 3, 4, 6 was done simultaneously. Table 1 contains values for bond lengths obtained. The geometry was optimized in the internal coordinates with the accuracy of 0.1 pm for bond lengths, 0.05° for bond angles, and 0.5° for dihedral angles.

The bond angles for individual molecules of linear ethers differ; the values of all optimized C—O—C angles being lower than the value of standard bond angle (109.5°) by about 4—1°. On the contrary, for O—C—C bond angles, the values are higher by 0.5° after optimizing internal coordinates. The values obtained for dihedral angles O—C——C—O were between 59.8° and 60.9° and for the C—O—C—C angles varied between 179.6° and 182.1°.

The values of the internal coordinates for crown ethers reported in the literature considerably differ. They were obtained *via* X-ray structure analysis of these ethers,

where the most advantageous arrangement of atoms in view of the crystal lattice leads to deformation of bond angles and bond lengths. The geometry of crown ethers was therefore optimized and the optimal values of the bond lengths, bond and dihedral angles are given in Tables 1 and 2.

Table 1

Optimalized bond lengths (d/pm)

Linear ethers				Crown ethers		
C—C	C—O	C—H^a	C—H^b	C—C	C—O	C—H
148.1	138.6	114.1	113.2	148.3	138.6	109.0

a) In CH_2 group; *b*) in CH_3 group.

Table 2

Optimized values of bond and dihedral angles of crown ethers

Ether	Bond angles/°		Dihedral angles/°		
	C—O—C	C—C—O	O—C—C—O	C—O—C—C	C—C—O—C
12-Crown-4	112.6	113.8	± 62.9	± 147.0	± 120.5
18-Crown-6	110.4	111.3	± 59.7	180.1	182.1

The individual degrees of freedom for molecules were optimized at first independently in the order: bond lengths, bond angles, and dihedral angles. In the following step, all degrees of freedom were optimized simultaneously. No relations for symmetry or equivalence were prescribed for internal coordinates in the optimization of the geometry of these systems.

Results and discussion

The dependences of the hydrogen bond energy of the associates ether—phenol on the distance of oxygen atoms calculated have the shape of the potential curve with one minimum. In the calculation of the energies for complexes, the hydrogen bond length and its surrounding was optimized, *i.e.* —OH and —OC bond length of phenol and the bond angle H—O—C. In regard to the hydrogen bond energy ($\sim -20\,kJ\,mol^{-1}$), no change of the bond lengths and angles of covalent bonds of ethers can be expected.

Table 3

Equilibrium geometry and energy for hydrogen bonds of the associates phenol and linear ethers

System	Name	Number of O atoms in chain	R_{O-O}/pm	ΔE_{HB}/kJ mol^{-1}
1	Phenol—diethyl ether	1	273.6	−17.81
2	Phenol—1,2-diethoxyethane	2	274.1	−20.90
3	Phenol—α-methyl ω-methoxy dioxyethylene	3	273.9	−17.98
4	Phenol—α-methyl ω-methoxy trioxyethylene	4	274.7	−21.53
5	Phenol—α-methyl ω-methoxy pentaoxyethylene	5	275.4	−22.01

Table 3 contains the values of the energies of hydrogen bonds phenol—linear ethers at the equilibrium distance of oxygen atoms. The calculations show that linear ethers with odd number of oxygen atoms in chain (system *1* and *3*) form with phenol a weaker hydrogen bond than ethers with even number of oxygen atoms in chain. For these ethers, as the chain length increases, the energy of the hydrogen bond as well as the equilibrium distance between oxygen atoms of phenol and ether increases too. The geometry of the associates has been selected so that the phenolic hydrogen would be bonded to the oxygen atom of ether in the linear chain which is nearest to the centre of the molecule. The hydrogen bond was then surrounded by the largest number of the —CH$_2$—CH$_2$—O— and was comparable with the bond crown ether—phenol.

The results from Table 4 show that with the increasing number of —CH$_2$—O—CH$_2$— groups in ring, the hydrogen bond energy decreases and the equilibrium distance of oxygen atoms increases.

Table 4

Equilibrium geometry and energy for hydrogen bonds of the associates phenol and crown ethers

System	Name	R_{O-O}/pm	ΔE_{HB}/kJ mol^{-1}
7	Phenol—1,4-dioxan	271.1	−18.84
8	Phenol—12-crown-4	272.8	−18.53
9	Phenol—18-crown-6	273.6	−18.38

The results calculated show that the phenol molecule is bound to etheric oxygens with lone electron pairs *via* weak hydrogen bond of $E = -(18-22)$ kJ mol^{-1}. It is also supported by the equilibrium distance of oxygen atoms,

which is only little smaller than the sum of van der Waals radii of oxygen atoms. Figs. 1 and 2 show the optimal configuration of the associates 1,2-diethoxyethane—phenol and 1,4-dioxan—phenol calculated by the PCILO method.
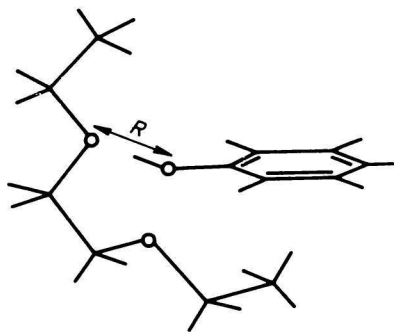

Fig. 1. Optimum configuration of 1,2-diethoxyethane—phenol associate calculated by the PCILO method.
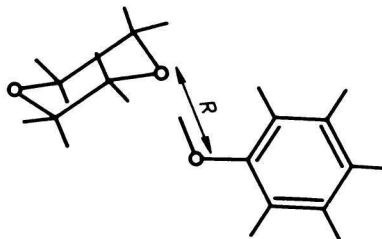
Fig. 2. Optimum configuration of 1,4-dioxan—phenol associate calculated by the PCILO method.

Only two of the systems studied were measured experimentally, *viz.* diethyl ether—phenol and 1,4-dioxan—phenol. The enthalpy of the system diethyl ether—phenol measured by the IR method in the near region is $-22.63 \, kJ \, mol^{-1}$ [18]. CCl_4 was used as solvent. *Gramstad* [19] reported for this system the enthalpy of $-20.09 \, kJ \, mol^{-1}$ measured under the same conditions. This system was also measured calorimetrically by the method of pure base; the enthalpy obtained has the value of $-22.83 \, kJ \, mol^{-1}$ [20].

The system 1,4-dioxan—phenol was measured in the IR region in CCl_4. The authors [21] reported the value for the enthalpy $-20.92 \, kJ \, mol^{-1}$. The calorimetric measurement of the enthalpy in this system gave the value $-21.40 \, kJ \, mol^{-1}$ [20]. The measurement was done by the method of pure base. The enthalpy of the system 1,4-dioxan—phenol reported earlier [18] was $-22.00 \, kJ \, mol^{-1}$. The measurement was performed by the IR method in the near region in CCl_4. The last value of the enthalpy for this system obtained by the UV measurement using isooctane as solvent was $-23.01 \, kJ \, mol^{-1}$ [22].

Interaction enthalpies obtained experimentally are higher than the energies calculated by about $2 \, kJ \, mol^{-1}$, which is a very good agreement.

The reason for these differences is complex. In the first place it should be noted that we compare experimentally measured enthalpies with the energies calculated by the PCILO method, although the difference between these quantities ($p\Delta V$) is very small for liquid systems. One has to reckon with some unreliability of the PCILO results since interactions of saturated molecules with phenol from the conjugated π-system were calculated. A similar study of hy-

drogen bonds using the PCILO method showed that this method does not provide so reliable results in the association conjugated system—saturated system as in the interaction of molecules without double bonds. On the other hand, one has to expect some unreliabilities in the experimental data. Moreover, the experimental enthalpies are measured in the real medium and we cannot neglect the solvent effect on the enthalpies measured.

Table 5

Charge shifts and charge transfer in hydrogen-bonded phenol complexes studied

System	$\Delta Q_E/mC$	$\Delta Q_H/mC$	$\Delta Q_O/mC$	$\Delta Q_T/mC$
1	19.1	38.0	−57.9	−0.8
2	17.6	40.3	−60.6	−2.7
3	13.8	38.4	−56.4	−4.2
4	15.8	40.1	−58.9	−3.0
5	15.4	45.3	−57.6	−3.1
6	21.0	36.1	−57.4	−0.3
7	19.8	38.2	−60.1	−2.1
8	17.7	43.7	−48.4	13.0

Table 5 shows the charge shifts and charge transfer of the system under study. ΔQ_E represents the charge shift to ether-bonded oxygen atom, ΔQ_H — charge shift on hydrogen from the —OH phenol group, ΔQ_O — charge shift on phenol oxygen, ΔQ_T — total charge transfer. Charge shifts and charge transfer are small; it corresponds to a weak hydrogen bond of individual associates. The charge shift is defined as

$$\Delta Q = Q(R) - Q(\infty) \qquad (1)$$

where $Q(R)$ is the charge on the atom at equilibrium configuration of the associates, $Q(\infty)$ is the charge on the atom in isolated molecule.

Conclusion

The semiempirical PCILO method was used for calculations of the energies of weak intermolecular interactions because of reliability and rate. It is supported by a comparison of the values calculated and determined experimentally. Linear and crown ethers form with phenol weak hydrogen bonds with the energy of $-(17.8\text{—}22.1)\,kJ\,mol^{-1}$, which is also confirmed by the equilibrium distance of oxygen atoms 271.0—275.5 pm. Hydrogens from phenolic ring do

not interact with lone electron pairs of oxygen atoms of crown ethers because of the size of phenolic ring.

References

1. Hobza, P. and Zahradník, R., *Weak Intermolecular Interactions in Chemistry and Biology.* Academia, Prague, 1980.
2. Weller, Th., *Int. J. Quantum Chem. 12*, 805 (1977).
3. Lochmann, R., *Int. J. Quantum Chem. 12*, 841 (1977).
4. Remko, M., *Advan. Mol. Relax. Interact. Processes 14*, 37 (1979).
5. Remko, M. and Polčin, J., *Advan. Mol. Relax. Interact. Processes 11*, 249 (1977).
6. Lochmann, R., *Int. J. Quantum Chem. 12*, 795 (1977).
7. Christensen, J. J., Eatough, D. J., and Izatt, R. M., *Chem. Rev. 74*, 351 (1974).
8. Izatt, R. M., Tery, R. E., Haymore, B. L., Hansen, L. D., Dalley, N. K., Avondet, A. G., and Christensen, J. J., *J. Amer. Chem. Soc. 98*, 7620 (1976).
9. Vögtle, F., Sieger, H., and Müller, W. M., *Top. Curr. Chem. 98*, 107 (1981).
10. Vögtle, F. and Müller, W. M., *Naturwissenschaften 67*, 255 (1980).
11. Van Zon, A., de Jong, E., Rinhondt, D. N., Torny, G. J., and Onwenzen, Y., *Rec. Trav. Chim. Pays-Bas 100*, 453 (1981).
12. Schori, E., Grodinski, J., Lutz, Z., and Shoper, M., *J. Amer. Chem. Soc. 93*, 7133 (1971).
13. Live, D. and Chan, S. I., *J. Amer. Chem. Soc. 98*, 3708 (1976).
14. Dobler, M., *Chimia 38*, 415 (1984).
15. Diner, S., Malrieu, J. P., Jordan, F., and Gilbert, M., *Theor. Chim. Acta 15*, 100 (1969).
16. Diner, S., Malrieu, J. P., and Claverie, P., *Theor. Chim. Acta 13*, 1 (1969).
17. Kožár, T. and Tvaroška, I., *Theor. Chim. Acta 53*, 9 (1979).
18. West, R., Powel, D. L., and Lee, M. K. T., *J. Amer. Chem. Soc. 86*, 3227 (1964).
19. Gramstad, T., *Spectrochim. Acta 19*, 497 (1963).
20. Arnet, E. M., Joris, L., Morfy, T. S. S. R., Gorrie, T. M., and Schleyer, P. R., *J. Amer. Chem. Soc. 92*, 2365 (1970).
21. Fritzsche, H., *Ber. Bunsenges Phys. Chem. 68*, 459 (1964).
22. Baba, H. and Suzuki, S., *J. Chem. Phys. 35*, 1118 (1961).