

Study of the interaction in the system poly(2,6-dimethylphenylene oxide)—solvent

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Dedicated to Professor Ing. RNDr. A. Tkáč, DrSc., in honour of his 60th birthday

In the present paper the model interaction of poly(2,6-dimethylphenylene oxide) with various solvents (chloroform, carbon tetrachloride, benzene, toluene, xylenes) is studied. As a model the interaction of 2,6-dimethyl hydroquinone (which reproduces the electron density distribution in poly(2,6-dimethylphenylene oxide) very well) with molecules of individual solvents was used. The semiempirical CNDO/2 method with the limited configuration interaction has been applied for all calculations. Theoretically obtained results were correlated with experimental data.

В работе изучается модельное взаимодействие поли(2,6-диметилфениленоксида) с различными растворителями (хлороформ, тетрахлоорметан, бензол, толуол, ксилолы). В качестве модели было выбрано взаимодействие 2,6-диметилгидрохинона, который хорошо отражает распределение электронной плотности поли(2,6-диметилфениленоксида) в среде молекул отдельных растворителей. Расчет проводился полуэмпирическим методом CNDO/2 с ограниченным конфигурационным взаимодействием. Вычисленные величины были прокоррелированы с экспериментальными данными.

The solvation of polymer molecules with solvent molecules is the basic condition of the process of polymer dissolution. This process causes the release of polymer chains from the surrounding environment. The interruption of the nonbonding interactions between polymer molecules and their compensation with stronger interactions polymer—solvent is the basic assumption for the transport of polymer molecules into the solution. The study of the interaction polymer—solvent can therefore grant us valuable information about the characteristics of various solvents. The experimental study of the magnitude of interaction forces is made

impossible due to the series of successive processes which cannot be separated in the diffusion processes. The theoretical accesses founded on the available apparatus of quantum chemistry may grant us some information about the magnitude and character of interaction forces, although we are forced (for the numerical reason) to depart from the calculations of simplified model systems.

The study of model interaction of poly(2,6-dimethylphenylene oxide) (PPO) with various solvents (chloroform, carbon tetrachloride, benzene, toluene, xylenes) by the use of semiempirical CNDO/2 method of quantum chemistry is the aim of the present paper.

Results

The direct calculation of interaction energy of highly polymer molecule with solvent molecules has not been realized due to the limited capacity and rapidity of the present-day computers. Therefore, the model system of interaction of 2,6-dimethyl hydroquinone molecule with molecules of individual solvents was chosen. This model was used because 2,6-dimethyl hydroquinone well reproduces the electron density distribution in PPO. The semiempirical CNDO/2 [1] method was used for all calculations. As the dispersion energy contributions calculation requires inclusion of correlation effects by the study of weak intermolecular interactions, the limited configuration interaction method was applied. 10 lowest monoexcited and 10 lowest biexcited configurations were included in our calculations. There was used the experimental geometry [2] for all the studied systems.

A. System $\text{CHCl}_3\text{—C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$

From the analysis of the chemical shifts by the interaction of chloroform with aromatic compounds follows the formation of specific complex $\text{CHCl}_3\text{—aromatic molecule}$ [3—7]. Such symmetric model was used for the calculation of interaction energy in the system $\text{CHCl}_3\text{—C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$. The geometry of mutual approach of investigated molecules is shown in Fig. 1. The minimum of the total energy lies at the distance $d = 0.2651$ nm between two parallel planes (Fig. 1). Its value is lower than the sum of van der Waals radii for atoms C and Cl ($R_{\text{C}} = 0.165$ nm, $R_{\text{Cl}} = 0.165$ nm). The interaction energy for the optimum distance is $\Delta E = -29.09$ kJ mol⁻¹.

B. System $\text{CCl}_4\text{—C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$

The symmetric model for mutual approach of carbon tetrachloride and $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$ molecules was used for the calculation of their interaction

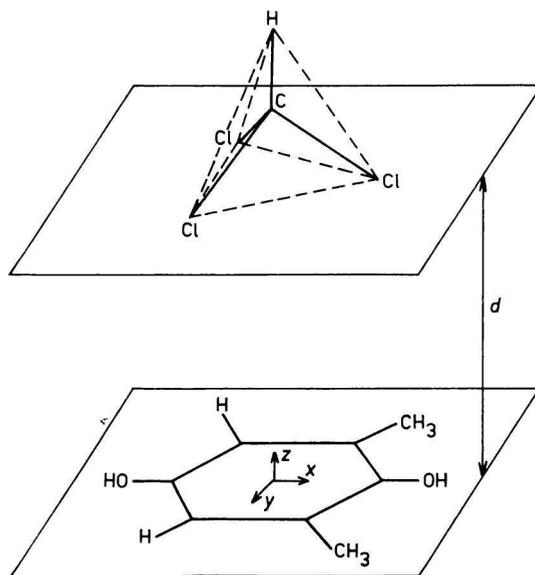


Fig. 1. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and $CHCl_3$ molecules.

energy (Fig. 2). This model follows from the interpretation of the chemical shifts changes by the interaction of carbon tetrachloride with various aromatic compounds [4—7]. The minimum of the total energy lies at $d=0.295$ nm. The interaction energy at this distance is $\Delta E = -18.08$ kJ mol⁻¹. The optimum distance is only a little lower than the sum of van der Waals radii of carbon and chlorine atoms ($R_C=0.165$ nm, $R_{Cl}=0.165$ nm).

C. System benzene— $C_6H_2(CH_3)_2(OH)_2$

By the interpretation of the ¹H-n.m.r. spectra of aromatic compounds [8—10] it was found out that there are formed the associates bonded through delocalized π systems of the benzene rings. Therefore, the symmetric model (Fig. 3) was used for the calculation of interaction energy of the benzene molecule with $C_6H_2(CH_3)_2(OH)_2$ molecule. The minimum of the total energy lies at the distance $d=0.305$ nm and at this distance the interaction energy is $\Delta E = -12.06$ kJ mol⁻¹.

D. System toluene— $C_6H_2(CH_3)_2(OH)_2$

By the calculation of interaction energy of toluene molecule with $C_6H_2(CH_3)_2(OH)_2$ molecule the model in which both aromatic rings are situated

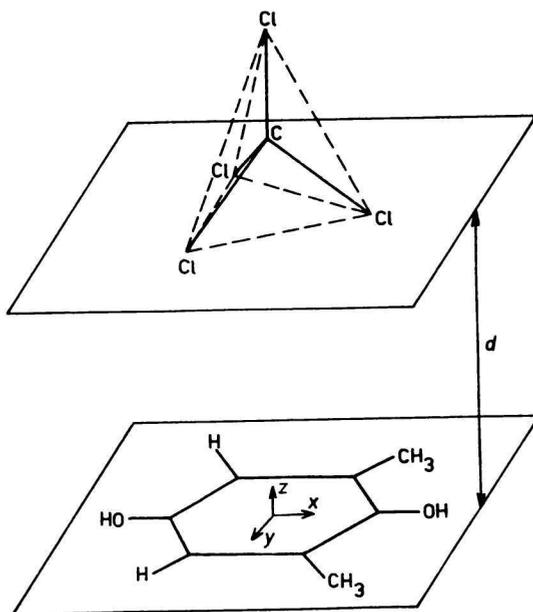


Fig. 2. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and CCl_4 molecules.

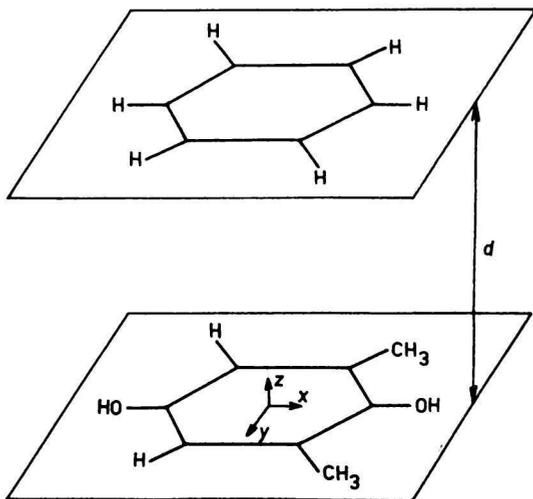


Fig. 3. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and benzene molecules.

symmetrically in the parallel planes [8—10] was proposed (Fig. 4). For the optimum distance $d = 0.295$ nm the interaction energy is $\Delta E = -18.92$ kJmol⁻¹.

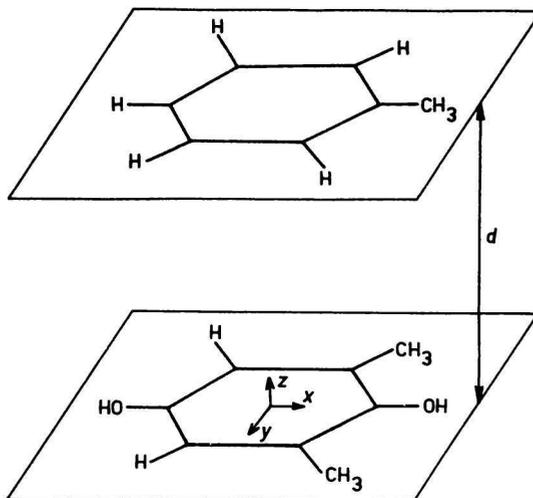


Fig. 4. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and toluene molecules.

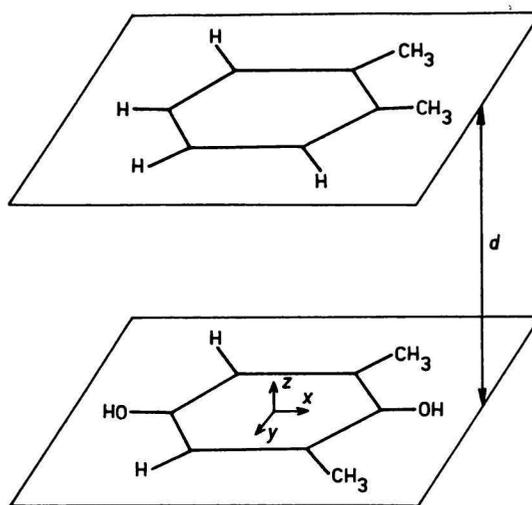


Fig. 5. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and 1,2-xylene molecules in configuration A.

E. System 1,2-C₆H₄(CH₃)₂—C₆H₂(CH₃)₂(OH)₂

For the interaction of mentioned molecules there was chosen again the model in which aromatic rings of both interacting molecules lie in the parallel planes [8—10]. Due to the asymmetry of 1,2-xylene molecule we have studied two various configurations of this molecule with respect to C₆H₂(CH₃)₂(OH)₂ molecule (Figs. 5 and 6). The optimum distance for configuration A is $d = 0.280$ nm and the interaction energy at this distance is $\Delta E = -19.60$ kJ mol⁻¹. The optimum distance for configuration B is also $d = 0.280$ nm with interaction energy $\Delta E = -19.67$ kJ mol⁻¹.

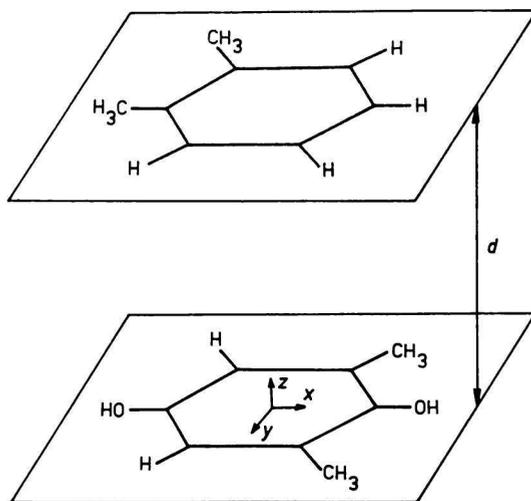


Fig. 6. Mutual orientation of C₆H₂(CH₃)₂(OH)₂ and 1,2-xylene molecules in configuration B.

F. System 1,3-C₆H₄(CH₃)₂—C₆H₂(CH₃)₂(OH)₂

Due to the asymmetry of the 1,3-C₆H₄(CH₃)₂ molecule there were studied two different configurations of this molecule with respect to C₆H₂(CH₃)₂(OH)₂ molecule (Figs. 7 and 8). The common feature of these two configurations is that the interacting molecules lie in mutual parallel planes [8—10]. The optimum distance for configuration A is $d = 0.280$ nm with interaction energy $\Delta E = -19.13$ kJ mol⁻¹, while for configuration B the optimum distance is $d = 0.290$ nm and interaction energy $\Delta E = -19.17$ kJ mol⁻¹.

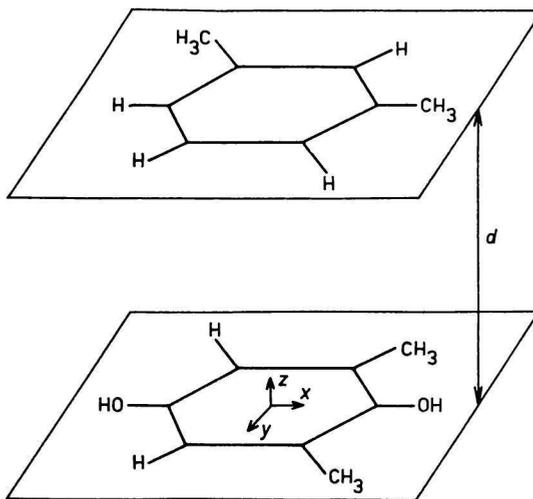


Fig. 7. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and 1,3-xylene molecules in configuration A.

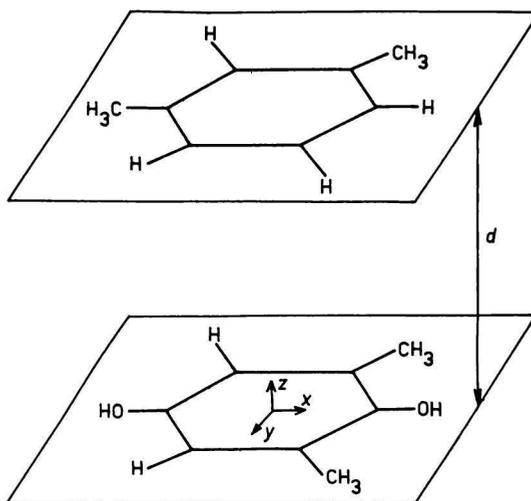


Fig. 8. Mutual orientation of $C_6H_2(CH_3)_2(OH)_2$ and 1,3-xylene molecules in configuration B.

G. System $1,4\text{-C}_6\text{H}_4(\text{CH}_3)_2\text{—C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$

The geometry of mutual approach of investigated molecules is in Fig. 9. As 1,4-xylene molecule is a symmetric molecule, it is sufficient to consider only one possible configuration. For the optimum distance $d = 0.290$ nm the interaction energy is $\Delta E = -18.71$ kJ mol⁻¹.

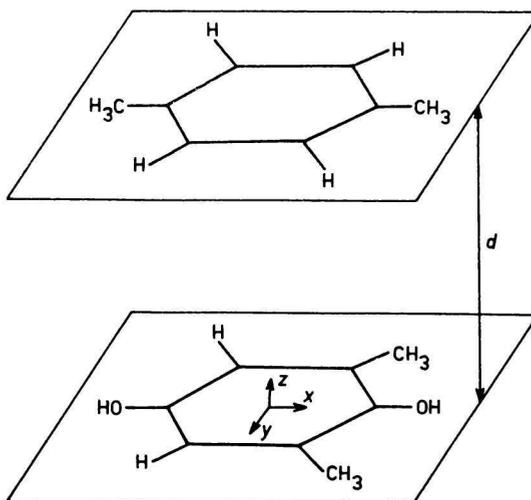


Fig. 9. Mutual orientation of $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$ and 1,4-xylene molecules.

Discussion

The calculation of intermolecular interactions in liquid phase strikes on the serious problems because there is a great number of molecules with various space orientations in mutual interactions. Despite of this there was found a good correlation between experimental data of intermolecular interactions in liquid phase and theoretically calculated values of interaction energy of couple molecules of respective liquid [11]. Calculations of this kind grant us also possibility of physical interpretation of the essence of the corresponding interactions.

Such a model of the couple molecules in mutual interaction was chosen for the calculation of the interaction of PPO (this was approximated by the $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{OH})_2$ molecule which well reproduces the electron density distribution in PPO) with various solvents (chloroform, carbon tetrachloride, benzene, toluene, xylenes). The above-mentioned CNDO/2 method was used for all

calculations. The dispersion energy inclusion was ensured by using the limited configuration interaction method. The most important results of our calculation are summarized in Table 1.

Table 1

Calculated characteristics of the intermolecular associates of $C_6H_2(CH_3)_2(OH)_2$ molecule with solvent molecules and experimental values of χ parameter of the interaction of PPO with solvents

Molecule	d/nm	Q/e	$E/kJmol^{-1}$	χ
$CHCl_3$	0.265	-0.0037	-29.09	0.482
CCl_4	0.295	-0.0013	-18.08	—
C_6H_6	0.305	+0.0002	-12.06	0.468
$C_6H_5CH_3$	0.295	+0.0006	-18.92	0.474
1,2- $C_6H_4(CH_3)_2^*$	0.280	+0.0004	-19.63	0.475
1,3- $C_6H_4(CH_3)_2^*$	0.285	+0.0008	-19.17	0.475
1,4- $C_6H_4(CH_3)_2$	0.290	+0.0013	-18.50	0.474

* The average values of configurations A and B.

Interaction of polar molecule $CHCl_3$ ($\mu_{calc} = 0.402 \times 10^{-30}$ Cm, $\mu_{exp} = 0.359 \times 10^{-30}$ Cm) with $C_6H_2(CH_3)_2(OH)_2$ molecule gives rise to the charge transfer complex ($\Delta E = -29.09$ kJmol $^{-1}$, $\Delta Q = -0.0037$ e, $d = 0.265$ nm). Its formation is conditioned partly by suitable energy values of frontier orbitals of the reacting molecules (Table 2) and partly by the strong polarizability of π -electron system of $C_6H_2(CH_3)_2(OH)_2$ molecule. The important factor for the stabilization of this

Table 2

Numerical values of energies (E/eV) of frontier orbitals of interacting molecules

Molecule	HOMO-2	HOMO-1	LUMO-1	LUMO-2
$CHCl_3$	-14.18	-14.18	+0.69	+1.87
CCl_4	-14.05	-14.05	+2.57	+2.57
C_6H_6	-13.32	-13.32	+4.55	+4.55
$C_6H_5CH_3$	-13.33	-12.38	+4.27	+4.55
1,2- $C_6H_4(CH_3)_2$	-12.70	-12.22	+4.21	+4.53
1,3- $C_6H_4(CH_3)_2$	-12.80	-12.06	+4.16	+4.40
1,4- $C_6H_4(CH_3)_2$	-13.08	-11.67	+4.04	+4.55
$C_6H_4(CH_3)_2(OH)_2$	-11.73	-9.72	+4.01	+4.98

associate is also the considerable diffusion of chlorine d orbitals, which due to their symmetry enable effective overlap with the π -electron system of $C_6H_2(CH_3)_2(OH)_2$ molecule.

An interesting result was achieved by the calculation of interaction of CCl_4 molecule with $C_6H_2(CH_3)_2(OH)_2$ molecule. Due to the interaction of couple nonpolar molecules there are only forces of dispersion character there. The creation of a relatively energy advantageous association of these molecules ($\Delta E = -18.08 \text{ kJ mol}^{-1}$, $d = 0.295 \text{ nm}$) may be explained by the strong polarizability of the π -electron skeleton of $C_6H_2(CH_3)_2(OH)_2$ molecule as well as of the highly symmetric tetrahedral CCl_4 molecule with strongly diffuse (and consequently easily polarizable) d orbitals of chlorine atoms. Stabilization of this system is supported also by a suitable symmetry of chlorine d orbitals which enables effective overlap with π -electron packing of $C_6H_2(CH_3)_2(OH)_2$ molecule. Owing to these facts the values of dispersion forces by the interaction of the given molecules are relatively high.

The lowest interaction energy was obtained for the system benzene— $C_6H_2(CH_3)_2(OH)_2$ ($\Delta E = -12.06 \text{ kJ mol}^{-1}$, $d = 0.305 \text{ nm}$). This result is not startling despite of the strong polarizability of π -electron systems of interacting molecules. Due to the planar structure of these molecules this polarizability is considerably anisotropic and its substantial part is orientated in mutual planparallel planes. The stability of the system is so conditioned by only weak dispersion forces which are supported by effective overlap of π -electron clouds of the interacting molecules.

Considerable stability of associates of $C_6H_2(CH_3)_2(OH)_2$ molecule with toluene molecule ($\Delta E = -18.92 \text{ kJ mol}^{-1}$), 1,2-xylene molecule ($\Delta E = -19.63 \text{ kJ mol}^{-1}$), and also 1,3-xylene molecule ($\Delta E = -19.17 \text{ kJ mol}^{-1}$) is supported partly by nonzero dipole moments of these molecules ($\mu_{\text{tolu}} = 0.033 \times 10^{-30} \text{ Cm}$, $\mu_{1,2\text{-xyl}} = 0.051 \times 10^{-30} \text{ Cm}$, $\mu_{1,3\text{-xyl}} = 0.048 \times 10^{-30} \text{ Cm}$) and partly by strong polarizability of these molecules, which is in comparison to benzene molecule increased by hyperconjugation effect of methyl groups. Therefore, the stability of the above-mentioned systems will be caused by forces of dispersion and induction character.

In the case of interaction of $C_6H_2(CH_3)_2(OH)_2$ molecule with nonpolar 1,4-xylene molecule the interaction energy is smaller ($\Delta E = -18.92 \text{ kJ mol}^{-1}$) than by the interaction with polar toluene, 1,2-xylene, and also 1,3-xylene molecules since there only dispersion forces contribute to the stabilization of systems. In comparison with benzene molecule the magnitude of these forces is much greater due to the increase of polarizability of this molecule caused by effective hyperconjugation effect of both methyl groups.

The values of theoretically obtained interaction parameters ΔE for all studied

model systems are in a good agreement with experimental values of χ parameter [12] (Table 1). The linear correlation of these quantities (correlation coefficient is 0.9919) indicates the suitability of the selection of model systems as well as of the used method which, however, does not give accurate quantitative results, but correctly reflects trends in the chemically similar systems.

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