

Optimum geometry of polychlorinated biphenyls *in vacuo*, solution and in the course of adsorption

^aV. JAKUŠ and ^bS. MIERTUŠ

^a*Department of Organic Technology, Faculty of Chemical Technology, Slovak Technical University, Detached Laboratory in Research Institute for Petrochemistry, CS-97104 Prievidza*

^b*Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, CS-81237 Bratislava*

Received 26 May 1989

The optimum geometry of the polychlorinated derivatives of biphenyl (PCB) was studied by the method of empirical potentials. It has been found for isolated molecules that the optimum values of the torsion angle are $\Theta = 48^\circ$ for biphenyl and its derivatives without Cl atoms in *ortho*-position, $\Theta \approx 68^\circ$ for PCB with one Cl atom in *ortho*-position, and $\Theta \approx 79^\circ$ for PCB with two Cl atoms in *ortho*-positions. The influence of solvation on the value of Θ was modelled by using continuum model and it was disclosed that owing to solvation the value of Θ increased by $6-7^\circ$ for the first group of derivatives, by $5-6^\circ$ for the second group and by 2° for the third one. The simulation of PCB adsorption on a surface representing stationary nonpolar phase in HPLC has shown that adsorption brings about greater changes in the values of Θ , *i.e.* by $7-10^\circ$ in the first and second group and by $5-6^\circ$ in the third group of PCB derivatives. The obtained results were used for interpreting the retention data of PCB in chromatography.

С помощью метода эмпирических потенциалов была исследована оптимальная геометрия хлорпроизводных бифенила (PCB). Было обнаружено, что в случае изолированных молекул оптимальное значение торсионного угла Θ равняется 48° для бифенила и производных без атомов Cl в *орто*-положении, для PCB с одним атомом Cl в *орто*-положении $\Theta \approx 68^\circ$, для PCB с двумя атомами Cl в *орто*-положении $\Theta \approx 79^\circ$. С помощью непрерывной модели моделировалось влияние сольватации на величину Θ . Обнаружено, что сольватация приводит к увеличению величины Θ для производных первой группы на $6-7^\circ$, второй на $5-6^\circ$ и третьей на 2° . Моделирование адсорбции PCB на поверхности, представляющей собой стационарную неполярную фазу в ВЭЖХ показало, что адсорбция приводит к большим изменениям величин Θ : на $7-10^\circ$ в первой и второй группе и на $5-6^\circ$ в третьей группе производных PCB. Полученные результаты были использованы при интерпретации данных по временам удерживания PCB в хроматографии.

The polychlorinated biphenyls (PCB) are industrially produced since 1930 and are widely used in different branches of chemical, electrotechnical and engineering industry. They are toxic and exceedingly stable in nature and for this reason they accumulate as pollutants of environment in soil, water and atmosphere and subsequently expand into noncontaminated regions. As for biphenyl and its derivatives, the problem of mutual twist of the phenyl rings of molecule has been investigated in many experimental [1—8] and theoretical [9—21] studies. The twist is characterized by internal torsion angle Θ (Fig. 1).

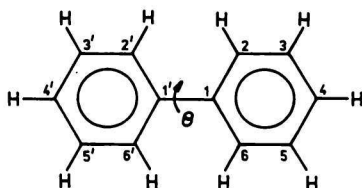


Fig. 1. Basic structure and numbering of atoms in biphenyl.

The theoretical calculation of the torsion angle Θ was carried out by different methods [9—21]. It results from these papers that the quantum-chemical semi-empirical methods are not suited for studying the molecule of biphenyl while the methods based on application of empirical potentials are more convenient for this purpose. The theoretically calculated values of the torsion angle of biphenyl vary within the range 16—90°. Recently, the *ab initio* calculations of the torsion angle of biphenyl were published [22—25]. They are in good agreement with the experimental value $44.4^\circ \pm 1.2^\circ$ [1].

In spite of many communications dealing with the problem of torsion angle of biphenyl, this problem still remains open. The potential curves and barriers to rotation were frequently determined with a lot of simplifications in empirical calculations. For instance, only the van der Waals interactions of the H...H type were taken into account while the interactions of the H...C and C...C type might also play an important role. The influence of medium (solvent) or sorption surface on the torsion angle of the phenyl rings of biphenyl has not yet been paid attention. Therefore the purpose of this study has been to investigate the internal rotation of biphenyl and polychlorinated biphenyls not only in the state of isolated molecules but also in solution and during adsorption on model surface with the aim to estimate the influence of these conditions on the value of Θ . The obtained results were also used for interpreting the interphase partition and chromatographic data of these substances especially with respect to high-performance liquid chromatography on reverse phases within the framework of partition as well as adsorption model of separation [26—28].

Method and models

For studying the internal rotation of biphenyl and PCB we used the method of empirical potential functions according to *Dashevskii* [29]. The reason for using the *Dashevskii* potential functions consisted in the fact that the nonbonding interactions between chlorine atoms, chlorine atom and carbon atom or hydrogen atom were completely parametrized only for these potential functions among their great variety [29—36]. The *Dashevskii* curves of potential functions have the form of the 6-exp type

$$E(r) = -Ar^{-6} + Be^{-Cr} \quad (1)$$

where parameters A , B , C were determined from a great number of structural data found by analysis. In Table 1 the parameters of potential functions of nonbonding interactions are given. In our calculations we took into account the standard geometries of biphenyl and PCB which were taken from paper [37] (except the torsion angle Θ which was optimized). The length of bond between two phenyl rings of biphenyl and PCB taken from paper [9] was kept constant during rotation (Table 2).

Table 1

Parameters of potential functions of nonbonding interactions according to *Dashevskii* [29]

Interaction	$A/(10^{-60} \text{ m kJ mol}^{-1})$	$B/(10^{-5} \text{ m kJ mol}^{-1})$	$C/10^{-10} \text{ m}$
H...H	167.891	1.1974	5.2
H...C	506.603	1.3733	4.13
C...C	1992.917	1.5784	3.513
C...Cl	5945.256	4.7311	3.513
Cl...Cl	12141.720	9.5878	3.513
H...Cl	1909.191	4.3961	4.194

Table 2

Interatomic distances of individual bonds for PCB molecules

Bond	$C_{\text{arom}}-\text{H}$	$C_{\text{arom}}-C_{\text{arom}}$	$C_{\text{arom}}-\text{Cl}$	$\text{C}-1-\text{C}-1'$
$l/\text{\AA}$	1.08	1.40	1.69	1.47

By using the *Dashevskii* empirical potential functions we performed optimization of the torsion angle of biphenyl and PCB as isolated molecules. The total energy of a molecule of biphenyl or PCB was expressed in terms of

dispersion [38], repulsion [39], and torsion energy as follows

$$E_T = E_{\text{disp}} + E_{\text{rep}} + E_{\text{tors}} \quad (2)$$

The torsion energy expresses the change in energy due to change in conjugation of the system and has the form

$$E_{\text{tors}} = \beta_0 \cos \Theta \quad (3)$$

where β_0 is a constant and Θ is the torsion angle of biphenyl or PCB. The value of β_0 is $-16.75 \text{ kJ mol}^{-1}$ for biphenyl and its derivatives, which means that in consistence with paper [9], the barrier to rotation does not exceed the value 20 kJ mol^{-1} for biphenyl.

Then we aimed at estimating the influence of solvent on the change in torsion angle Θ of PCB when passing from isolated molecule to a molecule in polar or nonpolar medium.

The total solvation Gibbs energy of the investigated substance in a given solvent x may be expressed as a sum of electrostatic, dispersion, repulsion, and cavitation contributions as follows

$$\Delta G_{\text{solv}}^x = \Delta G_{\text{elst}}^x + \Delta G_{\text{disp}}^x + \Delta G_{\text{rep}}^x + \Delta G_{\text{cav}}^x \quad (4)$$

Our approach is based on expressing the Gibbs energy of solvation (and its particular components) by means of continuum model. The details concerning the calculation of individual contributions to the Gibbs energy of solvation are given in paper [26].

The influence of adsorption of the investigated substances caught by modelled surface on their own geometry was also investigated. The adsorption energy of the investigated substance adsorbed on modelled surface may be expressed in terms of electrostatic, dispersion, and repulsion contributions as follows

$$\Delta E_{\text{ads}}^{\text{M-P}} = \Delta E_{\text{elst}}^{\text{M-P}} + \Delta E_{\text{disp}}^{\text{M-P}} + E_{\text{rep}}^{\text{M-P}} \quad (5)$$

where M and P denote molecule of adsorbed substance and surface, respectively.

The electrostatic contribution is given by the Coulombic forces operative in the system molecule—surface and can be expressed as follows

$$\Delta E_{\text{elst}}^{\text{M-P}} = -\frac{1}{4\pi\epsilon_0} \sum_i \sum_j \frac{Q_i Q_j}{r_{ij}} \quad (6)$$

where ϵ_0 stands for permittivity of vacuum, Q_i and Q_j are charges of atoms of a molecule of substance or surface, and r_{ij} is the distance between the i -th atom of a molecule of substance and the j -th atom of surface.

Our intention was to investigate the adsorption of biphenyl and PCB on such model surfaces that represent the chemically bonded C_{18} stationary phase used in RP-HPLC. These results are used in paper [28] for interpreting the chromatographic data in RP-HPLC by means of adsorption model. Surface modelling has been made by means of two models denoted P3 and P5 (Fig. 2). Since the ends of the C_{18} chains of chemically bonded phases are usually methyl groups, we decided to simulate these ends by methane molecules in models P3 and P5.

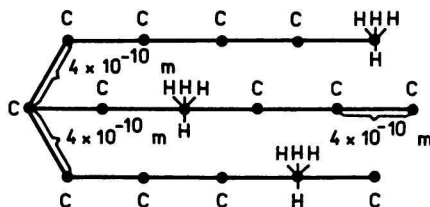


Fig. 2. Model of a section of surface P3 (view from above).

Model P3 consists of methane molecules three hydrogens of which are in tetrahedral arrangement and oriented to the molecule of PCB while the fourth hydrogen is directed to the opposite side. It comprises three rows. In the middle row there are 13 methane molecules distant 4×10^{-10} m from each other while two outer rows contain 12 methane molecules.

Model P5 consists of five rows of methane molecules, the number of methane molecules in individual rows being 13, 12, 13, 12, 13.

The dispersion and repulsion interactions of a biphenyl molecule or PCB with model surface were also studied by the Dashevskii method of empirical potential functions and the adsorption energies (eqn (5)) were calculated accordingly.

Results and discussion

We found by analysis of the dependence of total energy E_T of a molecule of biphenyl on torsion angle (Fig. 3) that the minimum of this energy (in isolated state) is at the torsion angle Θ equal to 48° . The calculated barriers to rotation ΔE for torsion angles $\Theta = 0^\circ$ and $\Theta = 90^\circ$ are equal to $19.00 \text{ kJ mol}^{-1}$ and 7.89 kJ mol^{-1} , respectively. A great number of papers the review of which is presented by Häfelinger and Regelmann in paper [24] have been concerned with these problems. Special attention is to be paid to *ab initio* calculations [24, 25] on the basis of which it has been found that the value of torsion angle is equal to 45.4° and the barriers to rotation ΔE for torsion angles $\Theta = 0^\circ$ and $\Theta = 90^\circ$ are $13.51 \text{ kJ mol}^{-1}$ and 6.91 kJ mol^{-1} , respectively.

The analysis of the dependence of total energy E_T of a molecule of 2-chlorobiphenyl on torsion angle Θ has shown that the minimum of this energy is at the torsion angle equal to 68° . The barriers to rotation ΔE calculated for torsion angles $\Theta = 0^\circ$ and $\Theta = 90^\circ$ are $506.274 \text{ kJ mol}^{-1}$ and $3.968 \text{ kJ mol}^{-1}$, respectively.

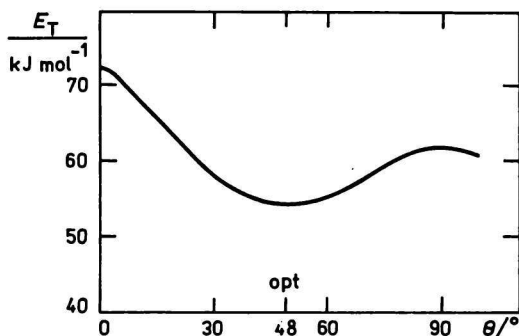


Fig. 3. Dependence of total energy E_T of biphenyl on torsion angle.

It is obvious that the substitution in individual positions by chlorine atoms results in a change in the value of Θ . By searching for minima of the total energy of PCB we obtained the values of the optimized torsion angles (*in vacuo*) given in Table 3. The polychlorinated biphenyls may be divided into three classes. The first class is represented by biphenyl and those PCBs which have no chlorine atoms in *ortho*-positions and exhibit the optimum torsion angle of about 48° . The second class comprises those PCBs which have a chlorine atom only in one *ortho*-position with the optimum torsion angle of about 68° . The third class is represented by those PCBs which are substituted by chlorine atoms in both *ortho*-positions and exhibit the optimum torsion angle of about 79° . Similar results obtained by *ab initio* calculations were also published by McKinney *et al.* [22] who found an extremely high barrier at 0° (and 180°) for *ortho*-substituted PCBs as well as a shift in energy minimum (from original 42° for biphenyl) towards 90° .

Furthermore, we used the method regarding the influence of medium (continuum model) and attempted to estimate the influence of solvent on the change in torsion angle Θ accompanying the passing from isolated molecule to a molecule in polar medium. For studying the influence of solvation on torsion angle we chose three derivatives, namely: biphenyl, 2,5,4'-trichlorobiphenyl, and 2,2',4,5'-tetrachlorobiphenyl which represented the above-mentioned three classes of compounds. For biphenyl with the values of torsion angle $\Theta = 18^\circ$, 33° , 48° , 53° , and 58° the Gibbs solvation energies and their particular contributions calculated for water and octanol, the total energy E_T of biphenyl molecule

Table 3

Homogeneous series of PCB with optimized torsion angle θ

Compound	Substituent	$\theta/^\circ$
I	H	48
II	2-Cl	68
III	2,2'-Cl	79
IV	2,3'-Cl	68
V	2,6-Cl	73
VI	2,5,4'-Cl	68
VII	2,4,4'-Cl	68
VIII	2,5,3'-Cl	67
IX	2,3,2',3'-Cl	78
X	2,3,2',5',-Cl	79
XI	3,4,3',4'-Cl	47
XII	2,5,2',5'-Cl	79
XIII	2,5,3',4'-Cl	67
XIV	2,4,2',5'-Cl	79
XV	2,4,2',4'-Cl	79
XVI	2,3,4,2',5'-Cl	79

and energy ΔG_{sum}^x which represents the sum of Gibbs solvation energy and energy of biphenyl molecule (*in vacuo*) ($G_T \approx E_T$) are presented for illustration in Table 4.

The analysis of the relationship between ΔG_{sum}^x (*i.e.* $G_T + G_{\text{solv}}^x$) and torsion angle of biphenyl has shown that the minimum shifts to higher torsion angle, *i.e.* 55.4° or 54.1°. However, the difference between energies ΔG_{sum}^x calculated for torsion angles 48° and 55.4° or 54.1° is small (Table 5). Similar situation was also

Table 4

Calculated values of the Gibbs solvation energies and individual contributions in water (w), total Gibbs energies (*in vacuo*) and sums of total and solvation Gibbs energy for biphenyl molecule

$\Delta G / (\text{kJ mol}^{-1})$	$\theta/^\circ$				
	18	33	48	53	58
ΔG_{elst}^w	-0.65	-0.75	-0.92	-0.98	-1.04
$\Delta G_{\text{disp, rep}}^w$	-93.44	-95.04	-97.90	-98.27	-98.80
ΔG_{cav}^w	87.04	88.11	90.04	90.10	90.43
ΔG_{solv}^w	-7.06	-7.68	-8.77	-9.16	-9.58
G_T	64.23	56.33	54.32	54.52	55.01
ΔG_{sum}^x	57.17	48.64	45.55	45.36	45.43

Table 5

Values of torsion angles of three selected PCB derivatives

Compound	Torsion angle <i>in vacuo</i> $\Theta/^\circ$	Torsion angle in octanol $\Theta/^\circ$	Torsion angle in water $\Theta/^\circ$
<i>I</i>	48	55.4	54.1
<i>VI</i>	68	74.8	73.2
<i>XIV</i>	79	80.6	80.7

observed for further two derivatives of biphenyl (2,5,4'-trichloro- and 2,2',4,5'-tetrachlorobiphenyl). The obtained values of torsion angles *in vacuo*, octanol, and water are listed in Table 5.

The results have shown that the torsion angle increases by about 6—7° for compounds of the first class, by about 5—6° for compounds of the second class, and by about 2° for compounds of the third class with respect to the optimized torsion angle *in vacuo*. Thus we may draw a conclusion that the solvation does not significantly influence the optimum torsion angle of all derivatives of PCB so that the study of solvation (*e.g.* interpretation of partition coefficient $\log P$ [27]) does not necessitate an additional reoptimization of the torsion angle of these derivatives.

Calculation of adsorption energy $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi, \Theta)$

The calculation of the adsorption energy $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi, \Theta)$ for interaction of PCB with model surface was performed with simultaneous optimization of position of PCB with respect to surface by taking into consideration:

a) Translation of PCB molecule with respect to surface characterized by distance r ,

b) rotation of molecule represented by angle φ ,

c) change in torsion angle expressed by angle Θ .

The parameter r represents the perpendicular distance between a carbon atom of surface and the centre of the connecting line of two phenyl rings of biphenyl (Fig. 4).

The angle of rotation is defined as an angle at which the whole molecule of PCB rotates round the axis x counterclockwise from 0° to 360° while four carbon atoms of its skeleton lie on the axis x (Fig. 4). The y — z projection of this rotation is represented in Fig. 5. A molecule of PCB is placed above the model surface so that it can rotate round the coordinate axis x (which is identical with

the axis of molecule and passes through atoms 1,1',4,4') at the angle of rotation φ and come near to the surface in the direction of the axis z (Fig. 4). It is valid $\varphi = 0^\circ$ if the ring of biphenyl denoted by marked numerals is in the xy plane and atoms 5',6' lie in positive direction of the axis y . The optimization of the distance was carried out with a precision of 0.01 Å and the optimization of the angle of rotation φ and torsion angle θ corresponded to a precision of 1° .

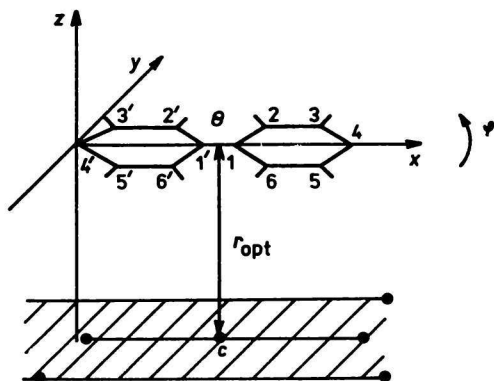


Fig. 4. Interaction of PCB molecule with model surface.

At first, we appreciated how the size of model surface affects the adsorption energy. When molecules of PCB approach the model surface P3 or P5 (without respecting the rotation of molecule and the change in torsion angle of molecule), the values $\Delta E_{\text{ads}}^{\text{M-P}}$ and r_{opt} given in Table 6 are obtained. The adsorption energies calculated for interaction of a molecule of PCB with surface P3 and surface P5 exhibit high statistical dependence (correlation coefficient $r = 0.992$, regression significance $RS = 8308.0$). Thus we can deduce that an increase in surface of the model is not necessary and the model surface P3 is sufficient for further calculations.

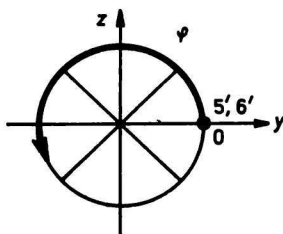


Fig. 5. Projection $y-z$ of the rotation of molecule.

Table 6

Values of adsorption energies $\Delta E_{\text{ads}}^{\text{M-P}}$ for interaction of PCB molecule with surface P3 or P5 and optimized distance r

Compound	$\Delta E^{\text{M-P3}}$	$r_{\text{opt}} / \text{Å}$	$\Delta E^{\text{M-P5}}$	$r_{\text{opt}} / \text{Å}$
I	-29.09	3.91	-30.55	3.91
II	-18.76	5.49	-19.92	5.48
III	-17.56	5.74	-18.81	5.73
IV	-20.06	5.47	-21.50	5.46
V	-17.77	5.63	-18.92	5.62
VI	-20.49	5.47	-21.87	5.46
VII	-21.70	5.45	-23.17	5.45
VIII	-20.66	5.46	-21.87	5.44
IX	-27.14	5.80	-28.91	5.80
X	-26.97	5.82	-28.72	5.81
XI	-33.37	4.70	-35.93	4.69
XII	-19.76	5.72	-21.36	5.71
XIII	-22.18	5.42	-23.87	5.41
XIV	-19.83	5.72	-21.46	5.71
XV	-19.96	5.72	-21.49	5.71
XVI	-28.10	5.81	-29.98	5.81

By optimizing the distance r and the angle of rotation φ (without considering the change in torsion angle Θ) of the PCB molecule interacting with surface P3, we obtain the adsorption energies $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi)$ (Table 7) the values of which are smaller than the values $\Delta E^{\text{M-P}}$ where only the distance r between interacting PCB molecule and surface P3 has been optimized. Table 7 shows that biphenyl exhibits two equally deep minima of $\Delta E_{\text{ads}}^{\text{M-P}}$ at angles $\varphi = 335^\circ$ and 155° , torsion angle $\Theta = 48^\circ$ and optimum distance $r_{\text{opt}} = 3.44 \times 10^{-10}$ m. As for the most stable position of biphenyl to surface, Fig. 6 shows that it assumes the form of roof in $y-z$ projection. The derivative of 3,4,3',4'-tetrachlorobiphenyl belonging to the first class of PCB occupies a similar position in $y-z$ projection as biphenyl. Like biphenyl, the derivatives of PCB belonging to the second and third class always assume positions of roof with respect to surface. Besides the position of biphenyl, the projections of position of 2,3'-dichlorobiphenyl and 2,3,4,2',5'-pentachlorobiphenyl are represented in Fig. 6.

It has been revealed by analysis of PCB positions with respect to surface that the optimum distance of interaction r_{opt} increases with the number of chlorine atoms, which is due to increasing length of the bond between carbon atoms and chlorine atoms of biphenyl. However, the value of adsorption energy (in absolute value) simultaneously increases, which results from stabilizing interaction between chlorine atoms and surface atoms.

Table 7

Calculated values of adsorption energies $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi)$, individual contributions with optimization of distance r and angle of rotation φ (without considering the change in torsion angle Θ) for interaction of PCB molecule with surface P3

Compound	$\Theta/^\circ$	$\varphi/^\circ$	r_{opt} Å	$\Delta E_{\text{elst}}^{\text{M-P}}$ kJ mol ⁻¹	$\Delta E_{\text{disp}}^{\text{M-P}}$ kJ mol ⁻¹	$\Delta E_{\text{rep}}^{\text{M-P}}$ kJ mol ⁻¹	$\Delta E_{\text{ads}}^{\text{M-P}}$ kJ mol ⁻¹
I	48	155	3.44	0.006	-66.22	25.14	-41.07
		335					
II	68	315	3.92	0.013	-66.83	25.43	-41.38
III	79	151	4.10	0.008	-64.41	24.46	-39.94
IV	68	156	3.89	0.013	-70.94	27.12	-43.81
V	68	132	4.01	0.008	-65.75	23.95	-41.81
VI	68	136	3.84	0.008	-83.64	32.14	-51.50
VII	68	145	3.59	0.007	-86.98	32.41	-54.58
VIII	67	146	4.25	0.029	-78.22	30.56	-47.63
IX	78	153	4.10	0.013	-83.56	31.85	-51.70
X	79	319	4.54	0.043	-89.38	35.08	-54.26
XI	47	328	3.49	0.008	-99.40	37.85	-61.55
XII	79	141	4.51	0.025	-71.98	27.74	-44.21
XIII	67	146	4.22	0.033	-85.98	33.93	-52.02
XIV	79	320	4.50	0.031	-75.75	29.11	-46.61
XV	79	152	4.04	0.004	-80.01	29.78	-50.22
XVI	79	319	4.53	0.042	-93.95	36.33	-57.58

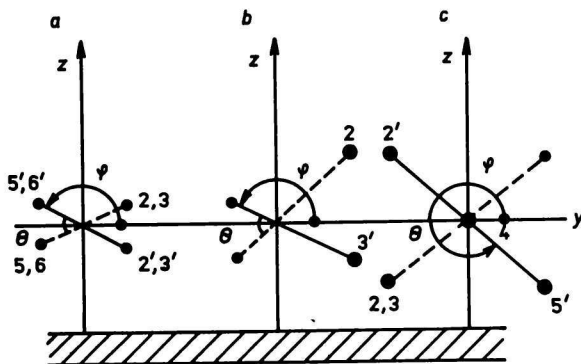


Fig. 6. Projections $y-z$ of a) biphenyl ($\Theta = 48^\circ$, $\varphi = 155^\circ$), b) 2,3'-dichlorobiphenyl ($\Theta = 68^\circ$, $\varphi = 156^\circ$), and c) 2,3,4,2',5'-pentachlorobiphenyl ($\Theta = 79^\circ$, $\varphi = 319^\circ$).

Table 8

Calculated values of adsorption energies $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi, \Theta)$, individual contributions with optimization of distance r , angle of rotation φ and the change in torsion angle Θ for interaction of PCB molecule with surface P3

Compound	$\Theta/^\circ$	$\varphi/^\circ$	$\frac{r_{\text{opt}}}{\text{Å}}$	$\frac{\Delta E_{\text{elst}}^{\text{M-P}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{\text{disp}}^{\text{M-P}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{\text{rep}}^{\text{M-P}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta E_{\text{ads}}^{\text{M-P}}}{\text{kJ mol}^{-1}}$
<i>I</i>	39	160	3.35	0.006	-69.36	26.78	-41.90
		340					
<i>II</i>	61	318	3.80	0.011	-69.55	26.18	-42.39
<i>III</i>	75	153	4.03	0.007	-66.13	25.13	-40.51
<i>IV</i>	60	159	3.76	0.01	-75.20	28.89	-45.22
<i>V</i>	65	136	3.85	0.006	-71.80	27.23	-43.18
		316					
<i>VI</i>	58	141	3.67	0.008	-91.04	34.98	-52.85
<i>VII</i>	59	149	3.49	0.01	-92.73	34.78	-56.45
<i>VIII</i>	58	151	4.06	0.031	-83.72	33.03	-48.87
<i>IX</i>	74	154	4.04	0.011	-85.94	33.15	-52.25
<i>X</i>	74	322	4.45	0.042	-90.99	35.49	-54.78
<i>XI</i>	37	340	3.40	0.013	-102.72	39.52	-63.20
		170					
<i>XII</i>	74	143	4.40	0.025	-75.25	29.38	-45.18
<i>XIII</i>	58	151	4.04	0.029	-91.54	35.62	-54.06
<i>XIV</i>	74	320	4.40	0.029	-78.47	30.43	-47.26
<i>XV</i>	72	155	3.93	0.003	-91.56	31.96	-51.87
<i>XVI</i>	74	322	4.43	0.038	-97.16	38.04	-58.48

For simultaneous optimization of distance r , rotation angle φ and torsion angle Θ of a PCB molecule interacting with surface P3 we obtain adsorption energies $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi, \Theta)$ the values of which are lower than values $\Delta E_{\text{ads}}^{\text{M-P}}(r, \varphi)$ (Table 7).

It results from Table 8 that the torsion angles in all three classes of PCB decrease during the adsorption. The change in torsion angle is approximately equal to 9–10° in the first class of PCB, 7–10° in the second class, and 5–6° in the third class. This influence is a little more significant than the influence of solvation on change in torsion angle of PCB molecule (Table 5). It is interesting that the angle increases because of solvation and decreases because of adsorption.

The obtained results have contributed to elucidating the influence of medium (solvent, adsorption surface) and simultaneously have been used for interpreting the values $\log P$ [27] as well as the mechanisms of separation in RP-HPLC [26, 28].

References

1. Almenningen, A., Bastiansen, L., Fernholt, B. N., Cyvin, S. J., and Samdal, S., *Theochem, J. Mol. Struct.* 128, 59, 77, 95, 115 (1985).
2. Eaton, V. J. and Steele, D., *J. Chem. Soc., Faraday Trans. 2*, 1601 (1973).
3. Charbonneau, G. P. and Delugeard, Y., *Acta Crystallogr.*, B33, 1586 (1977).
4. Bonadeo, H. and Burgos, E., *Acta Crystallogr.*, A38, 29 (1982).
5. Bree, A. and Edelson, M., *Chem. Phys. Lett.* 55, 319 (1978).
6. Takeuchi, H., Suzuki, S., Dianoux, A. J., and Allan, G., *Chem. Phys.* 55, 153 (1981).
7. Cailleau, H., Baudour, J. L., and Zeyen, C. M. E., *Acta Crystallogr.*, B35, 426 (1979).
8. Geise, H. J., Lenstra, T. H., De Borst, C., and Moes, G. W. H., *Acta Crystallogr.*, C42, 1176 (1986).
9. Golebiewski, A. and Parczewski, A., *Z. Naturforsch.*, A25, 1710 (1970).
10. Golebiewski, A. and Parczewski, A., *Acta Phys. Pol.* A37, 879 (1970).
11. Almlöf, J., *Chem. Phys.* 6, 135 (1974).
12. Hoffmann, H. J. and Birner, P., *Z. Chem.* 15, 23 (1975).
13. Stoleiv, R. and Thingstad, O., *J. Mol. Struct.* 106, 333 (1984).
14. Casalone, G. L., Mariani, C., Mugnoli, A., and Simonetta, M., *Mol. Phys.* 15, 339 (1968).
15. Lindener, H. J., *Tetrahedron* 30, 1127 (1974).
16. Tinland, B., *J. Mol. Struct.* 3, 161 (1969).
17. Perahia, D. and Pullman, A., *Chem. Phys. Lett.* 19, 73 (1973).
18. Birner, P. and Hoffmann, H. J., *Int. J. Quantum Chem.* 21, 833 (1982).
19. Momicchioli, F., Baraldi, I., and Bruni, M. C., *Chem. Phys.* 70, 161 (1982).
20. Janssen, J. and Lüttke, W., *J. Mol. Struct.* 55, 265 (1979).
21. Koll, A., *Wiadomosci Chem.* 40, 231 (1986).
22. McKinney, J. D., Gottschalk, K. E., and Pedersen, L. G., *Theochem, J. Mol. Struct.* 104, 445 (1983).
23. Pedersen, L. G., Darden, T. A., Oatley, S. J., and McKinney, J. D., *J. Med. Chem.* 29, 2451 (1986).
24. Häfelinger, G. and Regelman, C., *J. Comput. Chem.* 6, 368 (1985).
25. Häfelinger, G. and Regelman, C., *J. Comput. Chem.* 8, 1057 (1987).
26. Miertuš, S., Jakuš, V., and Matisová, E., *Chromatographia* 30, 1720 (1990).
27. Miertuš, S. and Jakuš, V., *Chem. Papers*, in press.
28. Jakuš, V. and Miertuš, S., *Collect. Czechoslov. Chem. Commun.*, in press.
29. Dashevskii, V. G., *Zh. Strukt. Khim.* 11, 912 (1970).
30. Scott, R. A. and Scheraga, N. A., *J. Chem. Phys.* 45, 2091 (1966).
31. Jordan, F., *J. Theor. Biol.* 41, 375 (1973).
32. Kitaigorodskii, A. I. and Mirkaya, K. V., *Kristallografiya* 6, 507 (1961).
33. Magnasco, V., *Nuovo Cimento* 24, 425 (1962).
34. Flory, P. J., Brandt, D. A., and Miller, W. J., *J. Mol. Biol.* 23, 47 (1963).
35. Venkatachalam, C. M. and Ramachandran, G. N., *Conformation in Biopolymers*. (Ramachandran, G. N., Editor.) Vol. 1, p. 83. Academic Press, London, 1967.
36. Poltev, V. I. and Sukhorukov, B. I., *Zh. Strukt. Khim.* 9, 298 (1968).
37. Pople, J. A. and Beveridge, L., *Approximate Molecular Orbital Theory*. McGraw Hill, Book Company, New York, 1970.
38. London, F., *Z. Phys.* 63, 245 (1930).
39. Born, M. and Mayer, J. E., *Z. Phys.* 75, 1 (1932).

Translated by R. Domanský