Journal of Inclusion Phenomena and Macrocyclic Chemistry **46:** 19–25, 2003.

Complexation of Calix[4]arenephosphonous Acids with 2,4-Dichlorophenoxyacetic Acid and Atrazine in Water

O.I. KALCHENKO[1], A.V. SOLOVYOV[1], S.A. CHERENOK[1], N.F. STARODUB[2] and V.I. KALCHENKO[2,*]

[1] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya, 5, 02094, Kiev-94, Ukraine (E-mail: vik@ukrpack.net);* [2] *Palladin Institute of Biochemistry, National Academy of Sciences of Ukraine, Leontovicha, 9, 02030, Kiev-30, Ukraine*

(Received: 6 March 2002; in final form: 6 April 2003)

Key words: atrazine, calix[4]arenephosphonous acids, 2,4-dichlorophenoxyacetic acid, guest–host complexes, reversed phase HPLC

Abstract

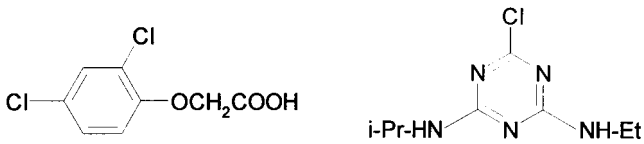
Calix[4]arene phosphonous acids possessing two or four dihydroxyphosphoryl groups linked with the *para*-positions of the macrocyclic skeleton directly or by an aminomethyl spacer have been synthesised and their complexation with the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) or atrazine (AT) in water has been investigated by the reversed phase HPLC method. The association constants of the 1 : 1 guest–host complexes of the herbicides (guest) with the calixarenes (host) in the range 772–5077 M^{-1} (2,4-D) and 2513–6785 M^{-1} (AT) have been determined from the relationship between the capacity factor of the guest and concentration of the calixarene host in the mobile phase. The association constants are dependent on the conformation and stereochemical mobility of the calixarene skeleton, the number of the dihydroxyphosphoryl groups at the upper rim, as well as the acid-base properties of the guest. Hydrophobic, electrostatic, and π-π-aromatic interactions in the guest–host complexes are discussed.

Introduction

Calixarenes, bowl-shaped macrocyclic compounds synthesized by condensation of *para*-substituted phenols with formaldehyde, are versatile platforms in the design of molecular receptors capable to recognize, bind and separate cations or anions or neutral organic molecules similar in size and properties [1, 2]. Water-soluble calixarene derivatives which can mimic enzymes have attracted much interest during the last decade [3].

The water-soluble derivatives have been synthesized by functionalisation of the calixarene lower or upper rim with fragments of glucoside [4], cyclodextrin [5], aminoacid [6], polyethylene glycol [7] or groups such as NR_3^+ [8], CO_2^- [9], SO_3^- [10] and PO_3^- [8, 11]. The sulfocalixarenes are the most investigated compounds within the water-soluble derivatives [3]. Sulfocalixarenes form complexes in water with uranyl–cation (Lg $K > 19$) [12], lanthanides [13], choline and acetylcholine ($Ks = 5 \times 10^4$ to 8×10^4 M^{-1}) [14], as well as with fullerenes [15]. The complexing ability of sulfocalixarenes and other water-soluble calixarenes is the basis of their specific biological activity [16].

In contrast to the sulfocalixarenes, their water-soluble phosphorus analogues are less investigated. The first water-soluble calix[n]arenes bearing proton-



2,4-D AT

Chart 1.

ionisable hydroxyphosphorylmethyl groups at the upper rim [C_{Ar}—CH_2—$P(O)(OH)_2$ were synthesized by Ungaro [11] and Shinkai [8]. Calixarenes possesing dihydroxyphosphoryl groups at the lower rim (C_{Ar}—O—P bond) [17–19] as well as at the upper rim bound to the *para*-positions by hydroxy(amino)methyl spacers [C_{Ar}—CH(X)—P bond] [20] were described recently. Hexakis(dihydroxyphosphorylmethyl)calix[6]arene, similar to sulfocalix[6]arene, is an effective uranophile [21], and cationic dye binder [8]. Amphiphilic calixarenes with dihydroxyphosphoryl groups at the lower [19] or at the upper [22] rim form nanoparticles [22] or stable Langmuir–Blodgett films at the air–water interface [19].

This article reports complexation studies of the water-soluble calix[4]renes, containing dihydroxyphosphoryl groups, linked with the upper rim directly (compounds

* Author for correspondence.

1, **2**) or by an aminomethyl spacer (compound **3**) with 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine (AT) in water solutions.

2,4-D and AT, the effective herbicides, have attracted considerable concerns as an environmental issue since they have been widely used and caused serious pollution in soil and groundwater. Development of selective receptors capable of molecular recognition and specific binding of 2,4-D and AT in water medium is an important stage in the design of sensors for determination of the herbicides in the environment [23, 24] as well as in the design of synthetic polymeric materials for herbicide-selective decomposition [25].

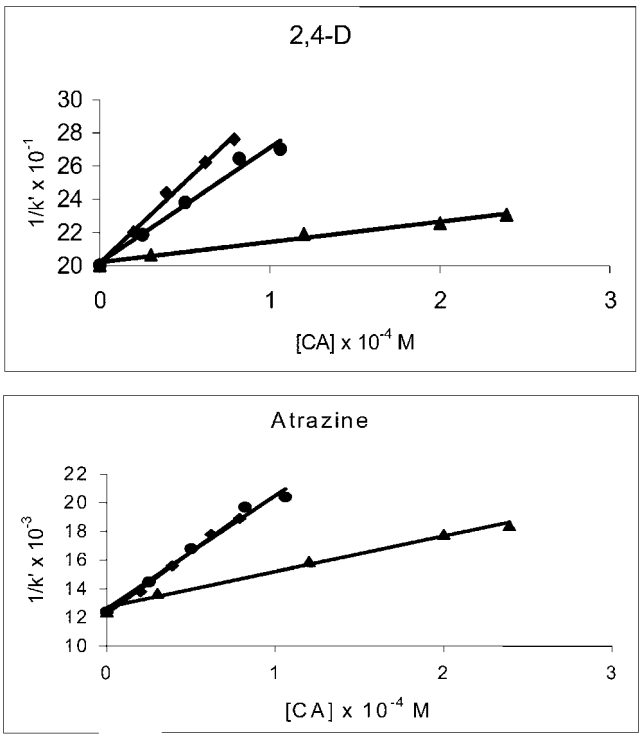


Figure 1. Plots of $1/k'$ *vs* concentration of calixarenes **1**-(●), **2**(▲), **3**(♦) for 2,4-D and AT.

Experimental

Materials

^{1}H NMR and ^{31}P NMR spectra were recorded on a VXR 300 instrument operating at 300 MHz and 121.5 MHz accordingly. The chemical shifts are reported from internal tetramethylsilane and external 85% H_3PO_4 standards. FAB mass spectra were obtained with a double focusing Kratos MS 50S instrument equipped with a standard FAB source and DS 90 data system, using *meta*-nitrobenzyl alcohol as a matrix. The melting point determinations were performed on a Boetius apparatus and are uncorrected.

General procedure of synthesis of calix[4]arene phosphonates **4**, **5**

At 170 °C to a solution of di-, and tetrabromotetrapropoxycalix[4]arene (0.01 mmol) in benzonitrile (10 mL) in presence of $NiBr_2$ (0.002 mmol for each bromine atom of calix[4]arene) the phosphites (0.24, 0.48 mmol accordingly) were added dropwise. The resulting solution was refluxed for 1 h. The reaction mixure was evaporated in vacuum (0.05 mm, 100 °C) to give oil. The oil was solved in methylene chloride and washed with water. Organic phase was dried over Na_2SO_4. Organic solvent was evaporated and resulting compound was purified by crystallization from hexane.

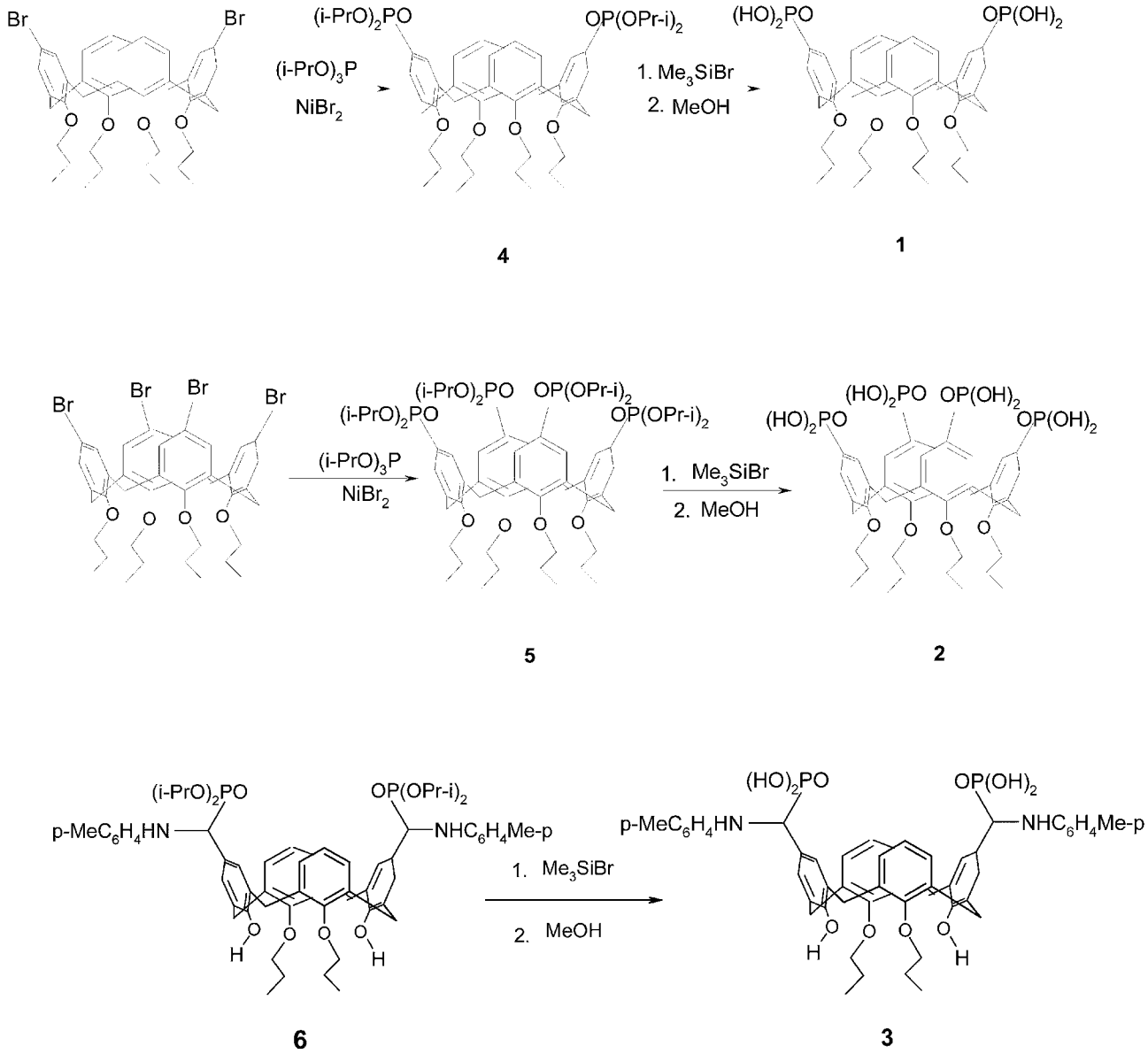
5, 17-Bis(diisopropoxyphosphonyl)-25, 26, 27, 28-tetrapropoxycalix[4]arene (4)
White solid: yield 60%; m.p. 180–182 °C; ^{1}H NMR ($CDCl_3$) 1.23, 1.41 (two d, 6H + 6H, J 7.0 Hz, diastereotopic C*H*$_3$CHP), 1.37 (t, 12H, J 7.0 Hz, C*H*$_3$CH$_2$CH$_2$O), 2.09 (m, 8H, CH$_3$*H*$_3$CH$_2$O), 3.30 (d, 4H, J 13.0 Hz, ArCH$_{2eq}$), 4.03 (t, 8H, J 7.0 Hz, OCH$_2$), 4.46 (d, 4H, J 13.0 Hz, ArCH$_{2ax}$), 4.64 (m, 4H, CH$_3$C*H*OP), 6.83 (t, 2H, J 7.0 Hz, ArH-p), 7.01 (d, 4H, J 7.0, ArH-m), 7.57 (d, 4H, J_{PH} 13.2 Hz, ArH); ^{31}P NMR δ 17.68; MS (CI) m/z 922 (M^+, 100%). M calculated 921.05. Anal. Calcd. for $C_{52}H_{74}O_{10}P_2$: P, 6.72 Found: P, 6.65.

*5, 11, 17, 23-Tetrakis(diisopropoxyphosphonyl)-25, 26, 27, 28-tetrapropoxy-calix[4]arene (***5***)*
White solid: yield 70%; m.p. 200–205 °C; ^{1}H NMR ($CDCl_3$) 0.99 (t,12H, J 7.5 Hz, C*H*$_3$CH$_2$O), 1.08, 1.27 (two d, 12H + 12H, J 7.5 Hz, diastereotopic C*H*$_3$CH), 1.97 (sextet, 8H, J 7.5 Hz, CH$_3$C*H*$_2$CH$_2$O), 3.31 (d, 4H, J 13.0 Hz, ArCH$_{2eq}$), 3.93 (t, 8H, J 7.5 Hz, CH$_2$O), 4.48 (d, 4H, J 13.0 Hz, ArCH$_{2ax}$), 4.55 (octet, 4H, J 7.5 Hz, CH$_3$C*H*), 7.28 (d, 8H, J_{PH} 13 Hz, ArH-m); ^{31}P NMR δ 17.3; MS (CI) m/z 1250 (M^+, 100%). M calculated 1247.88. Anal. Calcd. for $C_{64}H_{100}O_{16}P_4$: C, 61.53; H, 8.07; P, 9.92 Found: C, 61.78; H, 8.08; P, 9.75.

General procedure of synthesis of calixarene phosphonous acids **1**, **2**

Bromotrimethylsilane (0.8 and 1.6 mmol accordingly) was added to a solution of phosphorylated calix[4]arenes **4**, **5** (0.1 mmol) in 5 mL dry chloroform. The reaction mixture was stirred at room temperature for 30 h. The reaction mixture was evaporated under reduced pressure and excess of absolute methanol was added to the residue. The methanol solution was heated at 50 °C for 2 h and the solvent evaporated. The solid residue was dried in vacuum (0.05 mm) for 10 h.

*5, 17-Bis(dihydroxyphosphoryl)-25, 26, 27, 28-tetrapropoxycalix[4]arene (***1***)*
White solid: yield 96%. M.p. 80–85 °C; ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 6H, CH$_2$CH$_2$C*H*$_3$, J 7.5 Hz), 1.1 (t, 6H, CH$_2$CH$_2$C*H*$_3$, J 7.5 Hz), 1.84–2.00 (m, 8H, 1.92 CH$_2$C*H*$_2$CH$_3$), 3.17 (d, 4H, ArCH$_{2eq}$, J 13 Hz), 3.68 (t, 4H, C*H*$_2$CH$_2$CH$_3$, J 7.5 Hz), 4.02 (t, 4H, C*H*$_2$CH$_2$CH$_3$, J 7.5 Hz), 4.44 (d, 4H, ArCH$_{2ax}$, J 13Hz), 6.63 (d, 4H, Ar—H, J_{PH} 14.4 Hz), 6.92 (t, 2H, Ar—H, J 7.2 Hz), 7.14 (d, 4H, Ar—H, J 7.2 Hz), 8.54 (wide s, 4H, OH). ^{31}P NMR δ 24.1;



Scheme 1.

Table 1. Capacity factors of the guests (k') depended on the calixarene concentration in the mobile phase

Guest	[Calixarene] × 10^{-4} M														
	1					**2**					**3**				
	0	0.25	0.50	0.82	1.06	0	0.30	1.20	2.00	2.39	0	0.20	0.39	0.62	0.79
2,4-D	0.499	0.457	0.420	0.378	0.370	0.499	0.484	0.455	0.433	0.433	0.499	0.454	0.410	0.381	0.362
AT	80.65	68.97	59.52	50.76	49.02	80.65	72.99	62.89	56.18	54.35	80.65	72.46	64.10	56.18	52.91

Table 2. Stability constants K_A of the host–guest complexes of 2,4-D and AT with calixarenes **1–3**

Guest	Calixarene host					
	1		**2**		**3**	
	K_A, M^{-1}	RSD, %	K_A, M^{-1}	RSD, %	K_A, M^{-1}	RSD, %
2,4-D	3657	6.18	772	24.22	5077	6.64
AT	6785	7.32	2513	26.58	6483	9.07

MS (FAB) 753 $[M + H]^+$; Anal. Calcd. for $C_{40}H_{50}O_{10}P_2$: C, 63.82; H, 6.69; P, 8.23 Found: C, 63.78; H, 6.65; P, 8.20.

*5, 11, 17, 23-Tetrakis(dihydroxyphosphoryl)-25, 26, 27, 28-tetrapropoxy-calix[4]arene (**2**)*

White solid: yield 92%; m.p. 119-124 °C; ^{1}H NMR ($CDCl_3$) 0.9 (t, 12H, $CH_3CH_2CH_2O$, J 7.5 Hz), 1.75 (m, 8H, $CH_3CH_2CH_2O$), 3.24 (d, 4H, J 13.0 Hz, $ArCH_{2eq}$), 3.86 (t, 8H, $CH_3CH_2CH_2O$), 4.41 (d, 4H, J 13.0 Hz, $ArCH_{2ax}$), 6.92 (d, 8H, J_{PH} 13 Hz, ArH-m); ^{31}P NMR δ 17.1; MS (FAB) 913 $[M + H]^+]^+$; Anal. Calcd. for $C_{40}H_{52}O_{16}P_4$: C, 52.63; H, 5.74; P, 13.57 Found: C, 52.78; H, 5.70; P, 13.52.

RP HPLC analysis

The Liquid Chromatographic system consisted of a high-pressure pump HPP 4001 (Laboratorni Pristroje, Praha, Czehoslovakia) connected to a Rheodyne sample 7120 injector with a 20-μl loop (Rheodyne, Berkeley, CA) and an ultraviolet-visible (UV-vis) detector LCD 2563 (Laboratorni Pristroje, Praha, Czehoslovakia). The column (150 $\times$ 3.3 mm i.d.) was packed with Separon SGX CN (5 μm) (Lachema, Czechoslovakia). The mobile phases (water solution of calixarene **1** at concentrations 0.25, 0.50, 0.82 and 1.06×10^{-4} M, calixarene **2** at concentrations 0.30, 1.20, 2 and 2.39×10^{-4} M, calixarene **3** at concentrations 0.20, 0.39, 0.62 and 0.79×10^{-4} M) were prepared by dissolving each calixarene in distilled water at ambient temperature (22 °C). Each of the concentrations was analysed five times. The concentrations of guest-substances in chromatographic solutions (the mobile phase was used as solvent) were $0.1 \times 10^{-4} - 1.0 \times 10^{-4}$ M. The volume sample injected was 0.5 μl. Each of the samples was analysed 3 times. All chromatograms were obtained at 30 °C. The flow rate was 0.8 mL/min, and the UV detector was operated at 254 nm. The dead time (t_0) was measured with EDTA disodium salt. The mobile phase was equilibrated with each of the investigated calixarene additives during 3 hours before each subsequent analysis.

Results and discussion

Synthesis of calix[4]arene phosphonous acids

The method of preparation of the calixarenephosphonous acids consists of hydrolysis of the corresponding alkyl or silyl esters [8, 11, 19, 20, 22], synthesised by phosphorylation of a calixarene platform.

Calix[4]arene phosphonous acids **1** and **2**, bearing at the upper rim of the macrocycle two or four dihydroxyphosphoryl groups, were synthesised in two steps starting from easily accessible tetrapropyl ethers of dibromocalix[4]arene – or tetrabromocalix[4]arenes [38] respectively (Scheme 1). The first stage is the Ni-catalysed Arbuzov reaction of the bromocalixarenes with triisopropylphosphite [26] that leads to the formation of bis-diisopropoxyphosphoryl- or tetrakis-diisopropoxyphosphorylcalixarenes **4** and **5**. Following consecutive treatment of esters **4** and **5** with trimethylbromosilane and methanol leads to acids **1** and **2** (Scheme 1).

Calix[4]arene diphosphonous acid **3**, in which two dihydroxyphosphoryl groups bound with the *para*-position of the benzene rings of the macrocyclic skeleton by aminomethyl groups, has been prepared recently [20] by a similar interaction of bisdiisopropoxyphosphoryl-*N*-tolylaminomethyldipropoxycalixarene **6** with trimethylbromosilane and methanol.

Calixarene phosphonous acids **1–3** similar to their precursors **4–6** exist in the conformation where all benzene rings of the macrocyclic skeleton are oriented up to the main plane of the macrocycle formed by four methylene links. This conformation is confirmed by observation of two doublets of an AB spin-spin system ($\Delta\delta$ 0.6-1.2 ppm, J_{HH} 13 Hz) of the axial and equatorial protons of the methylene links.

Complexation

The stability constants of the calixarene complexes with organic molecules in solution are usually determined by ^{1}H NMR spectroscopy [27], which detects change of the chemical shifts of the calixarene or guest molecule protons in the process of supramolecular host–guest interaction. However a solubility of calixarene phosphonic acids **1–3** is too poor for investigation by NMR method.

Recently the reversed phase high-performance liquid chromatography method was used for the determination of stability constants of the calixarene inclusion complexes with benzene derivatives [28–31]. Stability constants of complexes of diiminocalix[4]arene [31], dialkoxyphosphoryl derivatives of calix[4,8]arenes [26, 28] or calix[4]resorcinarene [29, 30], with different benzene guests (alkylbenzenes, halogenated benzenes, substituted benzaldehydes, phenols, benzoic acids etc.), as well as stability constants of complexes of sulfocalix[4]arene [32] with aminoacids (Ala, Arg, Asp, Gly, His, Lys, Phe, Pro, Trp, Tyr) in acetonitrile-water or methanol-water media were determined by this method. The stability constants of the benzene derivative complexes are in the range from 17 to 2795 M^{-1} dependent on the medium polarity, calixarene structure, nature, quantity and arrangement of the substituents in the aromatic guest molecules. The stability constants of the complexes of aminoacids with sulfocalix[4]arene are within the range 113–2587 M^{-1}. Utilisation of the HPLC method in the constant determination is based on the change of chromatographic characteristics of the guest-molecules, caused by calixarene additives (host-molecules) in the mobile phase. The detailed procedure of the constants determination is described in [28, 29, 32].

Similar to neutral dialkoxyphosphoryl derivatives of calix[4,8]arenes [26, 28] or calix[4]resorcinarene [29, 31], an addition of proton-ionisable dihydroxyphosphoryl derivatives of calix[4]arenes **1–3** to the water mobile phase leads to decrease of the capacity factors k' of 2,4-D and AT (Table 1). The decrease of the capacity factors is induced by formation of host–guest inclusion complexes which weakens the interaction of the soluble guest-molecules with

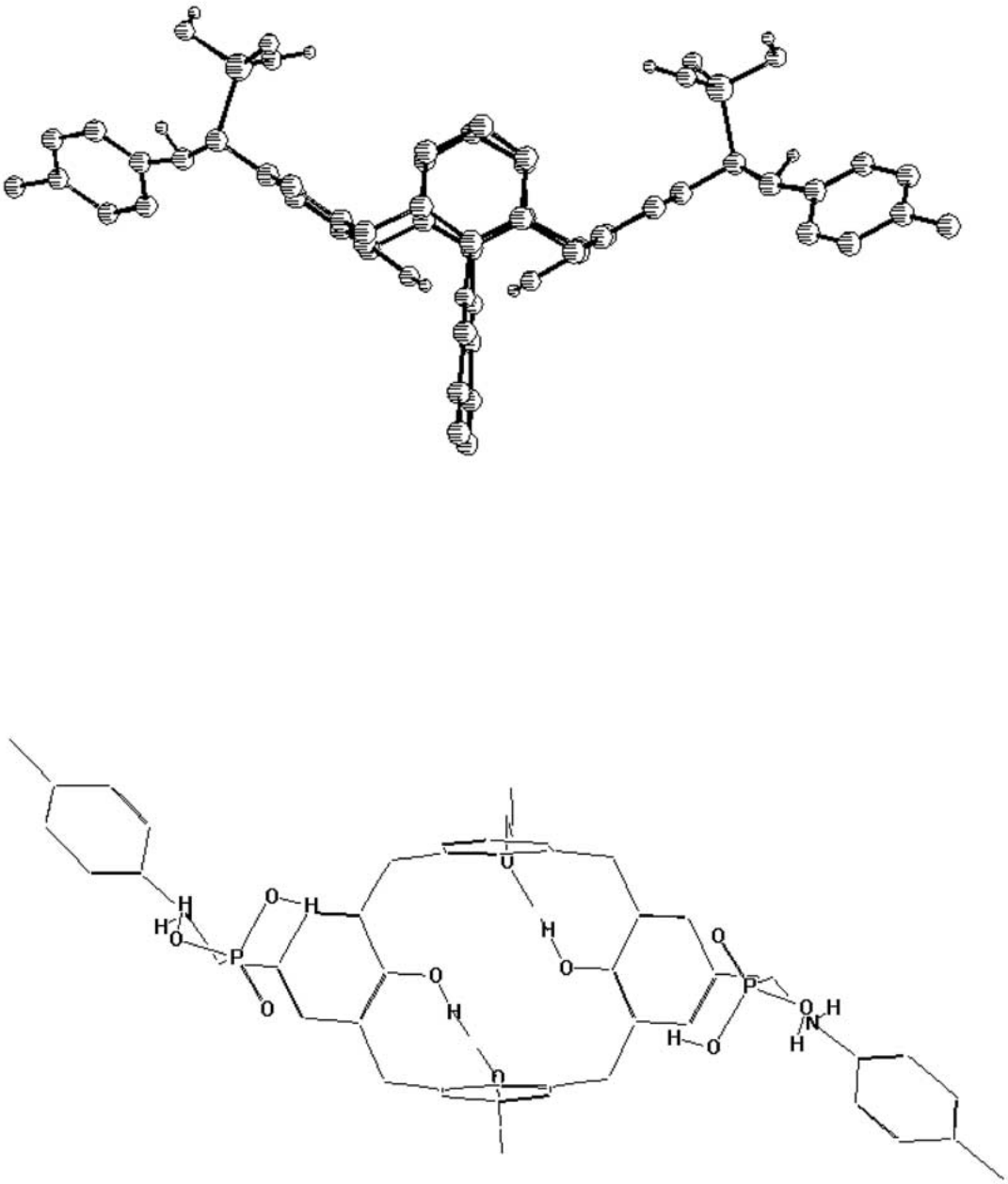


Figure 2. Molecular structure of calix[4]arene diphosphonous acid **3** (side and top view) obtained by MM calculation (PCMODEL, MM+).

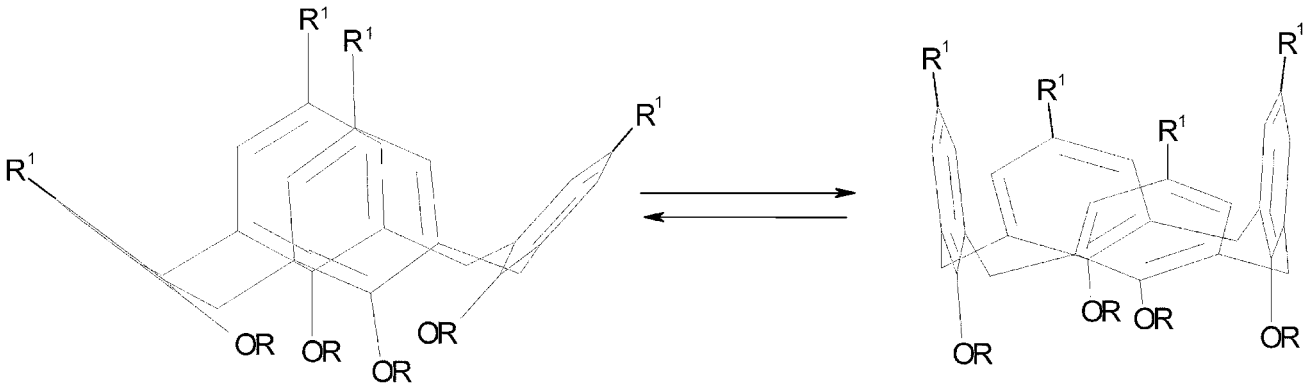


Figure 3. Flattened cone–flattened cone transformation of tetrapropoxycalix[4]arenes.

the stationary phase. The capacity factors of the solutes are decreased when the calixarene concentration in the mobile phase is increased (Table 1). As shown in Figure 1 the straight linear relationship $1/k'$ of 2,4-D or AT versus the calixarene **1–3** concentration (correlation coefficient 0.98–0.99) confirms formation of complexes of 1 : 1 stoichiometry. In this case the stability constants of the complexes K_A can be calculated from the dependence of the $1/k'$ values on the calixarene concentration [CA] in mobile phase by Equation (1).

$$1/k' = 1/k'_0 + K_A \times [\mathrm{CA}]/k'_0, \qquad (1)$$

where k'_0 and k' are the capacity factors in the absence and presence of calixarene in the mobile phase.

In accordance with the K_A values calculated by the equation and collected in Table 2 the complexes stability are determined by the structure of calixarenes **1–3** and the nature of the guest.

It is well known that the host–guest complexation in water solution is governed by the hydrophobic effect, electrostatic and π-π aromatic interactions [33]. In the case of 2,4-D the main role in the complexation with acids **1–3** is played by the hydrophobic effect. However, this effect is decreased by electrostatic repulsion between partially dissociated carboxylic groups of the guest and dihydroxyphosphoryl groups of the host in water. In fact, the stability constant is lowest (772 M^{-1}) for the 2,4-D complex with acid **2**, possessing four negatively charged phosphoryl groups at the upper rim of the macrocycle, repulsing COO^- groups of the guest 2,4-D in water. The higher stability constant of the 2,4-D complex with bis-aminophosphonic acid **3** (5077 M^{-1}) compared with the 2,4-D complex with calixarene diacid **1** (3657 M^{-1}) can be accounted for the larger volume of the molecular cavity of calixarene **3**, which possesses two phosphoryl-*N*-tolylaminomethyl substituents at the upper rim of the macrocycle (Figure 2).

Moreover the host–guest interaction is influenced by preorganization of the calixarene cavity in the complexation process. The macrocyclic skeleton of tetrapropoxycalix[4]arenes existing in the *cone* conformation is stereochemically non rigid due to the rapid conformational mobility between two C_{2v} structures (*flattened cone–flattened cone* interconversion) (Figure 3) [34–36]. Such conformational transformations that weaken the host–guest interaction take place in acids **1** and **2** obtained from tetrapropoxycalix[4]arene. At the same time the molecules of bis-aminophosphonic acid **3** constructed on the base of 1,3-dipropoxycalix[4]arene are stabilised in the stereochemically rigid *flattened-cone* conformation by two strong intramolecular hydrogen bonds ArO—H$\cdots$OPr at the lower rim of the macrocycle (Figure 2) [37]. For molecule **3** in this conformation the guest–host complexes can be stabilised additionally by π-π aromatic interactions of 2,4-D with two calixarene benzene rings oriented perpendicularly to the calixarene reference plane and parallel one to another.

The stability constants of the AT complexes (2513–6785 M^{-1}) are higher compared with the 2,4-D complexes (772–5077 M^{-1}) (Table 2). The nitrogen atoms of the exo-cyclic alkylamino groups of AT can be protonated by acids **1–3**. In this case, together with hydrophobic and π-π aromatic interactions, the electrostatic attraction of the positively charged nitrogen atoms of the guest to the negatively charged phosphoryl groups of the host will play an additional role in the stabilisation of the complexes.

Conclusion

In conclusion, calixarene phosphoric acids **1–3** efficiently bind herbicides 2,4-D and AT in aqueous solutions (K_A 772–6785 M^{-1}) due to their inclusion into the hydrophobic cavity formed by aromatic rings of the macrocyclic skeleton. The conformation and stereochemical rigidity of the calixarene macrocyclic skeleton, hydrophobic and π-π interactions as well as electrostatic forces between host and guest could play the main role in the complex formation.

Acknowledgement

This work was supported by the Ministry of Education and Science of Ukraine through grant 03.07/00045.

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