J Incl Phenom Macrocycl Chem (2008) 60:321–328
DOI 10.1007/s10847-007-9381-5

ORIGINAL ARTICLE

$1^3,1^7,5^3,5^7$-Tetraphenyl-$1^3,1^7,5^3,5^7$-tetrathio-3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane with an unusual conical-like conformation

Anna S. Balueva · Dmitriy V. Kulikov · Roman M. Kuznetsov · Aidar T. Gubaidullin · Louis Ricard · Sergey A. Katsyuba · Tat'yana P. Gryaznova · Andrey A. Karasik · Oleg G. Sinyashin

Received: 11 May 2007 / Accepted: 13 October 2007 / Published online: 6 November 2007

Abstract $1^3,1^7,5^3,5^7$-tetraphenyl-$1^3,1^7,5^3,5^7$-tetrathio-3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane **2b** was obtained by sulfurization of the corresponding macrocyclic tetraphosphine **1b.** The structure of the inclusion complex of tetrasulfide **2b** with DMF was investigated by the X-ray crystal structure analysis. A novel for this type of cyclophanes and relatively rare conical-like conformation of the macrocycle was found. A methyl group from one of the solvating DMF molecules penetrates the macrocyclic cavity of **2b** from the side of the wider rim. According to quantum-chemical simulations, this may be the reason of the unusual conical conformation of **2b** because the cavity of the macrocycles of this type is highly flexible.

Keywords 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4) tetrabenzenacyclooctaphanes · Conformation · Host–guest complexes · Quantum-chemical simulations

Electronic supplementary material The online version of this article (doi:10.1007/s10847-007-9381-5) contains supplementary material, which is available to authorized users.

A. S. Balueva · D. V. Kulikov · R. M. Kuznetsov · A. T. Gubaidullin · S. A. Katsyuba · T. P. Gryaznova · A. A. Karasik (✉) · O. G. Sinyashin
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Arbuzov Str. 8, 420088 Kazan, Russia
e-mail: karasik@iopc.knc.ru

L. Ricard
Laboratoire de Chimie du Phosphore et des Métaux de Transition DCPH Ecole Polytechnique, 91128 Palaiseau Cedex, France

Introduction

The recently synthesized $1^3,1^7,5^3,5^7$-tetra-R-3,7-di-X-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes **1** (R=Ph X=CH_2(**1a**), S(**1b**), SO_2(**1c**); R=Bn, X=CH_2 (**1d**), S (**1e**); R=Mes, X=S (**1f**)) [1–3] are the representatives of [n,1,n,1]-paracyclophanes. These cyclophanes draw an attention mainly as the receptors for different types of organic guests. So the sizes and the shapes of their intramolecular cavities are considered as the important parameters which determine the binding abilities of these macrocycles [4]. The numerous data on the structures of such cyclophanes and their inclusion complexes show that the frameworks of these cyclophanes are not rigid and the mutual arrangement of the phenylene rings of the diphenylmethane (or analogous) fragments varies from the "roof-like" [4–10] to skewed conformations [4, 11–19]. The partially twisted conformations of the spacers are the most typical. Accordingly the cavity's shapes vary from nearly "box-like" (cylindrical) to practically collapsed. Even small peripheral changes of the molecular structure which do not touch the basic macrocyclic framework may cause significant differences in the conformations of similar cyclophanes [4]. Significant changes in the conformations of the macrocycles sometimes are a result of the inclusion complex formation with different guest molecules [11, 20]. It demonstrates the ability of [n,1,n,1]-paracyclophanes to adapt to varying environments. Nevertheless the examples of asymmetrical conical conformations of these macrocycles are relatively rare and such conformations are usually forced by the formation of the inclusion complexes or dimers [4, 21, 22]. The X-ray analysis of four cage macrocycles (**1a**, **1d**, **1e**, **1f**) showed very similar structures with the roof-like conformations of spacers and the box-like cavities for all of

them in spite of the different nature of the bridging groups (CH_2 or S), various substituents at the phosphorus atoms (phenyl, benzyl or mesityl) and the different types of the solvate complexes formed [2, 3]. We proposed that the presence of two heterocyclic fragments probably fixed such conformation of the macrocycles due to the most efficient conjugation of the nitrogen lone electron pairs with π-systems of phenylene rings. The diazadiphosphacyclooctane fragments always adopt chair–chair conformation with the phosphorus lone electron pairs directed inward the cavity [2, 3]. It may be expected that the conversion of these tetraphosphines to the corresponding derivatives (sulfides or oxides) will lead to the partial filling of the macrocyclic cavities. It could lead to the restriction of the guest's access into the cavities of these compounds. Although tetrasulfides (**2a**) and tetraoxides (**3a**) of **1a** had been obtained previously [2] no data on their conformations and "host–guest" complexes are known yet.

We report here the synthesis, the unexpected results of the structural study as well as the quantum-chemical simulations of 3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane (**2b**) with conical-like intramolecular cavity.

Experimental

NMR spectra

MSL-400 (Bruker), standards: ^{31}P NMR (161 MHz): external 85% H_3PO_4; Avance DRX 400 (Bruker), standards: ^{1}H NMR (400 MHz): internal solvent. ^{13}C NMR spectra were of only poor quality due to low solubility; the most indicative signals (those of the CH_2 groups) had only very low intensity. The IR spectra were recorded as nujol mulls on a Specord M-80 spectrometer in the range 400–4,000 cm^{-1}. The melting point was determined on a Boetius apparatus and is uncorrected.

X-Ray structure determination for compound **2b**

Crystals suitable for X-ray diffraction were obtained from a DMF solution of the compound. Data were collected with a Nonius Kappa CCD diffractometer with graphite-monochromated MoK_α radiation (λ 0.71069 Å). The structure was solved by direct methods using SIR 97 [23] and refined with full-matrix least-squares procedures using the program SHELXL-97 [24]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in idealized positions, and no further refinement was applied. Illustrations were made using Platon [25]. Crystallographic data (excluding structure factors) for the structure **2b** have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 607373. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Crystal data

$C_{56}H_{52}N_4P_4S_6$ 6(C_3H_7NO), M 1535.83 g mol^{-1}, monoclinic, a = 27.610(5), b = 12.491(5), c = 23.178(5)Å, $\beta = 90.040(5)°$, $V = 7994(4)Å^3$, $T = 150$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-K_α) 3.07 cm^{-1}, $d_{calc} = 1.28(1)$ g cm^{-3}. A total of 13,743 reflections measured, 10,335 unique ($R_{int} = 0.034$) which were used in all calculations. The final $R(F^2)$ was 0.053 ($>2\sigma I$) and 0.075 (all).

$1^3,1^7,5^3,5^7$-tetraphenyl-$1^3,1^7,5^3,5^7$-tetrathio-3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane 2b

The mixture of 0.2 g (0.21 mmol) of **1b** [3], 0.027 g (0.84 mmol) of sulfur and 10 mL of DMF was heated until the mixture became homogeneous and was allowed to stand overnight. The precipitate formed was filtered off, washed carefully with DMF and MeCN and dried at 0.1 Torr for 2 h. The yield of **2b**: 0.17 g, 75%; mp 250–252 °C. ^{1}H NMR (DMF-d_7): δ 4.75 (dd, $^{2}J_{HH}$ = 15.75 Hz, $^{2}J_{PH}$ = 1.5 Hz, 8H, P–CH_A–N), 5.07 (dd, $^{2}J_{HH}$ = 15.75 Hz, $^{2}J_{PH}$ = 2.1 Hz, 8H, P–CH_B–N), 7.30 (d, $^{3}J_{HH}$ = 8.9 Hz, 8H, o-H in N–C_6H_4), 7.54 (d, $^{3}J_{HH}$ = 8.9 Hz, 8H, m-H in N–C_6H_4), 7.70–8.40 (m, 20H, C_6H_5). ^{31}P {^{1}H} NMR (DMF-d_7): δ 30.41. IR (KBr, nujol, ν/cm^{-1}): 630 (m, $\nu_{P=S}$), 640 (m, $\nu_{P=S}$), 692 (s, $\gamma_{C\text{-}Har}$), 740 (m, $\gamma_{C\text{-}Har}$), 780 (w), 812 (s), 840 (m), 862(m), 900(m), 1000 (w), 1104 (s), 1160 (m), 1212 (s), 1248 (m), 1266 (m), 1280 (w), 1312 (w), 1340 (w), 1376 (s), 1436 (s), 1460 (s), 1500 (vs, $\nu_{C=Car)}$, 1560 (w), 1590 (vs, $\nu_{C=Car}$), 3048 (w, $\nu_{C\text{-}Har}$). Anal. calc. for $C_{56}H_{52}N_4P_4S_6$ [1096]: C 61.31, H 4.74, N 5.11, P 11.31, S 17.52. Found: C 60.85, H 4.82, N 5.02, P 10.88, S 17.98%.

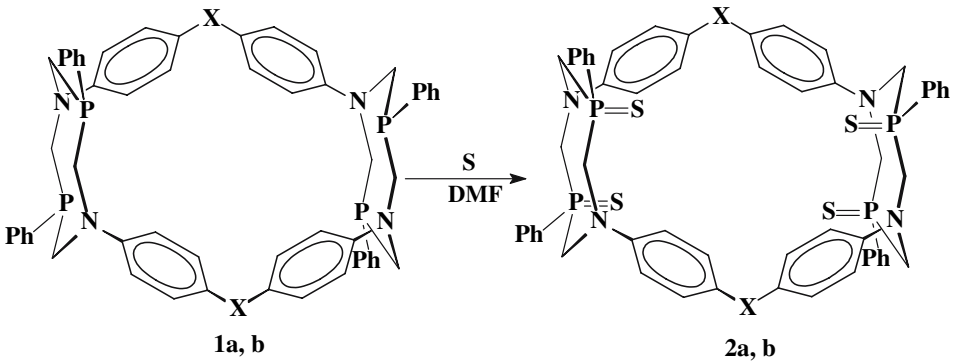
Computations

All quantum-chemical calculations were done using the Gaussian-98 [26] and PRIRODA [27] suites of programs. Density functional theory (DFT) was employed because this approach reproduces accurately geometry parameters, conformational behaviour and vibrational frequencies of 1,5-diaza-3,7-diphosphacyclooctanes [28]. We used Becke's three-parameter exchange functional [29] in

combination with the Lee-Yang-Parr correlation functional [30] and standard 6-31G* basis set (B3LYP/6-31G*), and Perdew-Burke-Ernzerhof functional [31] with basis set "basis1" [27] (PBE/basis1).

Results and discussion

$1^3,1^7,5^3,5^7$-tetraphenyl-$1^3,1^7,5^3,5^7$-tetrathio-3,7-dithia-1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphane **2b** was obtained by the reaction of tetraphosphine **1b** with elementary sulfur in boiling DMF.



X = CH_2 (1a, 2a); S (1b, 2b)

The compound **2b** is highly-melting air-stable solid which is restrictedly soluble only in DMF at the elevated temperature. The structure of the compound **2b** was determined on the basis of IR and NMR spectra. The presence of only one signal at δ_P 30.41 ppm in the ^{31}P NMR spectrum confirms the complete sulfurization of all four phosphorus atoms. It indicates that all of them remain available for the reagent attack up to the completion of the reaction.

The single crystals of **2b** were grown from DMF and the structure was studied by the single-crystal X-ray diffraction analysis, which showed that the convertion of three-coordinated phosphorus atoms to tetracoordinated ones unexpectedly led to more significant changes of the basic macrocyclic framework than of the diazadiphosphacyclooctane fragment's structures (Fig. 1a, b).

The heterocyclic units adopt the chair–chair conformations with the equatorial positions of the phenyl substituents and the axial P=S bonds. The geometrical parameters of the eight-membered rings are changed in comparison with the tetraphosphines **1**: their P–P distances are elongated from 3.84 Å (av. for **1** [3]) to 4.34–4.36 Å whereas N–N distances are shortened from 3.99 Å (av. for **1** [3]) to 3.51–3.56 Å. As a whole the macrocycle **2b** adopts an asymmetrical distorted conical conformation, whereas the conformations of parent tetraphosphines **1** are centrosymmetrical and their cavities can be described as cylinders [3]. The four nitrogen atoms are very roughly at the same plane (the dihedral angle N(1)–N(5)–N(26)–N(22) is 8.2°) and form the reference plane of the macrocycle. Two opposite phenylene rings are near ortogonal to the reference plane (the dihedral angles are 79.0 and 81.4°), whereas two other phenylene fragments are inclined to this plane at the angles of 122.7 and 113.2°. The noticeable divergence is also found for the diazadiphosphacyclooctane fragments: the dihedral angles between their mean planes formed by phosphorus and nitrogen atoms and the reference plane of the macrocycle are 106.3 and 107.5° correspondingly. The divergent phenylene and

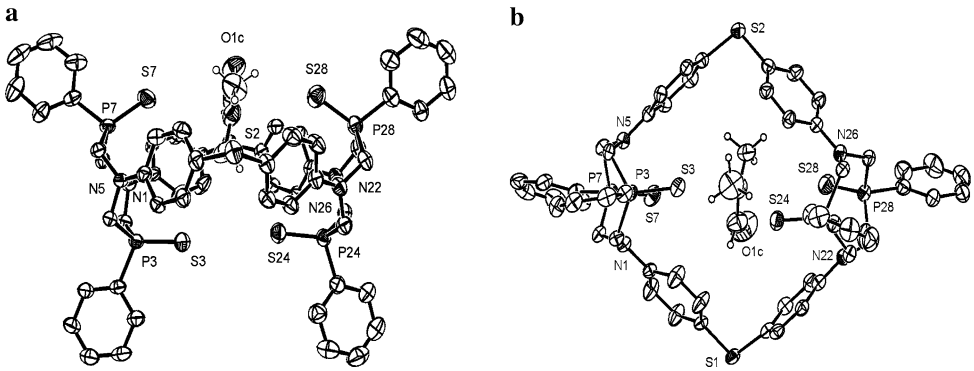


Fig. 1 50% probability ORTEP plot of the molecular structure of compound **2b** and DMF molecule inside the cavity (the position with occupancy 0.51 is shown). H atoms and the other DMF molecules are omitted. (**a**) side view of **2b**; (**b**) top view of **2b**

diazadiphosphacyclooctane fragments form the conical cavity with the pronounced wide and narrow rims. The strong differences in the distances between the corresponding atoms located on the wide and on the narrow rims of the cavity (sulfur and phosphorus atoms and carbon atoms of the divergent phenylene rings) are observed. Namely the distances S(7)–S(28) and S(3)–S(24) are 7.16 and 4.20 Å, the distances P(7)–P(28) and P(3)–P(24) are 10.4 and 7.9 Å, the distances C(13)–C(35) and C(11)–C(31) are 9.4 and 7.3 Å correspondingly. As a result, the bonds P(7)=S(7) and P(28)=S(28) are directed practically outward the cavity, so the cavity becomes available for the inclusion of the guest molecules.

In the crystal of compound **2b** there are six DMF molecules per a molecule of the macrocycle. Two of them are disordered in two positions with relative occupancies 0.51–0.49 and 0.56–0.44. The methyl group of one of the disordered DMF molecules penetrates the macrocyclic cavity from the side of the wider rim (Fig. 1a). The carbon atom of the methyl group of the proximate DMF molecule is near the center of the cavity, the shortest distance between one of hydrogen atoms of the methyl group and sulfur atom S(24) is equal to 2.94 Å. In spite of the disordering, the whole DMF molecule practically lies in the plane, which is perpendicular to the reference plane of macrocycle and passes through two bridging sulfur atoms (Fig. 1b). The position of the methyl group indicates some C–H$\cdots\pi$ interactions like in the case of 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes **1,** which also form the crystalline inclusion complexes with two or one DMF molecules penetrating their cavities [3]. The parameters of the interactions are the following: the distance between the center of gravity (C_g) of the aromatic ring and the hydrogen atom of the DMF methyl group is 3.26 Å and the angle (C–H $-$ C_g) is 144.8°. The penetration of the guest molecule probably forces the macrocycle **2b** to bend and to open the cavity, because it is shielded by the sulfur atoms in comparison with parent tetraphosphines, which do not show the significant structural distortions caused by the formation of the inclusion complexes. Nevertheless the absence of short contacts between the sulfur atoms of the narrow rim indicates that the change in the oxidation state of the phosphorus atoms is not the main reason of the macrocycle conformation's changes and the driving force of the conical distortion is the inclusion of the solvent molecule. The similar open slightly conical conformation of cyclophane was observed for the inclusion complex of nitromethane with one of dispiro[1,3,17,19-tetraoxa[3,1,3,1]paracyclophane-10,4′:26,4″-bispiperidinium] salts where strong C–H$\cdots\pi$ interactions were found [4].

Two DMF molecules (one of which is disordered) are located in the widest external part of macrocyclic "basket"

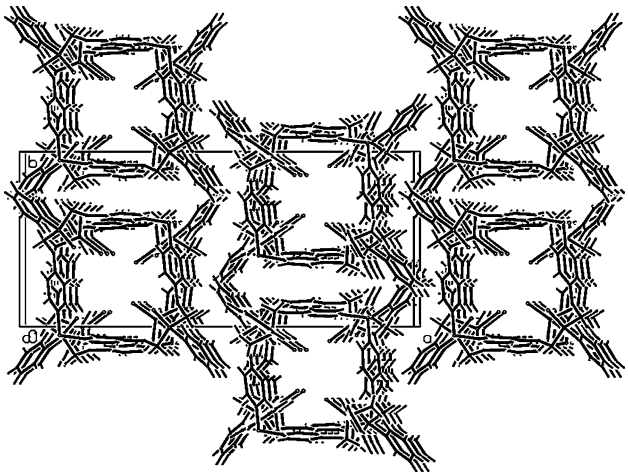


Fig. 2 Six channels of molecules in the crystal structure of **2** viewed along the *c* axis

which is restricted by the phenyl substituents on the phosphorus atoms of the wide rim, and the other solvating molecules are located between the macrocycle molecules. The molecules of **2b** form parallel stacks, the macrocyclic molecules in these stacks are turned to 90° with the respect to each other. Their cavities form channels (Fig. 2) like in the case of macrocyclic tetraphosphines **1a,c** [3], but these channels are strongly shielded by the exocyclic sulfur atoms. Nevertheless the DMF molecules penetrating the cavities are located near the axes of these channels. The packing coefficient of the molecules is relatively low (0.66) in spite of the sufficient amount of the solvate molecules in the crystal.

It should be mentioned that DMF molecules can be completely removed by the washing with acetonitrile which does not form the solvate with the cyclophanes **2a** and **2b**. The loss of DMF destroys the crystals of **2b** and the solvent-free **2a, b** are the powders. The attempts to obtain the solvate complexes of the compounds **2a,b** with other organic compounds were unsuccessful because of their low solubility in practically all available solvents (THF, dioxane, acetone, organic halides, organic esters, aromatic hydrocarbones, DMSO).

The ^{1}H NMR spectra of **2a** [2] and **2b** in DMF-d_7 are similar and give the evidence of some flexibility of macromolecules in solutions. The proton signals of all phenylene rings of **2a,b** appear as a single AA′BB′ spin system. The absence of the difference between the two rims of the cyclophanes indicates either existence of the molecules in cylindrical conformation or the fast conformational equilibrium in solution between conical and cylindrical forms of the macrocycles. The corresponding protons of all methylene groups of **2a,b** are also equivalent. In the case of **2b** their signals are two doublets of doublets. The values of both coupling constants $^2J_{PH}$ are low (1.5 and

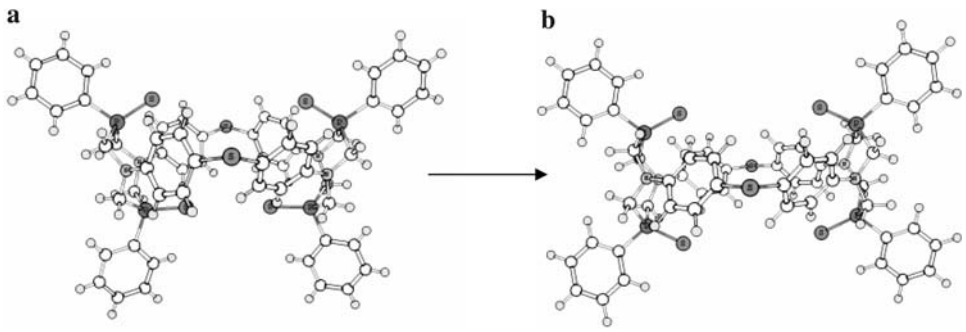


Fig. 3 Starting geometry of the molecule **2b** taken from X-ray of **2b**·DMF complex (**a**); and the geometry of the same molecule after optimisation (**b**)

2.1 Hz). The spectral picture is typical for disulfides of 1,5-diaza-3,7-diphosphacyclooctanes [32] and gives the evidence that the chair–chair conformation of the heterocyclic fragments with the pseudo-axial P=S bonds is not predominant in the solution. The keeping of this conformation with the significant difference of the S–P–C–H torsion angles for axial and equatorial protons (about 170° and 55–73° respectively) would lead to the different values of stereospecific coupling constants $^2J_{PH}$ for these protons (8–14 and 0–5 Hz respectively [33]). The observed low values of both coupling constants probably correspond to the equilibrium between the chair–chair and chair–boat conformations of the diazadiphosphacyclooctane fragments of **2a,b**.

We tested the validity of the above conjectures by quantum-chemical computations. As might be expected conical conformation observed in the crystal and taken as starting geometry for the optimisation did not correspond to a stationary point of the potential energy surface of the isolated molecule **2b**. During the optimisation the cone transformed to the cylindrical conformation of the macrocycle (Fig. 3).

At the same time the optimisation of the isolated complex **2b**·DMF resulted in the geometry very similar to the X-ray starting structure discussed above: the methyl group of the DMF molecule penetrated the macrocyclic cavity which adopted the conical conformation (Fig. 4).

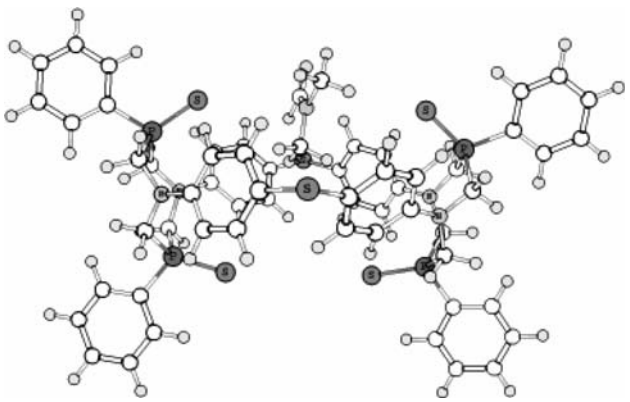


Fig. 4 The optimised geometry of the **2b**·DMF inclusion complex

So, the inclusion of the DMF guest molecule may cause the transformation of the cylindrical conformation of the macrocycle to the conical conformer. To evaluate the energy cost of this transformation, we computed the energy (E_{cone}) of the isolated molecule **2b** in the fixed conical conformation, adopted by **2b** in the complex with DMF, and subtracted the energy of the optimal cylindrical form of the isolated **2b** ($E_{cylinder}$). Depending on the computational method used, the value of $E_{cylinder} - E_{cone}$ amounted to 0.4–1.3 kcal mole^{-1} only. This small energy rise, demonstrating high conformational flexibility of the molecule **2b**, is easily compensated by the energy of the **2b**·DMF inclusion complex formation: depending on the computational method used, E(**2b**·DMF) − E(**2b**) − E(DMF) ≈ 4–5 kcal mole^{-1}. The value seems to be typical for hydrogen bonding and can be ascribed to the above mentioned C–H···π interactions between the methyl group of DMF, penetrating the cavity of the macrocycle, and the aromatic fragments of the latter. As all three protons of the methyl group participate in the short contacts, the energy of the interaction per one C–H···π bond is equal to ca. 1.5 kcal mole^{-1}, and, naturally, can be far outweighed by "crystal packing" effects. So, it is hardly possible to decide on the basis of the data available whether the cone conformation is a result of crystal forces or the C–H···π bonding or, most probably, of the both. Nevertheless, in spite of the weakness of the host–guest interaction, it is sufficient enough to transform the conformation of the isolated host molecule **2b** from the cylinder to the cone because of high conformational flexibility of the macrocycle **2b**.

To evaluate possible influence of oxidation/coordination state of the phosphorus and nature of the X groups, bridging the phenylene fragments, on conformational behaviour of the described cyclophanes we optimised also the structures of several related molecules (**1a,b** and **2a**). X-ray coordinates of the cone conformation of the molecule **2b** (Fig. 3a) were taken as starting geometry for all the molecules. In all cases the result of the optimisation was the same: in the absence of the "guest-molecule" the conical conformation transformed to the cylindrical conformation (Fig. 5). The only difference between the P(III)

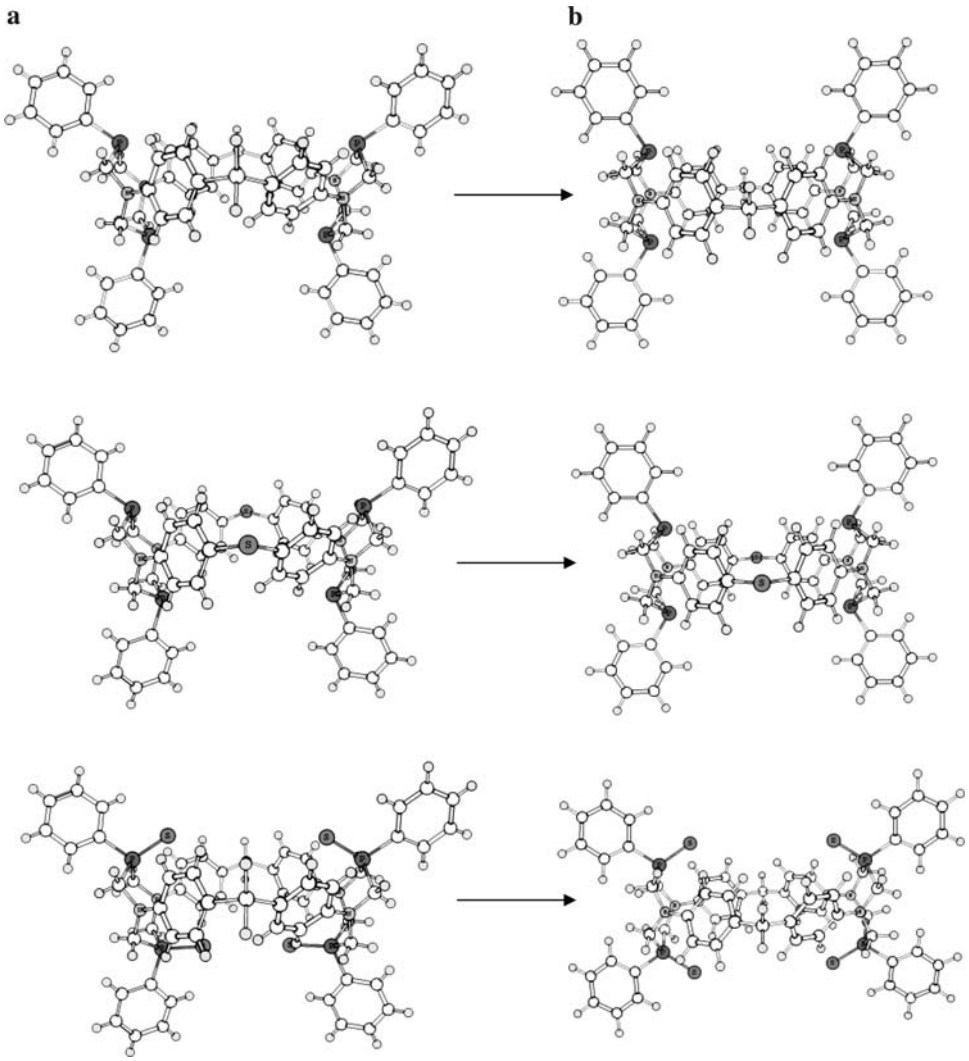


Fig. 5 Starting geometry of the molecules **1a**, **1b** and **2a** (from top to bottom, respectively) taken from X-ray of **2b**·DMF complex (**a**); and the geometry of the same molecules after optimisation (**b**)

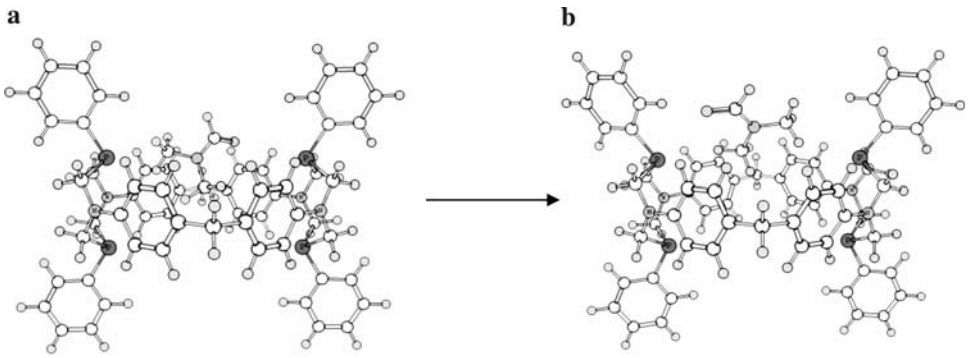


Fig. 6 Starting geometry of the molecule **1a,** taken from X-ray, and DMF molecule placed above the macrocycle (**a**). The geometry of the same molecules after optimisation (**b**)

and P(IV) molecules was that the roof-like conformations of spacers between two 1,5-diaza-3,7-diphosphacyclooctana moieties, typical for P(III) compounds, changed to partially twisted conformations in case of P(IV) molecules **2a,b** (Figs. 5 and 3, respectively).

To find out whether the interaction with DMF may cause the trasnformation of the cylindrical P(III)-based macrocycle to the conical conformer, we have taken the starting geometry of the molecule **1a** in the cylinder conformation from the X-ray data [2] and placed a molecule of DMF above the center of the macrocycle (Fig. 6a). As a result of the optimization, the molecule **1a** adopted cone conformation while the DMF guest-molecule shifted upword (Fig. 6b). Nevertheless, the methyl group of the DMF

molecule penetrated the cavity of the macrocycle; hence the DFT computations predicted the **1a**·DMF inclusion complex formation in vacuum. The computed formation energy of this complex amounted to 7.5 kcal mole^{-1}, irrespective of the computational method used. To evaluate the energy cost of the cylinder–cone transformation of the macrocycle **1a**, we computated the energy (E_{cone}) of the isolated molecule **1a** in the fixed conical conformation, adopted by **1a** in the complex with DMF (Fig. 6b), and subtracted the energy of the optimal cylindrical form ($E_{cylinder}$) of the isolated **1a** (Fig. 5a). Depending on the computational method used, the value of $E_{cylinder} - E_{cone}$ amounted to 0.8–1 kcal mole^{-1}, which is much less than the energy of the **1a**·DMF inclusion complex formation.

So, the computations demonstrate that the conical conformation does not correspond to a minimum (or even stationary point) of potential energy surface for the free macrocycles of the type discussed above, irrespective of the coordination/oxidation state of the phosphorus atoms and the nature of the bridges (–CH_2– or –S–) between phenylen groups of the macrocycles. Nevertheless, the cavity of the cyclophanes is so flexible that the inclusion of the DMF guest molecule may easily cause the trasnformation of the cylindrical shape to the conical conformer.

In summary, the results of the structural investigation of the macrocycle **2b** and other closely related compounds indicate that the frameworks of 1,5(1,5)-di(1,5-diaza-3,7-diphosphacyclooctana)-2,4,6,8(1,4)-tetrabenzenacyclooctaphanes have the sufficient conformational flexibility to accomodate the guest molecules via widening-narrowing of the cyclophane rim. The possibility of the adaptation of the cavity shape is important for the formation of the metal complexes inside the cavity of the cage tetraphosphines.

Acknowledgements Financial support from Russian Foundation for Basic Research (Grant No. 06-03-32754 and No. 05-03-33008), President of Russia Grant for the support of leading scientific schools (Grant No. 5148.2006.3) is gratefully acknowledged. The authors are also indebted to all staff-members of the Supercomputer center of the Kazan Scientific Centre of the Russian Academy of Sciences and especially to Dr. D. Chachkov for technical assistance in the computations and valuable advice.

References

1. Balueva, A.S., Kuznetsov, R.M., Litvinov, I.A., Gubaidullin, A.T., Nikonov, G.N.: Cyclo-bis{1-[p-(p-phenylenomethyl)phenyl]-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane} as the first representative of a new type of nitrogen-containing macroheterocyclic phosphines. Mendeleev Commun. 120–121 (2000)
2. Kuznetsov, R.M., Balueva, A.S., Litvinov, I.A., Gubaidullin, A.T., Nikonov, G.N., Karasik, A.A., Sinyashin, O.G.: Sintez novyh macrociklicheskih aminometilfosfinov na osnove 4,4′-diaminodifenilmetana i ego proizvodnyh. (Synthesis of new macrocyclic aminomethylphosphines based on 4,4′-diaminodiphenylmethane and its derivatives.) Izv. Akad. Nauk. Ser. Khim. 142–147 (2002) [Russ.Chem.Bull. 51, 151–156 (2002)]
3. Balueva, A.S., Kuznetsov, R.M., Ignat'eva, S.N., Karasik, A.A., Gubaidullin, A.T., Litvinov, I.A., Sinyashin, O.G., Lonnecke, P., Hey-Hawkins, E.: Self-assembly of novel macrocyclic aminomethylphosphines with hydrophobic intramolecular cavities. Dalton Trans. 442–447 (2004)
4. Huuskonen, J., Buston, J.E.H., Scotchmer, N.D., Anderson, H.L.: Water-soluble macrocyclic receptors for small neutral guests. New J. Chem. **23**, 1245–1252 (1999)
5. Baxter, I., Colquhoun, H., Hodge, P., Kohnke, F.H., Williams. D.J.: Sulfone-linked paracyclophanes. Chem. Commun. 1991–1992 (1998)
6. Odashima, K., Itai, A., Iitaka, Y., Koga, K.: Host-guest complex formation between a water-soluble polyparacyclophane and a hydrophobic guest molecule K. J. Am. Chem. Soc. **102**, 2504–2505 (1980)
7. Krieger, C., Diedrich, F.: Structure of host-guest complexes of 1', 1''-dimethyldispiro[1,6,20,25-tetraoxa[6.1.6.1]paracyclophane-13,4':32,4''-bispiperidine] with benzene and p-xylene. Chem. Ber. **118**, 3620–3631 (1985)
8. Apel, S., Czugler, M., Griffin, V.J., Nassimbeni, L.R., Weber, E.: Structure and kinetics of novel cyclophane inclusion compounds. J.C.S. Perkin Trans. **2**, 1949–1953 (1997)
9. Adams, H., Carver, F.J., Hunter, C.A., Osborne, N.J.: Amide-aromatic hydrogen-bonds in host–guest recognition. Chem. Commun. 2529–2530 (1996)
10. Ottens-Hildebrand, S., Meier, S., Nieger, M., Vogtle, F., Weber, E.: A new tetra-lactam host compound and its complexes with ethanol and dimethyl sulfoxide. Supramolecular Chem. **5**, 133–138 (1995)
11. Apel, S., Nitsche, S., Beketov, K., Seichter, W., Seidel, J., Weber, E.: 4,4'-(Fluorene-9,9-diyl)diphenol: a new versatile building block for clathrate type and macrocyclic host-guest inclusion. J.C.S. Perkin Trans. **2**, 1212–1218 (2001)
12. Lindeman, S.V., Shklover, V.E., Struchkov, Yu.T., Ponomarev, I.I., Siling, S.A., Vinogradova, S.V., Korshak V.V.: Molekulyarnaya i kristallicheskaya struktura heksazociklana na osnove 4,4'-diaminofenilovogo efira (Molecular and crystal structure of hexazocyclane based on 4,4'-diaminodiphenyl ether). Izv. AN SSSR. Ser. Khim. 2015–2023 (1984) [Russ. Chem. Bull. 33, 1838–1845 (1984)]
13. Weber, E., Pollex, R., Czugler, M.: A new channel-forming host macroring. X-ray crystal structure of its inclusion compound with DMF. J. Org. Chem. **57**, 4068–4070 (1992)
14. Habicher, T., Diederich, F., Gramlich, V.: Catalytic dendrophanes as enzyme mimics: synthesis, binding properties, micropolarity effect, and catalytic activity of dendritic thiazolio-cyclophanes. Helv. Chim. Acta. **82**, 1066–1095 (1999)
15. Ratilainen, J., Airola, K., Nieger, M., Bohme, M., Huuskonen, J., Rissanen, K.: Macrocyclic ethers and their inclusion complexes. Chem.-A Eur. J. **3**, 749–754 (1997)
16. Kus, P., Jones, P.G.: Synthesis of new tetraoxacyclophanes containing benzophenone. Pol. J. Chem. **74**, 965–978 (2000)
17. Blokhin, Yu. I., Gusev, D.V., Sokolinskaya, R., Bel'sky, V.K., Nifant'ev. E.E.: Sintez i struktura oligotioarilenocyklofosfonitov (Synthesis and structures of oligothioarylenecyclophosphonites). Izv. Akad. Nauk. Ser. Khim. 2313–2315 (1996) [Russ. Chem. Bull. 45, 2196–2198 (1996)]
18. Blokhin, Yu.I., Gusev, D.V., Bel'sky, V.K., Stash, A.I., Nifantyev, E.E.: The synthesis and the structure of the first representatives of oligoarylenecyclanes. Phosphorus, Sulfur, Silicon Relat. Elem. **102**, 143–145 (1995)
19. Weber, E., Helbig, C., Seichter, W., Czugler, M.: A new functional cyclophane host. Synthesis, complex formation and crystal

structures of three inclusion compounds. J. Incl. Phenom. Macrocyc. Chem. **43**, 239–246 (2002)
20. Brown, G.R., Chana, S.S., Stoddart, J.F., Slawin, A.M.Z., Williams, D.J.: New cyclophane hosts: a hexaoxocyclophane. J.C.S. Perkin Trans. **1**, 211–212 (1989)
21. Allott, C., Adams, H., Bernard P.L.Jr., Hunter, C.A., Rotger, C., Thomas, J.A.: Hydrogen-bond recognition of cyclic dipeptides in water. Chem. Commun. 2449–2450 (1998)
22. Adams, H., Carver, F.J., Hunter. C.A.: [2]Catenane or not [2]catenane? J. Chem. Soc. Chem. Commun. 809–810 (1995)
23. Altomare, A., Burla, M.C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori G., Spagna, R.: SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data (1999)
24. Sheldrick, G.M.: SHELXL-97. Universität Göttingen, Germany (1997)
25. Spek, A.L.: Platon, A multipurpose crystallographic tool. Utrecht University, The Netherlands (1999)
26. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B.G., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle E.S., Pople, J.A.: Gaussian 98 (Revision A.2). Gaussian, Inc., Pittsburgh, PA., USA (1998)
27. Laikov, D.N., Ustynyuk, Yu. A.: Priroda-04: a quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing. Russ. Chem. Bull. **54**, 820–826 (2005)
28. Karasik, A.A., Naumov, R.N., Balueva, A.S., Spiridonova, Yu.S., Golodkov, O.N., Novikova, H.V., Belov, G.P., Katsyuba, S.A., Vandyukova, E.E., Lönnecke, P., Hey-Hawkins, E., Sinyashin O. G.: Synthesis, structure and transition metal complexes of amphiphilic 1,5-diaza-3,7-diphosphacyclooctanes. Heteroatom. Chem. **17**, 499–513 (2006)
29. Becke, A.D.: Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. **98**, 5648–5652 (1993)
30. Lee, C., Yang, W., Parr, R.G.: Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. **B37**, 785–789 (1988)
31. Perdew, J.P., Burke, K., Ernzerhof, M.: Generalized gradient approximation made simple. Phys. Rev. Lett. **77**, 3865–3868 (1996)
32. Baimukhametov, F.Z., Zheltukhin, V.F., Nikonov, G.N., Balueva, A.S.: Sintez novyh fosfinov i P-heterocyklov na osnove fosfonatov, soderzhaschih allil'nuyu gruppu. (Synthesis of new phosphines and P-heterocycles from phosphonates containing allyl group. Zh. Obshch. Khimii. **72**, 1858–1873 (2002) [Russ. J. Gen. Chem. 72, 1754–1759 (2002)]
33. Arbuzov, B.A., Erastov, O.A., Nikonov, G.N., Ionkin, A.S.: Spektry PMR i prostranstvennoe stroenie stereoizomerov proizvodnyh 4,6-dizameschennyh 2,5-difenil-1,3,2,5-dioxaborafosforinanov. (PMR-spectra and three-dimensional structure of stereoisomers of 4,6-sisubstituted 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane derivatives. Izv. Akad. Nauk. Ser. Khim. 2501–2507 (1984). [Russ.Chem.Bull. 33, 2291–2296 (1984)]