Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 1779—1805, September, 2004

Reviews

Conformational rigidity and flexibility of the paracyclophane skeleton in substituted [2.2]paracyclophanes

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The character of distortions of the paracyclophane skeleton in various substituted [2.2]paracyclophanes was analyzed based on X-ray diffraction data. The rigidity of the skeleton is provided by ethylene bridges and flexibility of the benzene rings, which adopt a boat conformation. The flexibility of the skeleton is manifested in the displacement of the benzene rings with respect to each other and conformational changes of ethylene bridges. The changes in these characteristics are very sensitive to intra- and intermolecular steric factors and are indicative of the absence of strong specific stacking interactions between the be nzene rings. Precision X-ray diffraction study and quantum-chemical calculations for unsubstituted [2.2]paracyclophane and 4,7-benzoquinono[2.2]paracyclophane demonstrated that there are no attractive interactions between the benzene rings, and the electron density is localized predominantly on the outer surface of the rings. This fact can be considered as the "cage molecular" effect of the [2.2]paracyclophane skeleton.

Key words: [2.2]paracyclophane, [2.2]paracyclophane derivatives, influence of substituents and π—π interactions in the [2.2]paracyclophane skeleton.

1. Introduction

[2.2]Paracyclophane (PCP, **1**) and its derivatives have attracted attention for years. This interest is associated with both the theoretical concepts regarding the structure of this unusual molecule and synthetic problems, because chirality of substituted PCP derivatives makes it possible to use them in the asymmetric synthesis[1] and for resolution of enantiomers.[2] Substituted [2.2]paracyclophanes have found use in asymmetric catalytic processes[3] and as promising nonlinear-optical[4] and liquid-crystalline[5] materials, which stimulated studies in this area.

[2.2]Paracyclophane is a unique highly strained bicyclic system, in which two parallel benzene rings are linked by two $—C_2H_4—$ bridges, the benzene rings being nonplanar and adopting a boat conformation. The distance between the bottoms of the boats is ~3.1 Å. The distances between the opposite carbon atoms of the benzene rings linked by the ethylene bridges ("apex" or "bow and stern" atoms of the boat) are approximately equal to 2.8 Å.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1707—1732, September, 2004.

The molecular structure of [2.2]paracyclophane is unique since the benzene rings in this compound are located at a very short distance, which is substantially smaller than the lengths of the typical C...C contacts between isolated benzene rings (~3.5 Å). In systems with stacking interactions, in which attractive interactions occur between isolated aromatic π systems (in particular, in charge-transfer complexes), the distance between the planes of the benzene rings is generally no shorter than 3.2 Å. Hence, one can suppose that there are attractive interactions between the π systems of the benzene rings in PCP. In addition, the benzene rings in **1** are essentially nonplanar and adopt a boat conformation (the atoms at the bow and stern positions deviate by 0.12—0.18 Å from the plane of the atoms forming the "bottom"). Such a strong distortion of the geometry of benzene rings is also unusual.

Due to these two distinguishing features, the PCP molecule attracts considerable interest. The aim of the present review is to perform a comprehensive analysis of the crystallographic parameters of substituted [2.2]paracyclophanes, because X-ray diffraction studies provide reliable structural characteristics. Particular attention is given to analysis of distortions of the geometry of the benzene rings and the configuration of the paracyclophane skeleton as a whole under the influence of various substituents in the benzene rings. The problems of the synthesis, resolution of enantiomers, spectroscopic studies, and the practical use of [2.2]paracyclophane derivatives are beyond the scope of the present review. These problems have been considered in reviews,[6,7] the monograph,[8] and numerous original papers.[9]

The first attempt to study [2.2]paracyclophane by X-ray diffraction was made in 1953.[10] The general molecular structure of PCP **1** was established. However, the geometric parameters were determined in a crude way (even the errors in the atomic coordinates were not evaluated). The structure of PCP **1** was studied with higher accuracy at 293 and 93 K in 1960.[11] In the crystal structure (space group $P4_2/mnm$, $Z = 2$), the PCP molecule occupies a special position and has the symmetry D_{2h} (there are three independent atoms per asymmetric unity; two of these atoms, C(2) and C(3), are located on the symmetry plane *m*, whereas the C(1) atom occupies a general position). This is a rare example of the coincidence of the molecular symmetry (*mmm*) with the position occupied by this molecule in the crystal.[12]

The benzene rings are coplanar (Fig. 1) and are eclipsed relative to each other. The distance between the centroids of the rings is 2.978 Å. The rings adopt a symmetrical boat conformation with equal deviations of the C(2) and C(2A) atoms at the bow and stern positions from the C(1),C(1A),C(1B),C(1E) plane ("bottom" of the boat). The dihedral angle (α) between the plane of the "bottom" of the boat and the C(1),C(2),C(1E) plane is 14.0°. The C(2)...C(2B) distance (Δ) between the atoms at the bow or stern positions is 2.750 Å. In the aromatic ring, the C(2)—C(1) and C(1)—C(1A) bonds show a slight alternation (1.388 and 1.415 Å, respectively). The exocyclic C(2)—C(3) bond length (1.534 Å) is substantially larger than the typical C(sp^2)—C(sp^3) bond length (1.506 Å).[13] The C(3)—C(3B) bond in the ethylene bridge is also substantially weakened; its length (1.558 Å) is substantially larger than the typical C(sp^3)—C(sp^3) bond length (1.524 Å).[13]

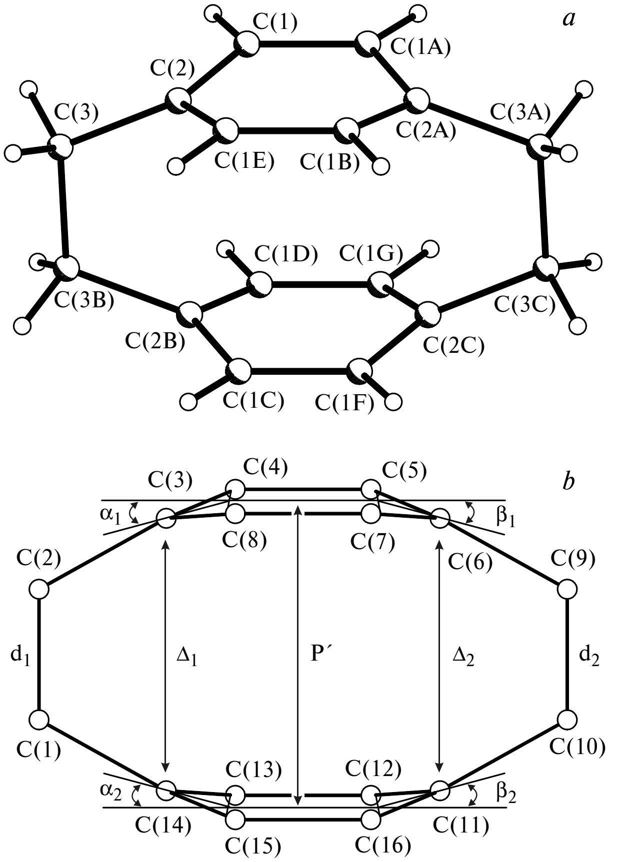


Fig. 1. Molecular structure of [2.2]paracyclophane[10] (**1**) (molecular symmetry D_{2h}): *a*, according to X-ray diffraction data; *b*, the schematic representation.

The above geometric parameters[11] determined at 93 K are insufficiently accurate (the *R* factor after the structure refinement was 10.5%). In the precision X-ray diffraction study[14] performed at 100 K (R = 4.63%), the geometric parameter were determined with higher accuracy: C(3)—C(3B), 1.579(1) Å; C(2)—C(3), 1.508(1) Å; C(1)—C(2), 1.400(1) Å; C(1)—C(1A), 1.392(1) Å; the C(2)...C(2B) distance (Δ) between the atoms at the bow or stern positions is 2.786(1) Å, the distance (*P*′) between the centroids of four coplanar atoms (C(1),C(1A),C(1B),C(1E) and C(1D),C(1C),C(1G),C(1F)), which form the bottom of the boat, and the distance (*P*) between the centroids of the benzene rings are 3.099(1) and 2.995(1) Å, respectively; the α angle is 12.4°. The main differences between these data and those obtained at 93 K[11] are the bridging bond length and the C(2)...C(2B) distance. Apparently, the bridging C(3)—C(3B) bond length (1.579 Å), the C(2)...C(2B) distance (2.786 Å), and the distance *P´* (3.099 Å) should be considered as the corresponding reference values.

The boat conformation becomes more flattened and the distance between the benzene rings in the cyclophane molecules decreases as the number of ethylene bridges increases. In the most strongly "tightened" [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane molecule,[15] in which the benzene rings are linked by six ethylene bridges, these rings are planar and the distance between their planes is 2.624 Å. The bridging $C(sp^3)—C(sp^3)$ bonds are also elongated (1.575—1.584 Å), whereas the exocyclic $C(sp^2)—C(sp^3)$ bond lengths (1.514—1.519 Å) have standard values. Interestingly, the bridging bond length is close to that found in unsubstituted PCP (**1**).

With the aim of revealing the character of deformations of the benzene rings and changes in the bridging bonds under the influence of various substituents (electron-donating or electron-withdrawing substituents and substituents with different effective volumes) in the PCP skeleton and ethylene bridges and determining the characteristic features of π coordination of the PCP fragment to the metal atoms, we analyzed the results of our and original structural studies and the data retrieved from the Cambridge Structural Database (CSD),[16] where the structures of more than two hundreds of various paracyclophanes are available. We restricted ourselves to the structures of substituted [2.2]paracyclophanes, in which the benzene rings are not involved in fused systems (anthracene, naphthalene, indene, benzofuran, *etc.*) and contain no additional bridging fragments ($—SO_2—N(R)—SO_2—$, $—PPh_2—PdCl_2—PPh_2—$, *etc.*). We found 153 such compounds, among which alkyl- and aryl-substituted derivatives and π complexes are most widely represented.

Since different atomic numbering schemes were used in publications, we unified the numbering of atoms in the PCP skeleton (see Fig. 1, *b*). We also give the following main parameters characterizing the structure of the PCP skeleton: the folding angles of the substituted ("upper") ring along the C(4)...C(8) and C(5)...C(7) lines (α_1 and β_1) and the "lower" ring along the C(13)...C(15) and C(12)...C(16) lines (α_2 and β_2), which characterize the conformation of the benzene rings and deviations of the C(3), C(6) and C(11), C(14) atoms at the bow and stern positions from the corresponding C(4),C(5),C(7),C(8) and C(12),C(13),C(15),C(16) planes ("bottoms" of the boats); the $C(sp^2)...C(sp^2)$ distances between the bow or stern atoms, *viz.*, C(3)...C(14) and C(6)...C(11) (Δ_1 and Δ_2), which characterize the degree of extension of the $C(sp^2)—C(sp^3)—C(sp^3)—C(sp^2)$ bridges; the distance (*P´*) between the plane of the bottom of the lower ring and the centroid of the bottom of the boat of the upper ring, which characterizes the degree of proximity of the rings; the $C(sp^3)—C(sp^3)$ bond lengths in the C(1)—C(2) and C(9)—C(10) ethylene bridges (d_1 and d_2) and the C(3)—C(2)—C(1)—C(14) and C(6)—C(9)—C(10)—C(11) torsion angles (τ_1 and τ_2, respectively), which characterize the distortion of the ethylene bridges and the relative displacement and twist of the benzene rings.

It should be noted that the interplanar distances or the distances between the centroids of the benzene rings (*P*), which are sometimes used for the description of the structures of [2.2]paracyclophanes,[8,17,18] only approximately characterize the degree of their proximity. This is associated with the fact that the benzene rings often differ in the type of puckering (differ in the angles α_1, β_1 and α_2, β_2) and are shifted with respect to each other in the direction perpendicular or parallel to the ethylene bridges. As a result, the centroids and the atoms at the bow and stern positions are not located precisely above each other. Hence, we use the distance between the centroid of the bottom of the boat of the upper ring and the plane of the bottom of the lower ring (*P´*).

The relative arrangement of the rings, which characterizes the "skew" of the PCP skeleton, is pictorially represented in the projection of the PCP skeleton onto the plane of the "lower" ring (superposition of the rings). The character of distortions (skew) of the PCP skeleton is qualitatively described by the shifts of the rings in the direction parallel or perpendicular to the ethylene bridges and the twist of the rings about the line connecting the centroids of the bases of the rings.

2. Substituted [2.2]paracyclophanes

One would expect electron-donating substituents containing atoms with lone electron pairs (O or N) to substantially influence the electronic state of the PCP molecule and the character of interactions between the π systems of the benzene rings, resulting in a change in the geometric parameters of the molecule. Let us consider the molecules containing OH, OR, R (R = Alk and/or Ar), and other heteroatomic substituents in benzene rings.

2.1. The OH and OR substituents

Data on selected substituted PCP are given in Table 1. Generally, the electronic effect of the electron-donating OH group on the geometry of the benzene ring is manifested in an increase in the endocyclic *ipso*-angle by 2—3°. The character of distortions of the PCP skeleton can also vary, because the OH group is involved in various hydrogen bonds.

Table 1. Parameters characterizing the structure of the paracyclophane skeleton in selected [2.2]paracyclophanes containing the OH, OR, OC(=O)R (OC(=S)R), SO_3, SR, $P(=O)R_2$, or halogen substituents at position 4 of the benzene ring

Compound	Substituents	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P'
2[19]	4-OH	1.58	1.58	2.77	2.78	12.3	12.0	12.1	11.8	16.8	8.2	3.074
		1.58	1.58	2.77	2.78	11.7	12.4	12.6	11.3	15.0	0.0	3.068
3[20]	4-OH, 12-CH=N—CH(Me)Ph	1.57	1.57	2.75	2.74	11.7	9.9	11.6	14.8	0.8	8.0	3.026
		1.57	1.59	2.75	2.79	11.2	11.5	11.3	12.5	15.4	22.8	3.062
4[21]	4-OH, 5-C(=O)Ph	1.56	1.54	2.74	2.78	10.5	11.7	12.6	13.6	5.0	25.1	3.054
		1.55	1.56	2.75	2.78	13.8	12.4	9.0	13.4	4.0	21.1	3.067
5[22]	4-OH, 5-C(=O)Me	1.58	1.57	2.74	2.80	10.3	13.9	11.7	13.0	1.5	23.9	3.059
6[23]	4-OH, 5-CH_2—(Ph—2-OH—3,5-$(Me)_2$)	1.58	1.59	2.75	2.78	12.1	13.1	10.6	13.8	2.5	17.7	3.068
7[24]	4-OH, 5-CH_2NH—CH(Me)Ph	1.60	1.59	2.77	2.78	11.2	12.7	13.0	12.1	8.9	11.2	3.071
8[24]	4-OH, 5-CH_2NEt_2	1.57	1.58	2.75	2.77	10.2	13.4	11.6	13.7	6.8	16.5	3.040
9[24]	4-OH, 5-CH(Ph)—NHCH(Ph)Me	1.61	1.57	2.78	2.78	7.8	13.5	11.1	14.2	7.1	19.9	3.032
10[21]	4-OH, 5-C(Ph)=N—CH(Me)Ph	1.59	1.57	2.76	2.78	10.6	11.9	11.6	12.7	8.1	23.3	3.050
		1.59	1.57	2.76	2.78	12.1	12.2	8.8	13.1	0.9	25.0	3.042
11[21]	4-OH, 5-C(Ph)=N—CH(Me)Ph	1.61	1.58	2.75	2.80	9.9	14.6	12.0	10.4	1.7	23.6	3.049
12[22]	4-OH, 5-C(Me)=NCH_2CH_2OH	1.54	1.54	2.73	2.77	8.1	15.2	13.2	11.8	3.6	19.4	3.040
13[22]	4-OH, 5-C(Me)=NCH(Pr)CH_2OH	1.56	1.56	2.79	2.73	13.2	6.0	10.2	13.2	10.7	14.5	3.049
14[25]	4-OH, 5-CH=N—CH(Me)Ph	1.58	1.59	2.74	2.77	12.5	11.7	12.6	12.8	8.6	9.4	3.079
15[20]	4-OH, 5-C(Me)=NOH	1.60	1.59	2.75	2.80	10.1	13.2	12.2	12.4	6.1	20.9	3.059
16[26] *	4-OH, 5-C(Me)=N—$(CH_2)_3$—	1.57	1.56	2.76	2.80	10.4	13.2	12.9	12.8	12.9	22.8	3.051
		1.58	1.57	2.75	2.79	11.8	12.3	12.1	11.1	10.7	12.0	3.038
17[26] *	4-OH, 5-C(Me)=N—CH_2—	1.57	1.57	2.75	2.80	8.6	13.8	11.6	12.0	2.0	5.6	3.057
		1.58	1.52	2.74	2.78	9.9	13.1	11.7	12.5	10.6	6.5	3.053
18[27] *	4-OH, 5-C(Me)=N—$(CH_2)_3$—	1.60	1.57	2.76	2.80	12.6	11.8	9.6	14.5	7.3	22.2	3.060
		1.59	1.59	2.74	2.79	11.3	12.0	12.2	12.2	13.0	21.4	3.033
19[27] *	4-OH, 5-C(Me)=N—CH_2—	1.57	1.57	2.77	2.79	10.2	12.8	11.4	12.7	10.9	11.3	3.053
20[27] *	4-OH, 5-CH=N—$(CH_2)_3$—	1.60	1.58	2.75	2.80	10.2	13.0	7.0	15.4	7.6	24.1	3.020
		1.59	1.58	2.75	2.77	12.1	11.6	7.9	14.5	10.8	9.5	3.035
		1.58	1.58	2.74	2.79	10.5	12.7	11.0	10.9	7.0	23.2	3.032
		1.58	1.58	2.74	2.77	11.4	10.9	11.7	11.5	8.5	10.9	3.036
21[27]	4-OH, 5-C(Ph)=N—CH_2	1.59	1.58	2.76	2.79	9.2	12.2	11.4	10.6	8.2	24.4	3.045
	—CH_2N=CH—ПЦ	1.58	1.59	2.75	2.78	10.6	13.1	12.9	10.2	17.0	11.9	3.006
22[28] *	4-OMe, 7-CH(NHPh)—	1.59	1.57	2.74	2.78	11.5	12.3	11.2	12.2	14.9	17.1	3.065
		1.58	1.57	2.75	2.78	11.9	12.6	11.3	12.6	12.6	14.1	3.052
		1.59	1.58	2.78	2.76	12.6	11.6	10.8	12.7	18.9	20.8	3.061
		1.57	1.58	2.76	2.78	12.6	12.4	11.0	11.6	22.2	20.9	3.070
23[29]	4-OMe, 5-CH(OH)(*p*-Tol)	1.57	1.55	2.77	2.77	13.4	11.8	12.3	11.5	16.2	10.1	3.076
24[28] *	4-OMe, 5-CH(OH)—	1.57	1.58	2.78	2.78	11.6	11.6	12.3	13.1	18.7	14.1	3.078
		1.57	1.59	2.78	2.77	10.7	12.9	13.3	13.2	27.3	13.2	3.066
25[30]	4-OMe, 5-CH=NPh	1.56	1.57	2.76	2.76	11.9	11.7	12.2	3.8	8.8	11.7	3.071
26[21]	4-OMe, 5-C(Ph)=N—CH(Me)Ph	1.59	1.59	2.77	2.75	11.2	10.8	12.5	12.2	5.5	8.3	3.049
27[21]	4-OEt, 5-C(Ph)=N—CH(Me)Ph	1.57	1.59	2.78	2.76	10.9	11.5	12.8	13.5	18.2	7.6	3.062
28[31]	4-OCH_2OMe, 5-(Ph-*o*-OMe)	1.58	1.58	2.75	2.78	11.9	13.2	11.3	13.1	11.9	6.2	3.075
29[32]	4,7-$(OMe)_2$, 12,13,15,16-$(CN)_4$	1.58	1.58	2.74	2.73	13.9	13.9	11.3	11.3	8.2	9.1	3.058
30[32]	4,5,7,8-$(OMe)_4$, 12,13,15,16-$(CN)_4$	1.57	1.58	2.75	2.73	14.7	13.8	11.3	11.5	19.4	11.1	3.012
31[33]	4-OC(=S)NMe_2	1.58	1.59	2.78	2.78	11.7	12.5	10.8	11.8	4.0	11.1	3.066
32[19]	4-OC(=O)camphanyl (*R*)	1.58	1.59	2.78	2.77	12.5	12.1	12.4	12.1	24.3	20.0	3.077
		1.60	1.60	2.77	2.78	12.4	12.5	12.4	13.0	17.6	1.3	3.075
33[19]	4-OC(=O)camphanyl (*S*)	1.57	1.57	2.75	2.76	11.0	11.7	12.9	12.2	14.8	4.7	3.051
34[34]	4-SO_3^-	1.57	1.57	2.78	2.77	14.6	12.7	12.2	12.5	2.7	12.2	3.087
35[35]	4,4′-S—PCP	1.58	1.58	2.77	2.78	12.6	12.0	11.8	11.7	15.7	9.9	3.078
		1.58	1.57	2.76	2.77	13.1	11.2	11.9	12.1	2.1	7.7	3.065
36[36]	4,12-$(POPh_2)_2$	1.60	1.58	2.76	2.78	13.5	14.2	14.9	13.7	8.4	2.5	3.107

(*to be continued*)

Table 1 (*continued*)

Compound	Substituents	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P'
37[37]	4,16-Br_2	1.57	1.57	2.75	2.75	11.7	11.7	13.3	13.3	5.8	5.8	3.065
38[38]	4,13-Br_2	1.58	1.59	2.78	2.75	12.8	13.2	12.4	13.4	2.2	4.6	3.088
39[39]	4,15-Br_2	1.60	1.55	2.75	2.77	15.2	10.0	13.3	14.6	20.6	10.1	3.068
40[40]	4,12-Br_2	1.66	1.58	2.78	2.77	11.4	11.3	10.8	12.3	18.7	20.0	2.967
41[37]	4,16-Cl_2	1.57	1.57	2.75	2.75	11.9	11.9	12.4	12.4	3.9	3.9	3.056
42[41]	4,5,15,16-Br_4	1.59	1.59	2.76	2.76	14.4	14.4	12.5	12.5	14.8	14.8	3.093

Note. In structures containing several independent molecules (**2—4**, **10**, **16—18**, **20**, **22**, **24**, and **32**), the data are presented in several rows; for "dimeric" molecules (**21** and **35**) containing two paracyclophane fragments linked by a bridging fragment, data are also given in several rows, but these molecules are marked with asterisks.

* Since the molecule has a symmetrical structure and contains two cyclophane fragments linked by a bridging fragment, the composition of one half of the molecule is given.

Let us consider molecules **2** and **3** (see Table 1) containing only the OH group at position 4 of the upper ring (molecule **3** contains also the —CH=N—CH(Me)Ph substituent at position 12 of the lower ring).

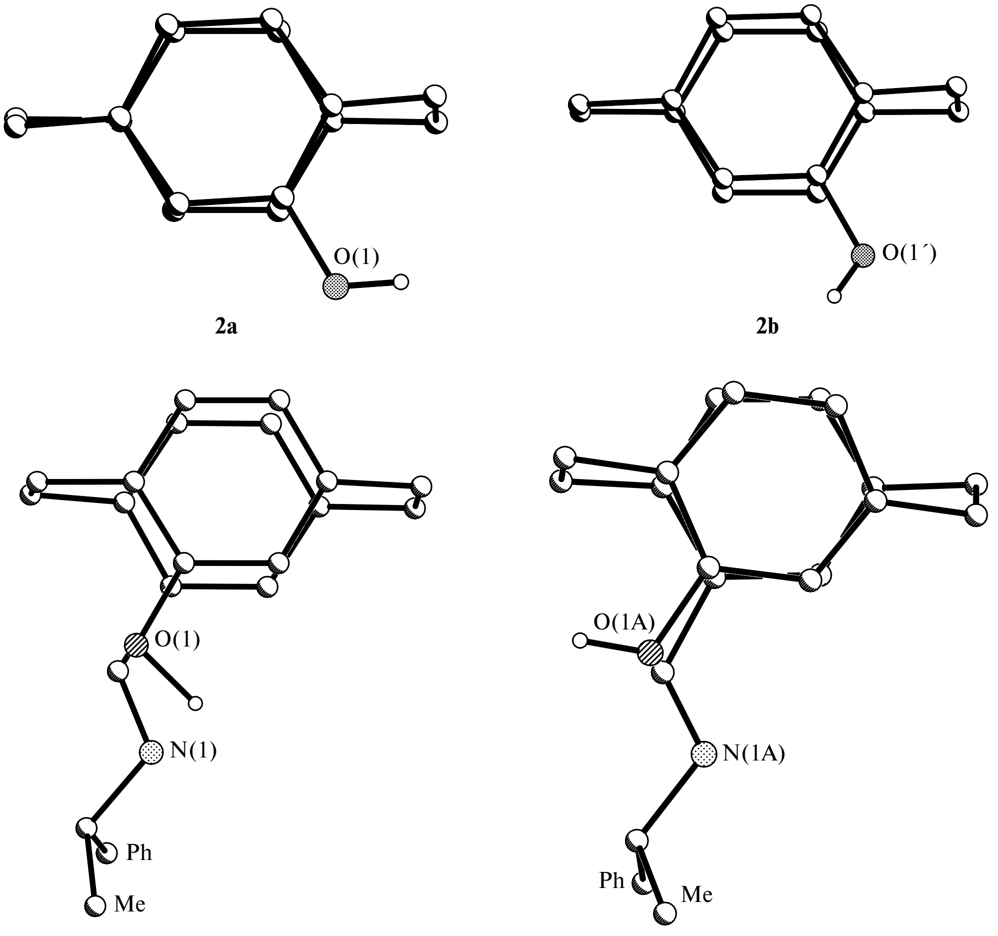
In these molecules, the upper and lower rings adopt the symmetrical C(3),C(6)-boat conformation. The OH group is coplanar with the plane of the bottom of the boat and is involved in intermolecular hydrogen bonding. The benzene rings are located at a closer distance than those in PCP **1**, in spite of the fact that these molecules have similar bridging bonds (*d* and Δ have similar values). Two independent molecules in the crystal structure of **3** are different. In one of them (less skewed), the rings are even more closely spaced, which is reflected in a decrease in the distances Δ and P'. The geometric parameters of the substituted ring are only scarcely affected by the OH substituent: the endocyclic C—C bond lengths are equalized, as in the PCP molecule and the unsubstituted ("lower") benzene rings, and the endocyclic *ipso*-angle is only slightly larger (aver., 121°). The bridging $C(sp^3)—C(sp^3)$ bond lengths (~1.58 Å) and the exocyclic $C(sp^2)—C(sp^3)$ bond lengths (~1.51 Å) are equal to the corresponding bond lengths in PCP **1**.

The conformation of the PCP skeleton in molecule **2** differs from that in **3** by a shift and a twist angle of the benzene rings. These differences are reflected in the τ_1 and τ_2 torsion angles and the type of the mutual arrangement of the rings (Fig. 2). The conformations of the skeletons in **2a** and **2b** differ only slightly, unlike the conformations of the skeletons in **3a** and **3b**. This fact can be related to the difference in the steric effects associated with intermolecular hydrogen bonding. In molecule **2**, the OH groups are involved in O—H...OH hydrogen bonds (two bonds in molecule **2a** and one bond in molecule **2b**; the O...O distance is 2.80 Å). In molecule **3b**, the OH group forms only one O—H...N hydrogen bond with the nitrogen atom of the —CH=N—CH(Me)Ph substituent, whereas the OH group in molecule **3a** is not involved in hydrogen bonding. It can be hypothesized that the mutual orientation of the benzene rings (the degree of skew) in the PCP skeleton depends substantially on the intermolecular steric factors.

The influence of intramolecular steric factors is pronounced in the crystal structures of the monoclinic (**10**) and orthorhombic (**11**) modifications of 4-oxy-5-(1-phenylethylimino)phenylmethyl[2.2]paracyclophane containing the bulky —C(Ph)—N=CH(Ph)Me substituent adjacent to the OH group. The phenyl ring of the substituent is located in the vicinity of the bridge and is almost orthogonal to the upper benzene ring of the PCP skeleton, resulting in a substantial parallel shift of the rings analogous to that observed in molecule **3a**. A similar situation is observed in compound **9**, in which the angle between the benzene rings is 5.4°. Therefore, these data confirm the assumption that the steric factors significantly affect the character of distortions of the PCP skeleton.

In addition to the OH group at position 4, molecules **4—21** contain various substituents with β-heteroatoms (O or N) in the adjacent position (position 5). The hydroxy group is involved in an intramolecular hydrogen bond with the N or O atom of the substituent to form the H-bonded ring. The hydrogen bond in molecules **9—21** is strong (the O...N distance is 2.5—2.6 Å). The hydrogen atom is located either in the vicinity of the oxygen atom or at equal distances from both atoms, whereas the hydrogen atom in molecules **11—13** is shifted to the nitrogen atom, resulting in the ziwtterionic structure of the H-bonded ring (O^-...H—N^+). However, this fact has no influence on the geometric parameters of the benzene ring in PCP.

The structures of molecules **4—21** are similar in that both rings adopt a virtually symmetrical flattened boat conformation (the α and β angles are in a range of 7.8—14.5°) and the C(3)...C(14) distance is slightly shortened compared to the C(6)...C(11) distance (2.74—2.78 and 2.77—2.80 Å, respectively). The differ-



2a **2b**

3a **3b**

Fig. 2. Projection of the PCP skeleton onto the plane of the unsubstituted ("lower") benzene ring (superposition of the rings) in two independent molecules of 4-hydroxy[2.2]paracyclophane (**2a** and **2b**) and 4-hydroxy-13-(methylphenylmethyliminomethyl)[2.2]paracyclophane (**3a** and **3b**).

ences are observed primarily in the character of deformations of the PCP skeleton, which, apparently, reflects the steric effect of the substituents. The most typical arrangement of the benzene rings is shown using molecule **10** as an example (Fig. 3). The main distortion of the skeleton in most molecules is associated with a parallel shift of the benzene rings.

Hence, analysis of the data (see Table 1) shows that molecules **2—21** containing the OH group at position 4 are characterized by similar symmetrical structures of both benzene rings (the α and β angles vary in a range of 7—15°), in which the C—C bond lengths are equalized and are similar to those in unsubstituted paracyclophane **1**. The benzene rings in molecules **2—21** are located at a closer distance from each other compared to those in unsubstituted paracyclophane **1**. The presence of substituents of different sizes and different hydrogen bond networks are responsible for the difference in the steric conditions, which affect the geometry of the molecules

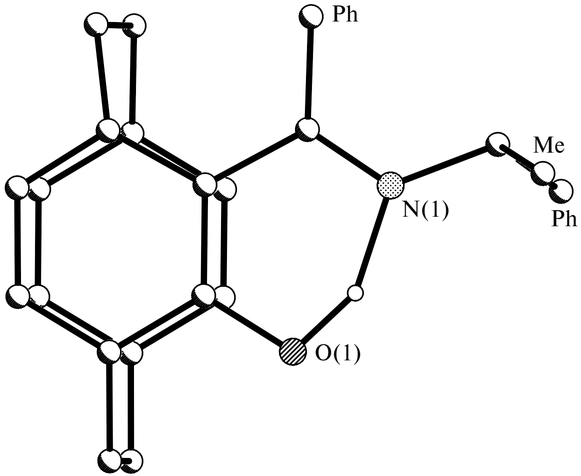


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Fig. 3. Superposition of the rings in the 4-hydroxy-5-(methylphenylmethylimino(phenyl)methyl)[2.2]paracyclophane molecule (**10**) containing the six-membered H-bonded ring.

and their packing in the crystals. This leads to substantial nonsystematic differences in the parameters characterizing the distortions of the PCP skeleton. The τ_1 and τ_2 torsion angles vary from 0.8 to 25.1°. The distances Δ_1 and Δ_2 between the atoms at the bow and stern positions and the bridging bond lengths d_1 and d_2 vary in ranges of 2.73—2.80 Å and 1.54—1.61 Å, respectively.

Compounds **22—28** contain the OAlk substituent at position 4 and various substituents at position 7 (**22**) or 5 (**23—28**). These substituents in compounds **22—28**, unlike those in compounds **2—21**, are not involved in intramolecular hydrogen bonds, which fix the orientation of the substituent with respect to the upper benzene ring. These molecules also have similar structures (see Table 1) and are structurally similar to compounds containing the 4-OH substituent. The differences are associated primarily with the character of distortions of the PCP skeleton.

The structure of **22** consists of two crystallographically independent molecules containing two PCP skeletons, which are linked by the —CH(NHPh)—CH(NHPh)—7,7′-bridge (Fig. 4). Hence, this compound serves as a convenient model for comparing the geometry of the skeletons. The benzene rings in all four PCP skeletons in molecule **22** adopt the same conformation. All characteristic parameters, *viz.*, the bridging C(1)—C(2) and C(9)—C(10) bond lengths (d_1 and d_2), the distances between the centroids (P'), and the distances between the atoms at the bow and stern positions (Δ_1 and Δ_2), differ only slightly. The presence of two symmetrically arranged substituents in the upper ring (at positions 4 and 7) leads to an identical twist of both bridges. However, the quantitative characteristics of the twist of the bridges in four skeletons are different, which can be related to the packing effects. The molecule is bulky, its fragments are rather flexible and can readily vary to fit the requirements of the closest packing in the crystal. The independent molecules differ in the twist angles of the Ph substituents with respect to the substituted benzene ring (36.6 and 49.1° in one molecule and 24.7 and 61.0° in another molecule) and the twist of the PCP skeletons with respect to each other (the angle between the planes of the upper benzene rings is 25.9° and 32.6° in two independent molecules). In addition, the crystal structure contains a water molecule and a solvent molecule (cyclohexane). The packing of the molecules containing such rather flexible fragments in the crystal is generally determined by the steric packing factors.

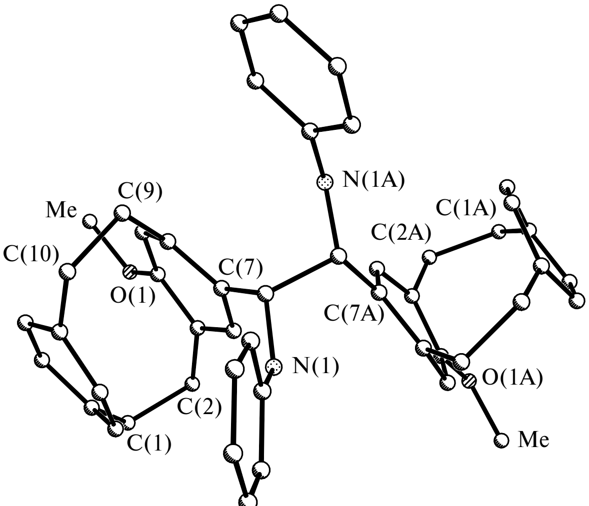

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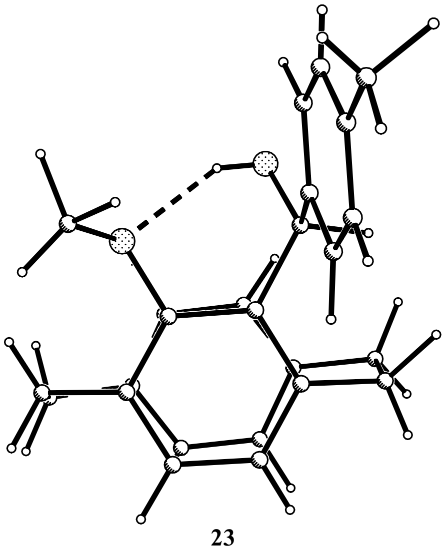
Fig. 4. Molecular structure of 1,2-bis(4-methoxy[2.2]paracyclophan-7-yl)-1,2-bis(phenylamino)ethane (**22**) (the hydrogen atoms are omitted).

In molecules **23—28**, the substituents are arranged asymmetrically (at positions 4 and 5) and the bridges are characterized by different twist angles (different τ_1 and τ_2 angles). The twist angle of the bridge substantially increases as the effective volume of the substituents increases (this can be seen, for example, from a comparison of molecules **24** and **25** or **26** and **27**).

To estimate the role of other factors influencing the distortion of the PCP skeleton, let us consider, for example, molecules **23** and **24** (Fig. 5) containing the similar 5-CH(OH)R substituents. However, the OH group in molecule **23** forms only a weak intramolecular OH...OMe hydrogen bond, whereas both OH groups in one crystallographically independent molecule of **24** form intermolecular OH...O(Me) hydrogen bonds, and the OH groups of another independent molecule are not involved in hydrogen bonding. In addition, the crystal structure of **24** contains a solvent molecule (toluene). The difference in the hydrogen bond network and the presence of the solvent are responsible for the difference in the conditions of the molecular packing in the crystals, resulting in the difference in the character of distortions of the PCP skeleton in molecules **23** and **24**.

Molecules **29** and **30** contain the completely substituted lower ring (four CN groups) and two OMe or four OMe substituents in the upper ring (**29** and **30**, respectively) and differ in the superposition of the benzene rings (Fig. 6) and the distance between these rings (see Table 1). A substantial shortening of the distance between the atoms at the bow and stern positions in these compounds (2.73—2.75 Å) is consistent with the possible occurrence of attractive interactions between the oxygen atoms of two OMe groups and the CN groups in compound **30**, in which the length of the O(2)...C and O(1)...C contacts is 2.90 Å. Other analogous contacts in **29** and **30** are substantially longer (3.11—3.21 Å).

Compounds **31—33** are representatives of [2.2]paracyclophanes containing the ester group O—C(=X)R at position 4. Molecules **32** and **33** are enantiomers of 1(*S*)-camphoric acid ester of 4-hydroxy[2.2]paracyclophane, in which the PCP skeletons have similar geometric parameters and differ only in the mutual orientation of



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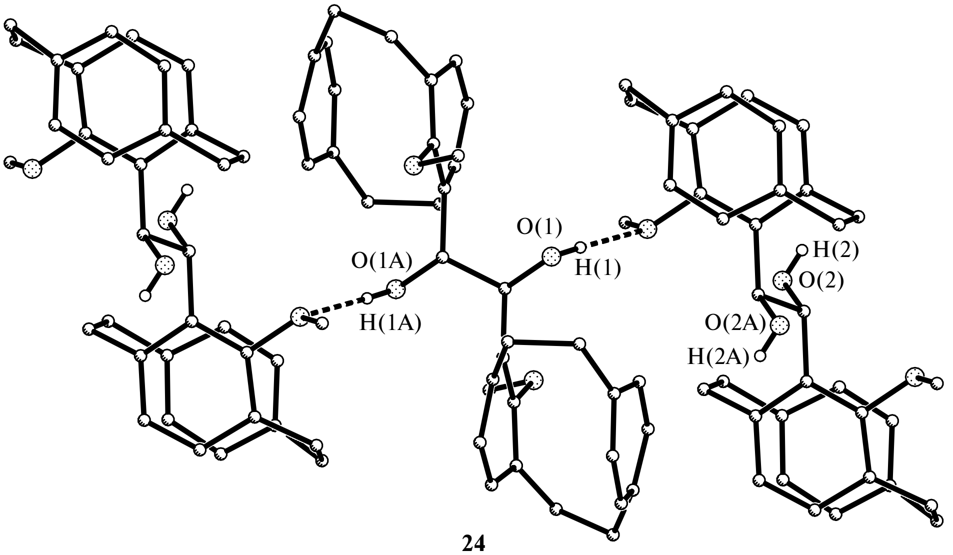

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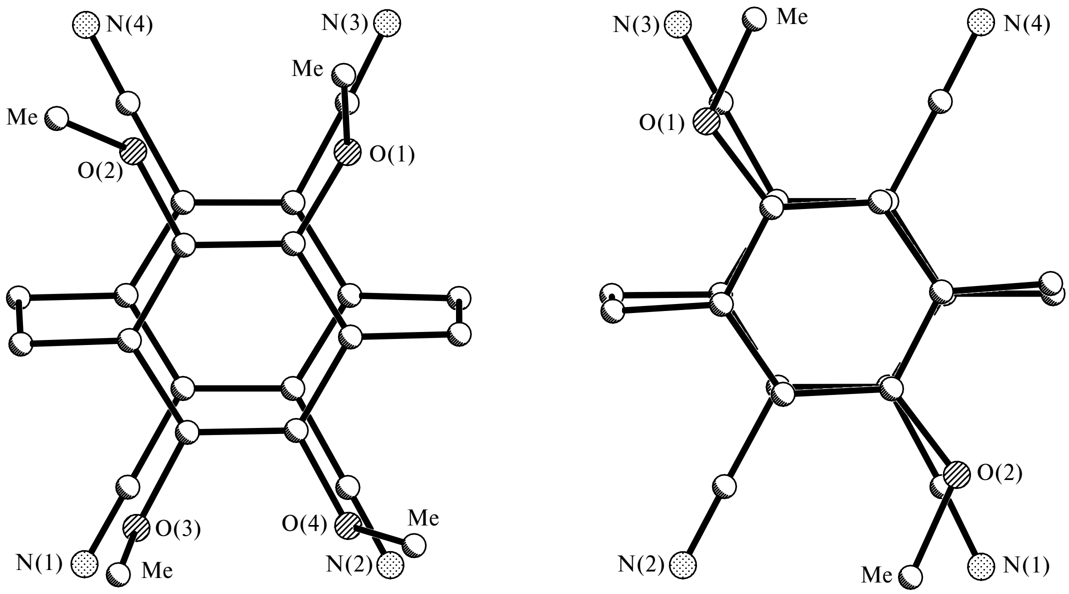
Fig. 5. Various hydrogen bond networks in molecules containing similar substituents (CH(OH)R) at position 5: 4-methoxy-5-(*p*-tolylhydroxymethyl[2.2]paracyclophane (**23**) and two independent molecules of 1,2-dihydroxy-1,2-bis(4-methoxy[2.2]paracyclophan-5-yl)ethane (**24**) (the hydrogen atoms, except for the hydroxy H atoms, are omitted).

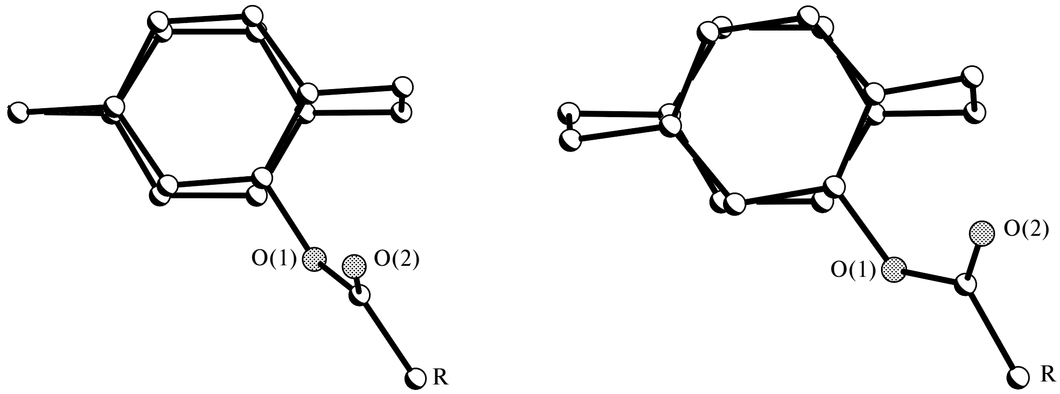
the rings in the skeleton. In one of two independent molecules of **32** (**32a**) and in molecule **33**, the twist makes the main contribution to the distortion of the skeleton (the τ_1 and τ_2 angles differ by 16 and 10°, respectively). In another independent molecule (**32b**), the distortion (Fig. 7) is characterized by the parallel shift of the rings. Undoubtedly, this difference in the configuration of the PCP skeletons in these three molecules is a consequence of the difference in the steric conditions of the molecular packing. In molecule **31**, the benzene rings are shifted parallel to the ethylene bridge analogously to the shift in molecule **30** (see Fig. 6).

The decisive influence of the steric factors on the character of the mutual arrangement of the benzene rings in the PCP skeleton is also clearly seen in the complex of copper dichloride with 4-[phenyl(2-pyridyl)hydroxymethyl][2.2]paracyclophane (**43**)[42] containing one highly overcrowded substituent at position 4 (Fig. 8). Compared to unsubstituted PCP **1**, the skeleton in molecule **43** is strongly distorted and is characterized by the parallel shift of the rings. Although the distance between the atoms at the bow and stern positions in the complex is equal to that observed in unsubstituted PCP **1** (2.78 Å), the rings in the complex are located at a closer distance (3.069 Å) and are unsymmetrically puckered (α_1 and β_1 are 17.0 and 13.6°; α_2 and β_2 are 11.9 and 14.7°) with retention of the usual C(3),C(6)-boat-like conformation. The rings are noncoplanar, and the dihedral angle between their planes



29 **30**

Fig. 6. Superposition of the rings in the 4,7-bis(methoxy)- (**29**) and 4,5,7,8-tetrakis(methoxy)-12,13,15,16-tetracyano[2.2]paracyclophane (**30**) molecules.



32a **32b**

Fig. 7. Superposition of the rings in two independent molecules of 4-camphanoyloxy-[2.2]paracyclophane (**32**).

is 6.6°. The exocyclic C(4)—C(17) bond has a standard length (1.534 Å), but the exocyclic C(17)—C(4)—C(3) and C(17)—C(4)—C(5) bond angles (124.1 and 117.9°, respectively) differ substantially from the standard values.

Therefore, the above analysis shows that the character of distortions of the boat-like conformation of the benzene rings, the arrangement of the ethylene bridges with respect to the rings, and the mutual arrangement of the rings in the PCP skeleton depend predominantly on the steric rather than electronic factors.

2.2. Other heteroatomic substituents

A total of 12 structures containing heteroatomic substituents different from OH and OR (two structures with the S atom, two structures with the $SiMe_2$ group, one structure with the P atom, one structure with the $GeMe_2$ bridging group, and six structures containing the Br or Cl atoms) were described. (The geometric parameters of selected molecules are given in Table 1.)

It should be noted that the lengths of the bonds between the C atoms and the substituents in the PCP skeleton and the *ipso*-angles in these structures have values typical of the corresponding atoms in substituted benzene derivatives. The main differences in the structures of these molecules are associated with the character of distortions of the PCP skeleton. Molecule **35** and isomers **37—41** are most typical in this respect.

Molecule **35** consists of two PCP skeletons linked by the sulfur atom (Fig. 9). Steric intramolecular hindrances occur between the sulfur atoms and the adjacent atoms of

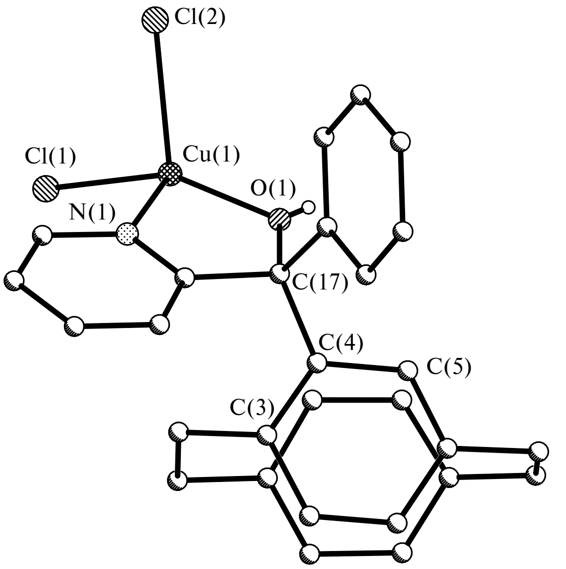


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Fig. 8. Molecular structure of the highly sterically overcrowded complex of copper dichloride with 4-[phenyl(2-pyridyl)hydroxymethyl][2.2]paracyclophane (**43**); the hydrogen atoms are omitted.

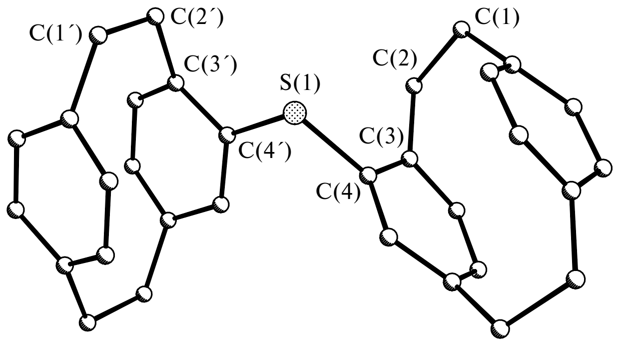
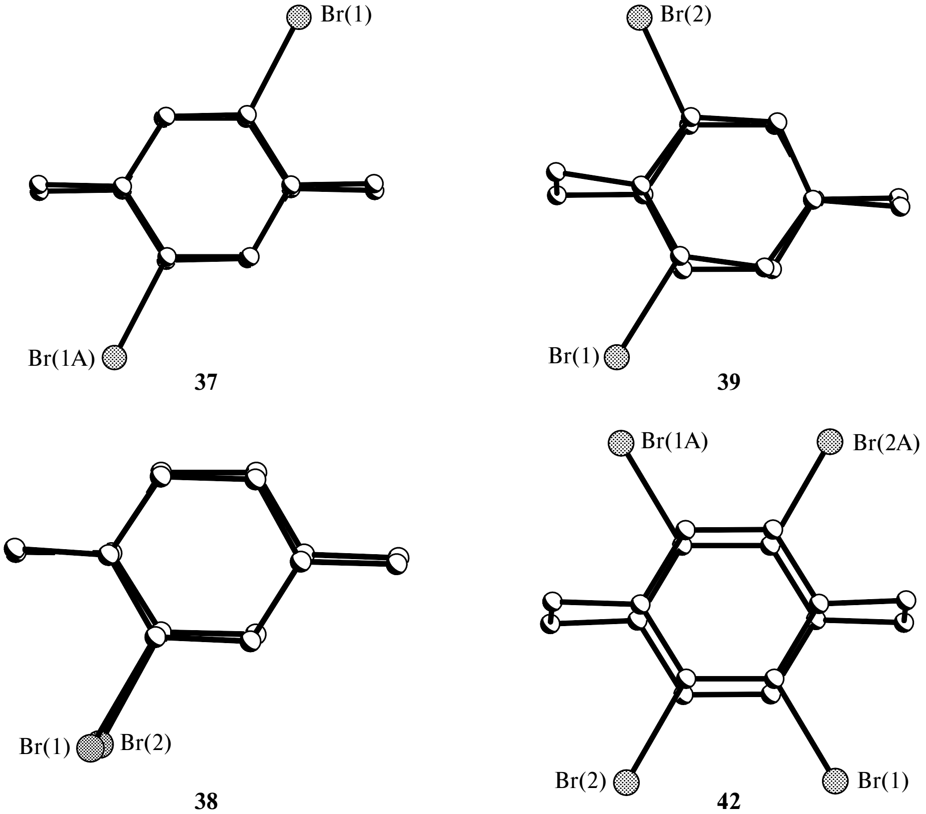


Fig. 9. Molecular structure of bis([2.2]paracyclophan-4-yl) sulfide (**35**); the hydrogen atoms are omitted.

the ethylene bridges; the S...C(2) and S...H—C(2) distances (3.183 and 2.86 Å) are larger than the S...C(2´) and S...H—C(2´) distances (3.089 and 2.69 Å). As a consequence, the second skeleton is more flattened; the torsion angles about the bridging C(1)—C(2) and C(1´)—C(2´) bonds in the first and second skeletons are 15.7 and 2.1°, respectively. In both skeletons, the benzene rings are shifted away from the sulfur atom. The related PCP—$SiMe_2$—PCP (**44**)[43] and PCP—$GeMe_2$—PCP (**45**)[44] molecules have similar structures.

In isomeric molecules **37**—**40**, the PCP skeleton is skewed in different ways (Fig. 10). The molecules have similar geometric parameters (except for the significantly elongated bridging C(1)—C(2) bond in **39** and **40**) and



37 **39** **38** **42**

Fig. 10. Superposition of the rings in 4,16-dibromo[2.2]paracyclophane (**37**), 4,13-dibromo-[2.2]paracyclophane (**38**), 4,15-dibromo[2.2]paracyclophane (**39**), and 4,5,15,16-tetrabromo[2.2]paracyclophane (**42**).

differ primarily in the torsion angles. In compounds **37** and **38**, the PCP skeleton is undistorted. In compound **39**, the angle between the rings is 4.3° (the twist angle). In compound **40**, the rings are not only twisted by 5.7° but also shifted in the parallel direction. In tetrasubstituted molecule **42**, the benzene rings are only shifted in the parallel direction. These differences in the character of distortions of the PCP skeleton are indicative of the influence of interatomic interactions on the molecular packing in the crystals, because there are no systematic changes in the skeleton depending on the positions of the bromine atoms and intramolecular contacts with the bridging atoms. The PCP skeleton has the most skewed conformation in molecules **39** and **40**, the bridges in these molecules are more strongly twisted (the τ_1 and τ_2 angles are as high as 20°) compared to other molecules.

2.3. The CN, COR, Alk, and Ar substituents

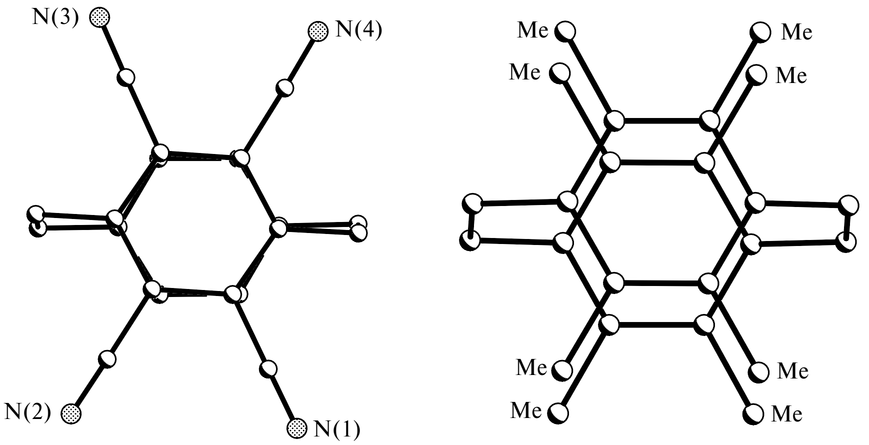
More than 40 structures of substituted [2.2]paracyclophanes containing the C(PCP)—C bonds were retrieved from the CSD. Selected molecules, which differ in the position and effective volumes of the substituents, are listed in Table 2. These molecules are of most interest from the point of view of the steric effects.

On the whole, these molecules are structurally similar. In all molecules, the benzene rings adopt the symmetrical C(3),C(6)-boat conformation characterized by the similar α and β angles. In most molecules, the bridging bond lengths are in a range of 1.57—1.59 Å. The exceptions are tetra- and octasubstituted molecules **47** and **49**, in which these bonds are shorter (aver., 1.56 Å). Besides, these molecules have the shortest (2.74 Å) and longest (2.82 Å) distances between the atoms at the bow and stern positions (the minimum and maximum extension of the ethylene bridges, respectively). The benzene rings in octamethyl[2.2]paracyclophane **49** are strongly shifted in the parallel direction, which apparently reflects the presence of steric hindrance between the Me groups in the PCP skeleton (Fig. 11). In compound **47** containing only one substituted ring, the shift is virtually absent. The distance between the rings (P') in molecule **49** is also substantially larger than that in molecule **47**.

In molecules **50**, **60**, and **61**, the τ_1 and τ_2 angles are larger than 20°. Apparently, this is also associated with intramolecular steric interactions. In molecule **50**, the 9-fluorenylidene substituent $CH=C_{13}H_{10}$ is tilted with respect to the PCP skeleton (Fig. 12) giving rise to steric hindrances with the ethylene bridge. However, the skeleton in molecule **62** is less twisted, in spite of the fact that it also contains the bulky substituent. In the molecule consisting of two PCP skeletons, which are linked by the highly overcrowded

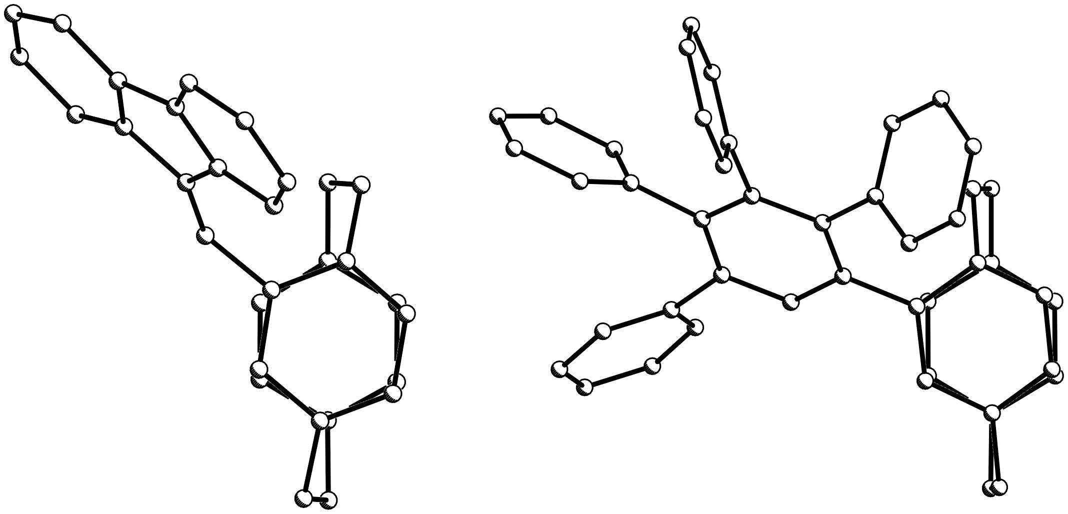
Table 2. Parameters characterizing the structure of the paracyclophane skeleton in selected 4-substituted [2.2]paracyclophanes containing the C(PCP)—C bond

Compound	Substituents	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P'
46[45,46]	4-COMe	1.58	1.57	2.76	2.78	14.5	13.1	12.1	12.0	12.8	11.9	3.093
47[32]	4,5,7,8-$(CN)_4$	1.55	1.57	2.74	2.74	13.7	14.0	12.9	12.1	9.4	11.5	3.074
48[47]	4,15-$(CHO)_2$, 5,16-$(CH(OEt)_2)$	1.57	1.57	2.76	2.76	13.0	13.0	14.3	14.3	14.8	14.8	3.108
49[48]	4,5,7,8,12,13,15,16-Me_8	1.56	1.56	2.83	2.83	16.4	16.4	16.9	16.9	15.4	15.4	3.152
		1.56	1.56	2.81	2.81	17.1	17.1	15.9	15.9	15.1	15.1	3.162
50[49]	4-$CH=C_{13}H_8$	1.59	1.59	2.78	2.77	12.2	11.9	12.7	12.7	29.2	25.7	3.077
51[50]	4-CH_2—PCP (*rac*)	1.581	1.585	2.792	2.779	13.7	12.3	12.2	12.4	17.1	8.7	3.101
52[50]	4-CH_2—PCP (*meso*)	1.579	1.582	2.767	2.771	6.8	11.5	12.5	11.8	3.5	4.7	3.068
		1.579	1.577	2.775	2.773	12.7	11.8	12.5	11.9	1.4	14.1	3.069
53[51]	4-*o*-Tol	1.584	1.573	2.796	2.771	12.8	11.8	12.5	12.0	3.0	11.3	3.075
54[51]	4-(2,6-Me_2—Ph)	1.588	1.581	2.799	2.781	15.1	13.5	8.7	15.9	5.1	20.1	3.110
55[51]	4-(2,4,5-Me_3—Ph)	1.576	1.587	2.790	2.775	12.7	11.9	12.5	12.0	14.0	15.0	3.090
		1.587	1.575	2.783	2.773	12.8	11.9	12.6	11.4	15.4	9.5	3.077
56[52]	4-PCP	1.58	1.58	2.79	2.77	13.8	12.3	11.6	12.2	3.8	4.0	3.085
		1.59	1.59	2.78	2.78	13.1	11.5	11.6	11.8	8.8	14.7	3.077
57[53]	4-(9-$C_{10}H_7$)	1.57	1.56	2.77	2.76	12.6	12.2	13.6	12.9	3.3	3.8	3.079
		1.59	1.57	2.79	2.76	13.1	11.7	13.2	11.8	8.0	11.2	3.083
58[53]	4-(2-Me—C_9H_7)	1.58	1.57	2.80	2.79	14.6	13.8	12.9	12.5	11.3	7.5	3.116
59[54]	4,16-$(CH=CHPh)_2$	1.58	1.58	2.76	2.76	12.6	12.6	12.3	12.3	8.6	8.6	3.069
60[54]	4,12-$(CH=CHPh)_2$	1.58	1.58	2.77	2.76	12.7	12.2	12.2	11.9	20.6	22.9	3.081
		1.58	1.58	2.79	2.78	11.7	12.8	12.4	12.7	25.2	25.2	3.069
61[41]	4,7,12,13-$(CH=CHPh)_4$	1.59	1.58	2.77	2.76	12.8	12.1	12.6	12.5	22.3	21.3	3.074
62[55]	4-Ph(Ph4)	1.58	1.59	2.79	2.78	12.7	12.9	12.9	12.2	15.0	11.3	3.089



47 **49**

Fig. 11. Superposition of the rings in 4,5,7,8-tetracyano- (**47**) and 4,5,7,8,12,13,15,16-octamethyl[2.2]paracyclophane (**49**).



50 **62**

Fig. 12. Superposition of the rings in the highly overcrowded 4-(9-fluorenylidenemethyl)[2.2]paracyclophane (**50**) and 4-[(2,3,4,5-tetraphenyl)phenyl][2.2]paracyclophane (**62**) molecules.

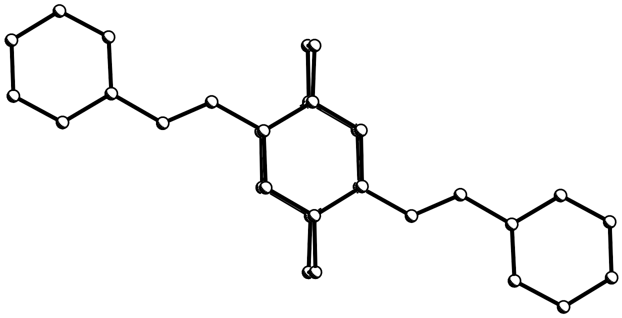
4,4´-CH(NH—(2,6-Me_2—Ph))—CH(NH—(2,6-Me_2—Ph)) bridge (**63**),[28] one skeleton is undistorted, whereas the rings in another skeleton are strongly shifted in the perpendicular direction. Molecules **59** and **60** differ in the position of the CH=CHPh substituent in the lower ring, the torsion angles differing by more than 10°. This leads to the difference in the character of distortions of the skeleton (Fig. 13).

There are no regularities in the character of distortions of the PCP skeleton, except for the general tendency for an increase in the degree of distortion with increasing bulkiness of the substituent. The wide ranges of the torsion angles (3.3—29.2°) and P distances (3.068—3.162 Å) are indicative of rather high flexibility of the PCP skeleton.

2.4. Quinones, semiquinones, and dihydrogenated rings

In these compounds, one benzene ring differs radically from the second ring, because the presence of the C=O (or C=C) groups or hydrogenation of one (or two) position of the benzene ring imposes rigid requirements on the geometric and conformational parameters (Table 3).

2.4.1. Quinones and quinodimethanes. In quinones **64** and **65**, the quinoid form is clearly pronounced. The C=O bond length (1.20 Å) and the C(5)=C(6) and C(8)=C(3) bond lengths (1.33 Å) are typical of double bonds. The exocyclic C(3)—C(2) bond length and the bridging C(2)—C(1) bond length are 1.50 and 1.56 Å, respectively. These lengths differ substantially from those observed in PCP **1**, in which the C—C bond lengths show a small al-



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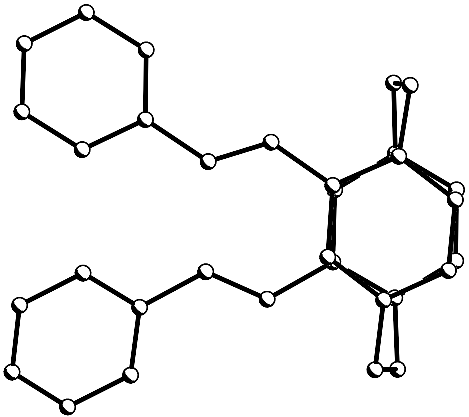


60

Fig. 13. Superposition of the rings in the isomeric 4,16- (**59**) and 4,12-bis(2-phenylethylidene)[2.2]paracyclophane (**60**) molecules.

ternation (the lengths are approximately equal to 1.40 Å), and the exocyclic C(2)—C(3) bond length and the bridging C(1)—C(2) bond length are 1.508 and 1.580 Å, respectively. In spite of this fact, the rings in compounds **64** and **65** adopt the nearly symmetrical C(3),C(6)-boat conformation (as in **1**). The average folding angles of the boat in the upper ring, α_1 and β_1 (17.4°), the distance P' (3.053 Å), and the distance Δ (2.705 Å) differ substantially from those in PCP **1** (12.4°, 3.099 Å, and 2.786 Å, respectively), *i.e.*, the rings in quinones are located at closer distances than those in [2.2]paracyclophane.

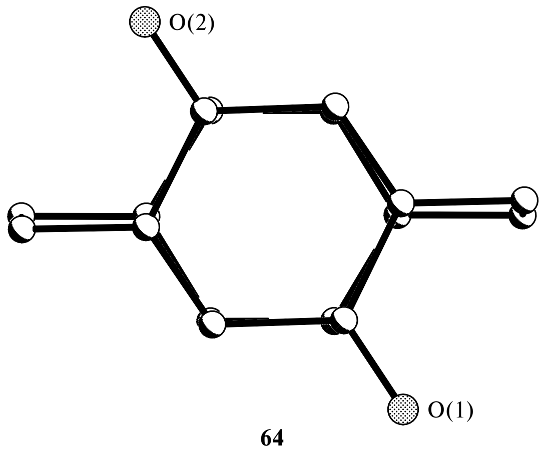
The τ torsion angles in molecule **65** are more than three times larger than those in **64**. This difference is clearly seen from Fig. 14, where the mutual orientation ("superposition") of the rings is shown. In molecule **64**, the rings are slightly shifted in the perpendicular direction. In the second molecule, the rings are twisted by approximately 7°. The latter fact is, apparently, associated with the presence of substituents in the lower ring, *i.e.*, with the steric intramolecular factors.

The [2.2]paracyclophane-4,7-tetracyanoquinodimethane molecule (**78**)[59] containing the quinoid ring $(CN)_2C=C_6H_4=C(CN)_2$ is structurally similar to quinone **65**. The distance between the atoms at the bow and stern positions (Δ_{aver} is 2.745 Å) in this molecule is somewhat larger than the corresponding distances in molecules **64** and **65**. The ring adopts the symmetrical C(3),C(6)-boat conformation, but the quinoid ring is more flattened (the average α_1 angle is 15.3°). The τ_1 and τ_2 torsion angles (21.0 and 25.8°) are similar to the angles characteristic of molecule **65**. The mutual arrangement of the rings is characterized primarily by the twist (the twist angle of 8°; Fig. 15). The C—C and C=C bond lengths in the quinoid ring are 1.459 and 1.349 Å, respectively, *i.e.*, the bonds are delocalized to a certain extent, unlike those in molecules **64** and **65**. Presumably, the

Table 3. Parameters characterizing the structure of the paracyclophane skeleton in quinones, semiquinones, and selected [2.2]paracyclophanes containing partially hydrogenated rings

Compound	Substituents	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P'
64[56]	4,7-$(=O)_2$	1.56	1.58	2.70	2.70	17.1	16.9	10.7	10.80	6.0	6.1	3.045
65[57]	4,7-$(=O)_2$, 12,15-$(NMe_2)_2$	1.55	1.55	2.71	2.71	17.4	17.4	11.8	11.8	21.5	21.5	3.061
66[58]	4,7-$(=C(CN)_2)_2$, 12,15-$(OMe)_2$	1.57	1.56	2.74	2.74	17.1	15.4	9.9	10.2	24.1	27.0	3.066
67[59]	4,7-$(=C(CN)_2)_2$, 13,16-$(OMe)_2$	1.58	1.57	2.71	2.73	15.2	13.1	9.8	10.3	20.3	18.0	3.021
68[60]	4-(=O), 3-OMe, 7-Ph, 3-H	1.54	1.57	3.07	2.72	3.9	8.1	12.9	14.3	39.3	22.5	3.100
69[61]	4-(=O), 3,7-Me_2, 3-H	1.55	1.58	3.07	2.73	1.6	9.8	13.0	12.9	43.3	19.6	3.084
70[61]	4-(=O), 3,7-$(CH_2CH=CH_2)_2$, 3-H	1.55	1.58	3.10	2.73	1.5	8.8	12.8	12.1	39.8	22.1	3.086
71[62]	4-(=O), 7-(H,Ph), 8-Ph	1.57	1.57	2.73	2.75	16.8	19.5	11.5	11.4	18.4	17.9	3.094
72[61]	4-(=O), 7-(H,Ph), 8-Ph	1.56	1.60	2.73	2.75	17.2	18.8	14.9	9.3	23.1	19.4	3.088
73[63]	4,7-$(OH,CH_2CH=CH_2)_2$	1.59	1.59	2.83	2.83	23.0	23.0*	13.5	13.5	14.8	14.8	3.063
74[63]	4,7-$(OH,Me)_2$	1.59	1.58	2.83	2.80	21.9	24.7*	13.5	12.6	19.3	16.6	3.033
75[63]	4,7-$(OH,Ph)_2$	1.59	1.58	2.81	2.82	23.9	24.2*	12.6	11.3	2.9	2.7	3.007
76[62]	4,7-(OH,*o*-PhOMe)$_2$	1.59	1.59	2.83	2.80	23.7	25.2*	9.9	12.1	21.3	22.6	2.990
77[62]	4,7-(OH,*o*-PhNMe)$_2$	1.58	1.58	2.81	2.81	24.4	25.7*	12.4	11.4	27.8	24.9	3.003
		1.58	1.58	2.81	2.80	26.1	25.3*	11.4	11.3	27.6	25.2	2.987

* The ring adopts the C(4),C(7) boat conformation.



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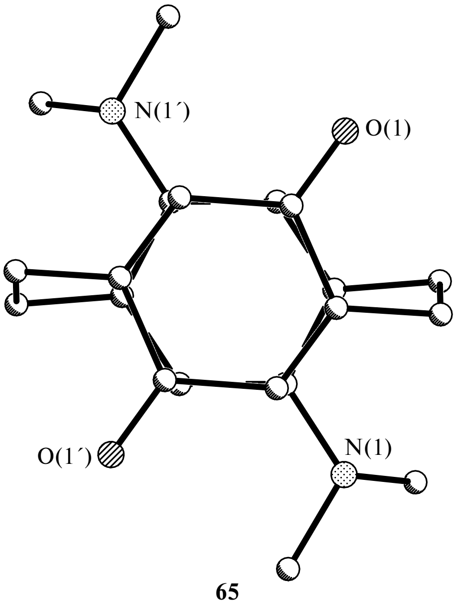

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Fig. 14. Superposition of the rings in the [2.2]paracyclophane-4,7-benzoquinone (**64**) and 12,15-bis(dimethylamino)[2.2]paracyclophane-4,7-benzoquinone (**65**) molecules.

replacement of the oxygen atom with the carbon atom (a decrease in electron donation to the system) leads to an increase in the distances between the bow and stern positions of the ring, a decrease in the folding angle, and bond delocalization in the ring, *i.e.*, the conformation of the ring becomes more similar to that of PCP **1**. Apparently, this fact is attributable to the purely electronic effect.

It should be noted that the conformation of the quinoid ring in these molecules is not unambiguously described in terms of the above-proposed characteristics. In particular, the deviations of the C(3) and C(6) atoms at the bow and stern positions in PCP **1** from the mean plane of the ring are twice as large as those of all other atoms (0.10 and 0.05 Å, respectively), which is unambiguously indicative of the C(3),C(6)-boat conformation. In the quinoid molecules, contrastingly, although the largest deviations are also observed for the C(3) and C(6) atoms at the bow and stern positions (0.15—0.13 Å), the deviations of two other atoms, *viz.*, C(4) and C(7), are also noticeable (0.10—0.13 Å), the deviations of the C(5) and C(8) atoms being small (0.01—0.03 Å), *i.e.*, there is a certain contribution of the C(4),C(7)-boat conformation. This contribution is particularly pronounced in molecule **78**, in which all four atoms of the ring, *viz.*, C(3),C(5),C(6),C(8), are strictly coplanar. The distances *P″* between the bottom of this C(4),C(7)-boat and the bottom of the C(3),C(6)-boat of the lower ring in these three molecules are substantially shorter (2.92—2.94 Å).

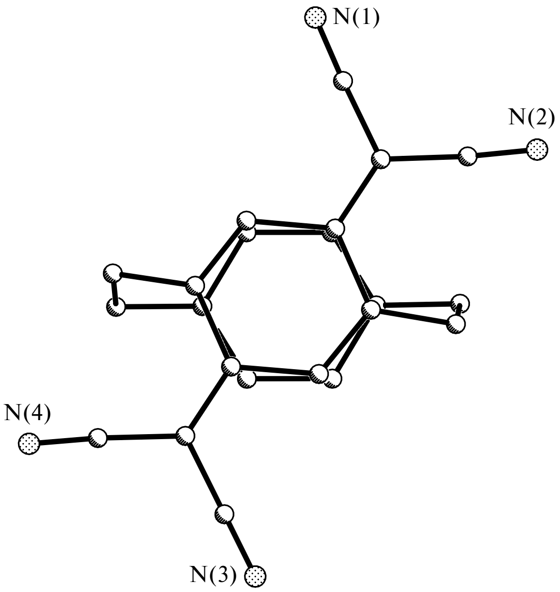

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Fig. 15. Superposition of the rings in the [2.2]paracyclophane-4,7-tetracyanoquinodimethane molecule (**78**).

It is of interest to compare the above-considered quinoid molecules with the paracyclophanequinone molecule **79**,[64] in which the quinoid ring is located between two benzene rings (Fig. 16). The geometric parameters of the central quinoid ring (C=O, 1.226 Å; C—C, 1.488 Å; C=C, 1.348 Å) have standard values, but the ring is strongly distorted and adopts a nearly twist conformation. Two planar fragments, *viz.*, C(11)—C(14)—O(2)—C(11A) and C(12)—C(13)—O1—C(12A) (the dihedral angle is 6.7°), are twisted by 33.7° along the C(11)—C(12) and C(11A)—C(12A) bonds, respectively. The ethylene bridges in the PCP skeletons are somewhat different (the C—C bond lengths are 1.580 and 1.570 Å, and the torsion angles are 15.5 and 18.8°). The conformation and geometry of the benzene rings are typical of the unsubstituted rings in PCP. The mutual arrangement of the rings in the skeleton of **79** is analogous to that in molecule **65**; the planes of the rings are twisted about a twofold axis (the

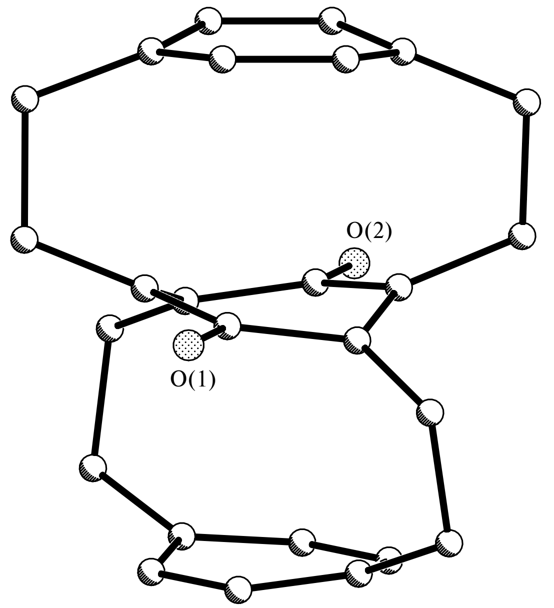

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Fig. 16. Molecular structure of paracyclophanequinone **79**; the hydrogen atoms are omitted.

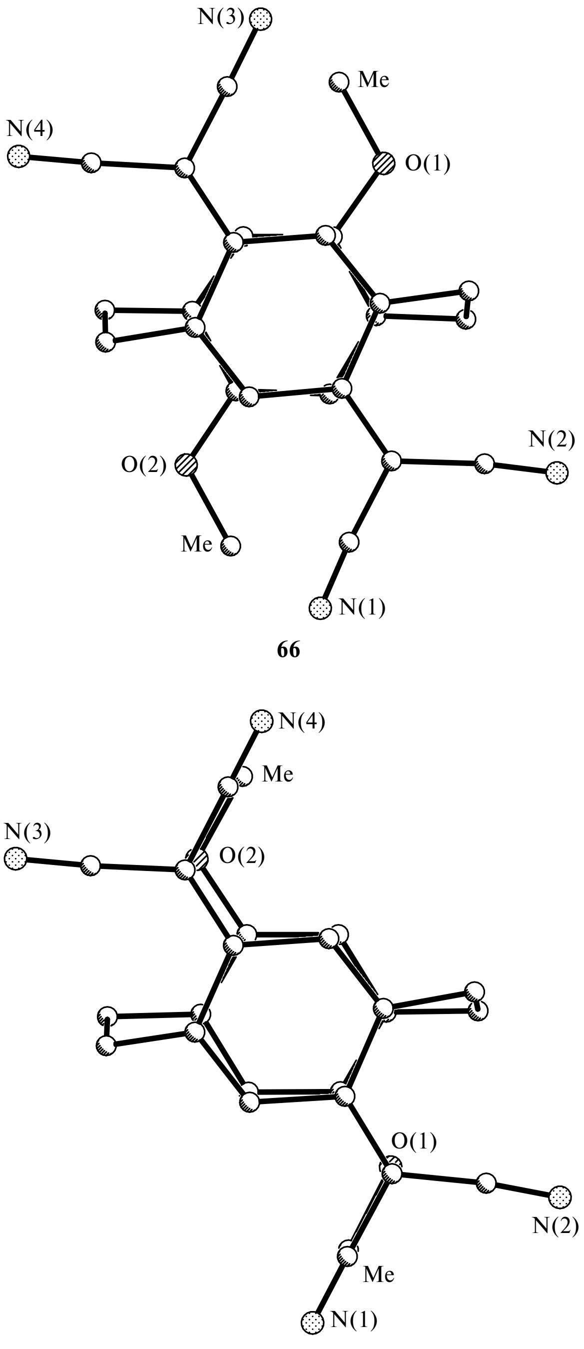


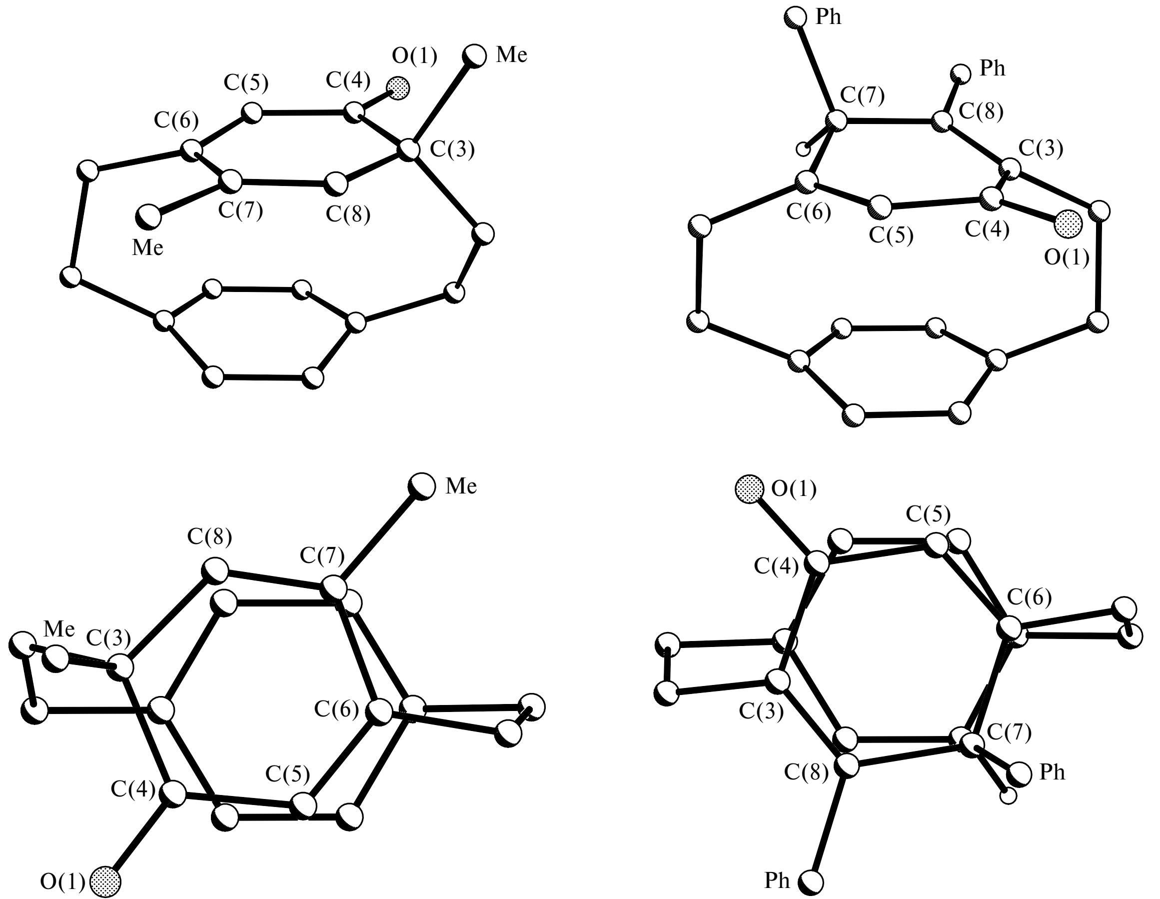
Fig. 17. Superposition of the rings in the isomeric 12,16-dimethoxy- (**66**) and 13,15-dimethoxy[2.2]paracyclophane-4,7-tetracyanoquinodimethane (**67**) molecules.

distance between the centroids of the rings $P = 2.96$ Å). In both PCP fragments, the distances Δ between the corresponding bow and stern positions have similar values (2.685 and 2.683 Å) and are shorter than those in molecules **64** and **65**. Therefore, in spite of a substantial distortion of the conformation, the geometric parameters of the quinoid ring in molecule **79** are similar to those in molecules **64** and **65**, with the only difference that the distances between the bow and stern positions are shorter.

Isomeric compounds **66** and **67** also contain the quinoid ring $(CN)_2C{=}C_6H_4{=}C(CN)_2$. However, the lower benzene rings in these compounds, in contrast to compound **78**, each contain two OMe groups (at positions 12, 15 and 13, 16). These molecules are also characterized by shortening of the C(3)...C(14) and C(6)...C(11) distances between the bow and stern positions (2.71—2.74 Å). The lower rings adopt the usual C(3),C(6)-boat conformation. The C(3),C(6)-boat makes the major contribution also to the conformation of the upper rings (as opposed to compound **78**). The shorter distance between the rings in molecule **67** can be related to an attractive interaction between the oxygen atom of the OMe group and the $C(CN)_2$ group (O...C, 3.06 Å). The character of the mutual arrangement of the rings is similar in both molecules (Fig. 17) and is analogous to that observed in molecule **65**.

The common feature of quinoid molecules **64—67** and **78** is a substantial distortion of the quinoid ring, the lower benzene rings being flattened in a similar fashion, and a decrease in the repulsion between the π systems of the PCP skeleton, resulting in shortening of the distances between the planes of the rings and the atoms at the bow and stern positions.

2.4.2. Semiquinones. Molecules **68—72** are representatives of semiquinoids. In three of these molecules (**68—70**), the *ortho* position 3 is hydrogenated, whereas the *para* position 7 is hydrogenated in mol-



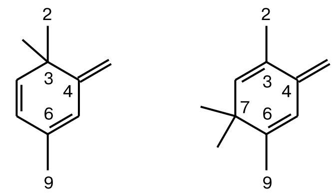
69 **72**

Fig. 18. Structures of the semiquinoid molecules and superposition of the rings in the 4-oxo-3,7-dimethyl-3*H*-[2.2]paracyclophane-*p*-semiquinone (**69**) and 4-oxo-7,8-diphenyl-7*H*-[2.2]paracyclophane-*o*-semiquinone (**72**) molecules; the hydrogen atoms are omitted.

ecules **71** and **72** (*o*- and *p*-semiquinones, respectively) (Fig. 18).

In each group of the molecules, the skeleton is distorted in a similar fashion. In molecules **68—70**, the PCP skeleton has an unsymmetrical structure. The bridging C(1)—C(2) bond is shorter than the C(9)—C(10) bond (aver., 1.55 and 1.58 Å). The C(3)—C(2)—C(1)—C(14) torsion angle (aver., 40.8°) is larger than the C(6)—C(9)—C(10)—C(11) angle (aver., 21.4°) by 20°. The C(3)...C(14) distance (aver., 3.08 Å) is substantially larger (by 0.3 Å) than the C(6)...C(11) distance (aver., 2.73 Å). In addition, the substituted ring is strongly flattened in the vicinity of position 3 (the α_1 angle is smaller than the β_1 angle by 6—8°), which corresponds to the flattened C(6)-half-chair conformation. Although the bridging C(1)—C(2) bond is shorter than the C(9)—C(10) bond, the C(3)—C(2)—C(1)—C(14) bridge (C(sp^3)—C(sp^3)—C(sp^3)—C(sp^2)) is more extended compared to the C(6)—C(9)—C(10)—C(11) bridge (C(sp^2)—C(sp^3)—C(sp^3)—C(sp^2)). This extension occurs due to an increase in the exocyclic C(2)—C(3) bond length (1.55—1.57 Å) compared to the C(6)—C(9) bond length (1.52 Å). In *p*-semiquinones **71** and **72**, such an asymmetry of the PCP skeleton is not observed. The rings adopt the nearly symmetrical C(3),C(6)-boat conformation, the hydrogenated ring being somewhat more puckered.

The C(3)...C(14) distance (Δ_1) between the bow or stern positions in *o*-semiquinones **68—70** is substantially longer (to 3.10 Å) compared to the distances in the molecules hydrogenated at the *para* position (2.74 Å), which reflects the difference in the configuration of the C(3) atom (sp^3 and sp^2). The exocyclic (C(3)—C(2)) and endocyclic (C(3)—C(4), C(3)—C(8), and C(7)—C(8)) bond lengths correspond to the canonical structural formulas of these rings.



The difference in the character of distortions of the PCP skeleton in these two groups of molecules (the τ_1

and τ_2 torsion angles) is, apparently, associated not only with the difference in hybridization of the C(3) atom at the bow position but also with the intramolecular steric factors resulting from the presence of substituents at positions 3, 7, and 8.

The common feature of semiquinoids **68—72** is that they have nearly equal distances P' (aver., 3.09 Å), which are similar to that typical of unsubstituted PCP, *i.e.*, the aromatic systems in semiquinoids and PCP **1** are arranged in a similar fashion and are located at larger distances than those in quinones. However, the molecules differ in the mutual arrangement of the rings. The rings in **68—72**, unlike those in PCP **1**, are substantially shifted and twisted (of the three components of distortion of the PCP skeleton, the perpendicular shift and twist play the major role) (see Fig. 18).

2.4.3. Dihydrogenated rings. In the molecules of diols **73—77**, the dihydrogenated ring contains the OH group and the alkyl (**73** and **74**) or Ph (**75—77**) substituent at positions 4 and 7. The hydroxy groups are involved in intra- or intermolecular hydrogen bonding.

The characteristic features of this group of compounds are associated with the sp^3 hybridization of the C(4) and C(7) atoms. First, the dihydrogenated rings adopt another conformation, *viz.*, the symmetrical C(4),C(7)-boat conformation; the average α_1 and β_1 angles are 24°; the unsubstituted rings adopt the usual symmetrical C(3),C(6)-boat conformation. Second, the ethylene bridges are substantially extended; the C(3)...C(14) and C(6)...C(11) distances are in a range of 2.80—2.83 Å. Third, the rings are far apart; the distances P'' between the bottoms of the C(4),C(7)-boat of the upper ring and the C(3),C(6)-boat of the lower ring, which are twisted with respect to each other by 60°, are in a range of 3.06—2.99 Å. In the quinoid molecules, the analogous average distance (as mentioned above) is 2.93 Å. The distances between the bottoms of the C(3),C(6)-boats in both rings (the analog of the distance P') are very large (3.23—3.26 Å).

The character of distortions of the PCP skeleton is similar in pairs of compounds **73**, **74** and **76**, **77**, and the distortion is virtually absent in compound **75**. The distortion of the skeleton (Fig. 19) includes primarily the twist component, whereas the shift of the rings is insignificant. Only in molecule **75**, the overall configuration of the PCP skeleton (the τ_1 and τ_2 torsion angles are close to 3°) is similar to that in the PCP molecules and quinone **64**.

The bond lengths in the hydrogenated ring correspond to the canonical form of 4,7-dihydrobenzene (the average C—C and C=C bond lengths are 1.52 and 1.32 Å, respectively). A substantial extension of the bridges results only in an increase in the C(3)—C(2)—C(1) and C(6)—C(9)—C(10) bond angles involving the C(3) and C(6) atoms of the hydrogenated ring (to 115°), whereas the C(14)—C(1)—C(2) and C(11)—C(19)—C(9) bond

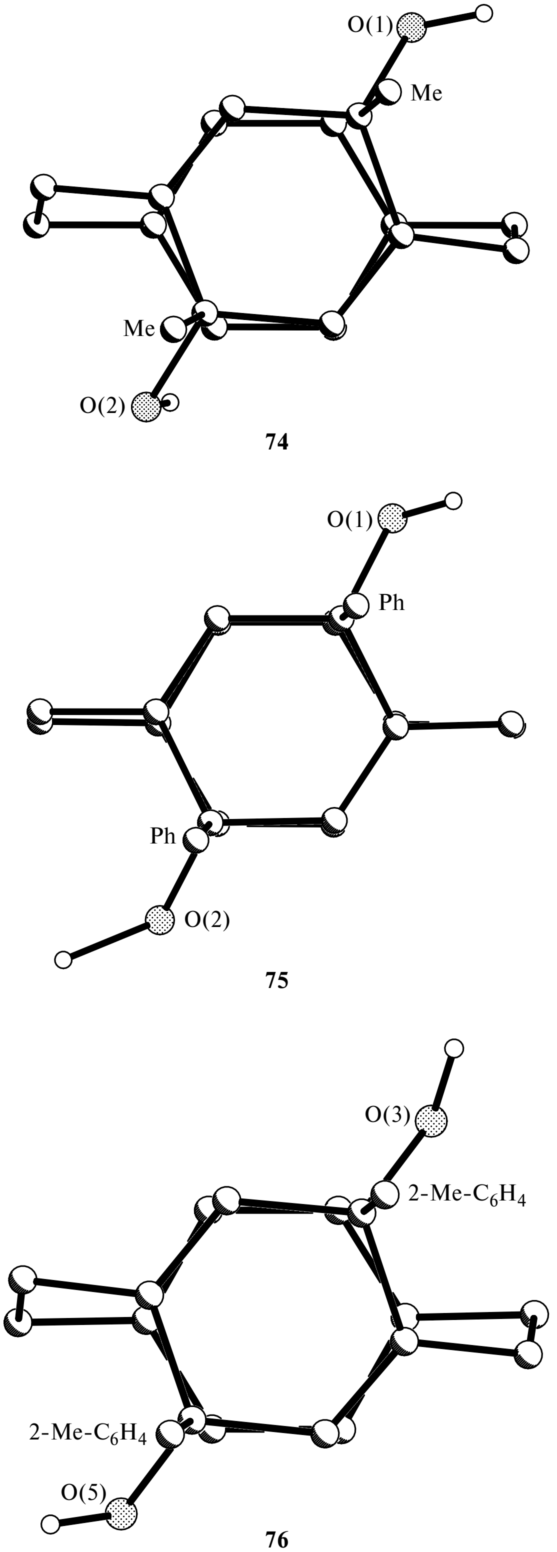


Fig. 19. Superposition of the rings in the dihydrogenated 4,7-dihydroxy-4,7-methyl- (**74**), 4,7-dihydroxy-4,7-phenyl- (**75**) and 4,7-dihydroxy-4,7-bis(2-methoxyphenyl)-4,7-dihydro[2.2]paracyclophane (**76**) molecules.

angles involving the atoms of the unsubstituted ring, *viz.*, C(14) and C(11), are smaller (110.5—112.2°). The bridging C(1)—C(2) and C(9)—C(10) bond lengths in molecules **73—77** have standard values, but all exocyclic bonds are shorter (their lengths vary in a range of 1.503—1.524 Å).

3. Substituents in ethylenic bridges

The ethylenic bridges serve as an important constituent of the PCP skeleton as a molecular cage. Up to this point, we have considered only molecules containing unsubstituted ethylenic bridges and noted their flexibility. As mentioned above, the changes in the structural features are accompanied primarily by the changes in the torsion angle, thus characterizing the extension or contraction of the bridges. It is also of interest to analyze the influence of the substituents in the bridges on the overall structure of the PCP skeleton.

Only 11 molecules containing substituents at the bridgehead atoms were found. Selected geometric characteristics of these compounds are given in Table 4.

The presence of one substituent in one ethylene bridge results in similar distortions of the PCP skeleton (**80—83**). The benzene rings adopt the symmetrical C(3),C(6)-boat conformation (the average folding angles of the boat are approximately equal to 12°). The bridging bond lengths vary in a range of 1.57—1.60 Å. The distances between the bow and stern positions vary in a range 2.76—2.79 Å. The τ_1 torsion angles in the substituted bridge (20—30°) are substantially larger than the τ_2 torsion angles in the unsubstituted bridge (3—17°). The skeleton is unsymmetrically twisted in a similar fashion about the line connecting the centroids of the benzene rings. The typical character of distortions of the skeleton is shown using molecule **83** as an example (Fig. 20).

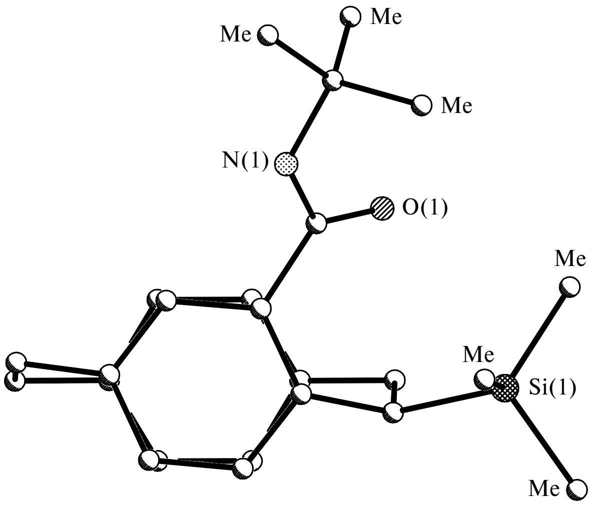


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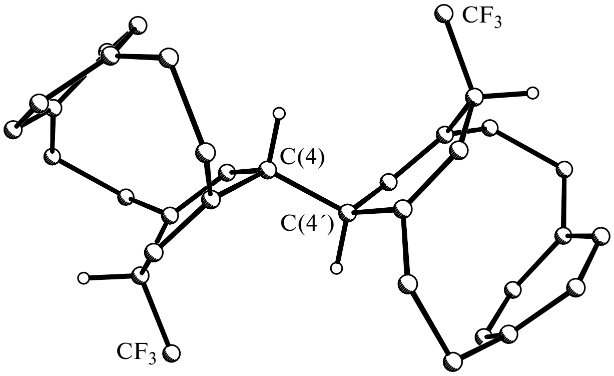
Fig. 20. Molecular structure and superposition of the rings in *N*-*tert*-butyl-2-trimethylsilyl[2.2]paracyclophanyl-4-carboxamide (**83**); the hydrogen atoms are omitted.

Molecules **84** and **85** are isomeric. The molecules contain two fluorine atoms in different positions at one of the carbon atoms in each bridge. The bridging C—C bond lengths (1.54 Å) are substantially smaller than those typical of the PCP skeleton. However, an "extension" of the —CH_2—CF_2— bridge (the distances Δ_1 and Δ_2) is similar to that observed in unsubstituted PCP **1** (2.80 Å). The exocyclic C(3)—C(9) and C(9)—C(10) bond lengths (1.50—1.51 Å) have standard values, and shortening of the bridging bond results only in an increase in the C(3)—C(2)F_2—C(1) bond angle (116°; in PCP **1**, this angle is approximately equal to 112°) compared to the C(2)F_2—C(1)—C(14) angle (113.5°). The PCP skeleton is only slightly distorted. The shift of the rings is analogous to that shown for molecule **47** in Fig. 11 or for molecule **75** in Fig. 19.

In the molecules containing the completely substituted —CF_2—CF_2— bridges (stereoisomers **86** and **87**), the situation is somewhat different. These molecules belong to 4,7-dihydrogenated paracyclophanes (like compounds **73—77**, see Table 3) and involve two PCP skeletons linked at positions 4 and 4´. In addition, each PCP skeleton contains the CF_3 substituent at position 7. For molecule **87**, the character of distortions of the skeleton is similar to that observed in 4,7-dihydrogenated paracyclophanes (Fig. 21, Table 3).

From a comparison of the mono- and disubstituted bridges, it follows that the C—C bond lengths in the —CF_2—CF_2— bridges and their extension (Δ) are substantially larger than those in the —CF_2—CH_2— bridges. The exocyclic C—CF_2 bond lengths have similar values. An extension of the —CF_2—CF_2— bridges is accompanied only by a slight decrease in the bond angles at the



87

Fig. 21. Molecular structure of 7,7´-bis(trifluoromethyl)-1,1,2,2,1´,1´,2´,2´-octafluoro-4,7,4´,7´-tetrahydro-4,4´-bi[2.2]paracyclophane (**87**); the bridgehead fluorine atoms and the hydrogen atoms in the PCP skeletons are omitted.

Table 4. Parameters characterizing the structure of the paracyclophane skeleton in selected [2.2]paracyclophanes containing substituents in the ethylene bridges

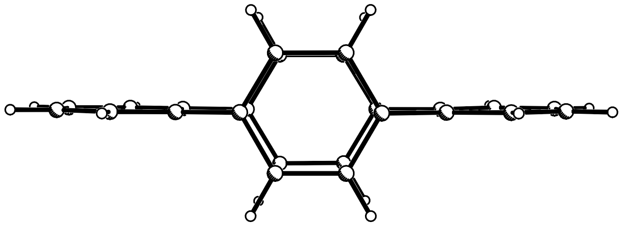
Compound	Substituents	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P'	C(3)—C(2)	C(1)—C(14)	C(6)—C(9)	C(11)—C(10)
80[65]	C(2)-SPh, 4-oxazole	1.58	1.57	2.78	2.78	13.8	13.2	12.9	12.9	23.5	2.9	3.107	1.52	1.53	1.52	1.52
81[66]	C(1)-CONPr$^{i}_{2}$, 4-OH, 5-SiEt$_3$	1.59	1.57	2.79	2.79	11.5	8.7	6.4	12.4	30.0	9.1	3.087	1.52	1.51	1.53	1.51
		1.59	1.56	2.80	2.76	11.4	14.6	11.4	11.5	29.7	11.4	3.079	1.53	1.50	1.52	1.51
		1.59	1.57	2.76	2.78	12.2	14.4	12.1	12.2	24.7	17.3	3.062	1.52	1.52	1.52	1.50
82[66]	C(1)-CONPr$^{i}_{2}$, 4-OH	1.60	1.59	2.78	2.77	11.3	12.0	12.2	12.3	20.4	13.1	3.032	1.53	1.51	1.51	1.51
83[66]	C(2)-SiMe$_3$, 4-CONHBu^t	1.59	1.59	2.78	2.79	15.0	13.5	11.5	11.5	26.1	16.3	3.107	1.53	1.52	1.52	1.51
84[67]	C(1)-F$_2$, C(9)-F$_2$	1.54	1.54	2.80	2.80	10.5	10.5	13.0	13.0	1.6	1.6	3.088	1.51	1.51	1.52	1.52
85[67]	C(1)-F$_2$, C(10)-F$_2$	1.54	1.54	2.79	2.79	10.9	11.7	13.0	12.7	5.5	1.5	3.086	1.50	1.52	1.51	1.51
86[68]	4,4´-(PCP—PCP), C(1),C(2)-F$_4$, 4-H, 7-CF$_3$	1.59	1.59	2.82	2.81	18.6	18.5	10.9	10.1	25.1	26.0	3.160	1.52	1.50	1.52	1.50
		*	*	2.83	2.82	17.1	18.8	10.2	10.3	*	*	3.078	*	*	*	*
87[68]	4,4´-(PCP—PCP), C(1),C2)-F$_4$, 4-H, 7-CF$_3$	1.59	1.59	2.86	2.86	18.5	17.7	11.0	11.3	29.5	30.8	3.173	1.51	1.50	1.52	1.50
		1.60	1.59	2.85	2.83	20.3	16.7	10.5	10.7	28.0	25.9	3.190	1.52	1.50	1.42	1.49
88[69]**	C(1),C(2)-C$_6$H$_4$, 9,10-C$_6$H$_4$	1.42	1.44	2.78.	2.80	12.1	12.4	11.8	13.2	3.3	1.7	3.100	1.50	1.50	1.51	1.50
89[70]**	C(1),C(2)-C$_6$H$_4$	1.43	1.55	2.77	2.81	11.0	12.3	11.3	13.1	1.8	3.7	3.082	1.51	1.50	1.54	1.49
90[70]**	C(1),C(2)-C$_6$H$_4$, C(9)=C(10)	1.42	1.31	2.76	2.81	15.1	11.6	13.7	12.2	1.7	1.7	3.106	1.48	1.52	1.53	1.53
91[71]**	C(1),C(2)-pyridazine	1.41	1.55	2.79	2.79	11.6	12.5	11.7	12.6	0.1	15.2	3.079	1.50	1.50	1.51	1.51
92[72]**	C(1),C(2)-C$_6$Ph$_4$, 9,10-C$_6$Ph$_4$	1.43	1.43	2.77	2.77	12.4	12.4	13.7	13.7	3.4	3.4	3.103	1.50	1.50	1.50	1.50
93[73]	C(1)=C(2), C(9)=C(10)	1.34	1.34	2.80	2.80	13.1	13.1	14.2	14.2	0.9	0.9	3.140	1.51	1.51	1.52	1.52

* The bridge is disordered.

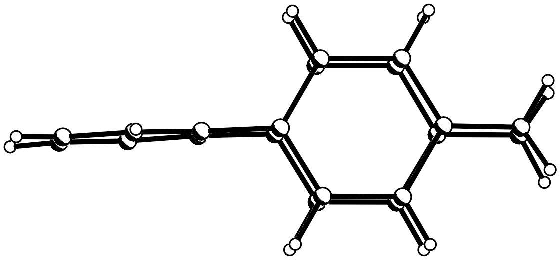
** The bridgehead atoms are involved in the aromatic ring.

C(2), C(9) and C(1), C(10) atoms (aver., 114.3 and 111.6°) compared to the less "extended" $—CH_2—CF_2—$ bridge (115.7 and 113.5°).

In molecules **88—92**, the bridges are involved in the aromatic rings (the $C_{Ar}—C_{Ar}$ bridges), whereas molecule **93** contains the —CH=CH— bridges. These molecules differ only in the bridging C(1)—C(2) and C(9)—C(10) bond lengths, whereas the orientations of the benzene rings and their conformations are similar. The bridging $C_{Ar}—C_{Ar}$ bond lengths (aver., 1.43 Å) are larger than the standard bond length in the benzene ring. A shortening of the bridging bond compared to that in PCP **1** leads only to an increase in the bond angles at the bridgehead carbon atoms to 116—118°. In compounds **89** and **91**, only one bridge is involved in the aromatic ring (benzene and pyridazine, respectively), resulting in the nonequivalence of the bridges. In addition to the difference in the bridging bond lengths, this is reflected in the bond angles. In the $—C_{Ar}—C_{Ar}—$ bridge, these angles (116.2—118.0°) are larger than those in the $—CH_2—CH_2—$ bridge (113.5—115.0°). The overall conformation of the PCP skeleton is similar to that in molecules **88** and **92** containing two aromatic bridges, which are characterized by a slightly larger shift of the coplanar benzene rings (the dihedral angle between the planes of the rings is 2.4°). The shifts of the ethylene bridge in the perpendicular and parallel directions make the major contribution to the character of distortion of the PCP skeleton in compound **91**, the perpendicular shift being rather pronounced (Fig. 22).



88



91

Fig. 22. Superposition of the rings in the 1,2:9,10-dibenzo[2.2]paracyclophane-1,9-diene (**88**) and 3,6-bis(methoxycarbonyl)-4,5-([2.2]paracyclophanyl-1,2)pyridazine (**91**) molecules, the substituents in the pyridazine ring are omitted.

Molecule **93** contains two identical —CH=CH— bridges and has a centrosymmetric structure. The bond length (1.34 Å) corresponds to the standard isolated double bond. Other parameters remain unchanged (see Table 4), except for the bond angles at the bridgehead atoms, which are approximately equal to 120° (119.1 and 118.7°). The PCP skeleton in **93**, like that in unsubstituted PCP **1**, is undistorted.

Hence, the overall conformation of the PCP skeleton remains unchanged regardless of the bond lengths in the bridges and the degree of their elongation, and only changes in the bond angles at the bridgehead atoms are observed.

4. π Complexes

Generally, the benzene rings in π complexes of various metals, in particular, in mono- and dibenzene complexes, are planar. It is of interest to analyze the structures of such complexes with [2.2]paracyclophane and reveal the effect of π-coordination on the structure of the benzene rings. Many structures of such compounds retrieved from the CSD belong to ruthenium [2.2]paracyclophane complexes, in which the ruthenium atom is η^6-coordinated by the benzene ring of the PCP skeleton. In addition, one structure with η^5-coordination and several structures with $2(\eta^3)$-, $3(\eta^2)$-, and $2(\eta^2)(\eta^3)$-coordination modes were described (the two last-mentioned modes are typical of Ru clusters, in which two or three ruthenium atoms are involved in coordination to one benzene ring of the PCP skeleton). There are also several structures of complexes with other metals (Fe, Cr, Rh, Ag, or In). A total of 27 complexes were structurally characterized.

We consider only the most typical η^6 complexes. The data for these complexes are given in Table 5. An analysis of these data shows that the PCP skeletons in complexes **94—104** are structurally similar. The coordinated ring retains the C(3),C(6)-boat conformation. These complexes have a number of structural features in common.

First, the coordinated and uncoordinated benzene rings are coplanar (the φ angle between the planes of the rings is no larger than 2.9°), except for complex **96**, and adopt the nearly symmetrical C(3),C(6)-boat-like conformation. In complex **96**, the φ angle is 6.4°, which is, apparently, attributable to the steric factors associated with the presence of the bulky $Me_3C_6H_3—Co(CO)_3$ substituent at position 4. It can be concluded that the π-coordination of one ring (or two rings in complex **106**) has no effect on the conformation of the rings and their mutual arrangement, which remains the same as that in unsubstituted PCP **1**.

Second, the distances between the bottoms of the boats P' (2.973—3.030 Å) are shorter than that in unsubstituted PCP **1** (3.099 Å). The exception is cation **100**,

Table 5. Parameters characterizing the structure of the paracyclophane skeleton in selected typical η^6-complexes with [2.2]paracyclophanes

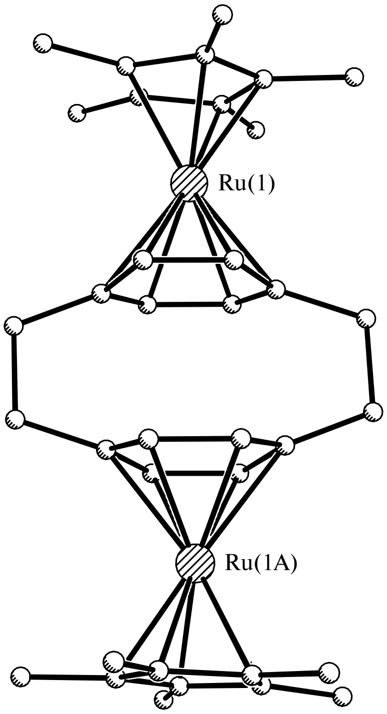
Compound	Refcode*	Composition of the complex	d_1	d_2	Δ_1	Δ_2	α_1	β_1	α_2	β_2	τ_1	τ_2	P	φ **
94	BIVVEH	$[PCP—Fe(Cp)]^+$	1.61	1.58	2.70	2.67	14.4	11.9	16.0	12.4	2.6	1.3	3.030	0.6
			1.60	1.61	2.70	2.70	13.0	14.5	12.4	11.9	3.3	5.9	3.020	8.0
			1.60	1.61	2.69	2.67	12.5	14.9	10.7	15.5	0.6	1.5	3.013	1.6
95	CPARCR	$PCP—Cr(CO)_3$	1.59	1.60	2.72	2.73	12.4	12.2	10.5	12.4	4.5	3.2	3.015	2.1
96	***	$(4-C_6H_3Me_3(Co(CO)_3)—PCP)—Cr(CO)_3$	1.58	1.57	2.74	2.74	15.8	12.1	14.0	11.6	10.7	0.1	3.028	6.4
97	DOPDIV	PCP—Ru(CHD)****	1.59	1.59	2.71	2.71	13.8	13.8	12.4	12.4	3.0	3.0	3.044	0.0
98	GIRLOI	$[PCP—Ru(Cl,2Py)]^+$	1.58	1.60	2.69	2.67	15.1	14.7	12.9	10.8	7.6	2.9	3.029	1.0
			1.59	1.61	2.69	2.65	12.3	13.0	11.0	12.9	8.2	11.8	2.986	2.9
99	JOBCUY	$PCP—Ru(2Cl,PyNH_2)$	1.64	1.56	2.70	2.64	12.5	11.7	14.1	14.8	3.2	5.5	2.997	2.0
100	KAHYIB	$[(Cp^*)Ru—PCP—Ru(Cp^*)]^{2+}$	1.59	1.59	2.63	2.63	9.5	9.5	14.5	14.5	3.0	3.0	2.945	0.0
			1.58	1.58	2.64	2.64	12.0	12.0	13.0	13.0	3.0	3.0	2.950	0.0
101	ZESRUK	$PCP—Ru(2Cl,PPh_3)$	1.57	1.56	2.68	2.67	13.7	13.7	10.8	10.8	9.7	10.0	2.973	1.6
102	VAVPUD	$[PCP—Ru(OEt)_3Ru—PCP]^+$	1.60	1.59	2.70	2.69	11.3	12.2	10.6	12.6	5.7	1.4	2.979	0.9
			1.61	1.59	2.71	2.68	12.1	13.3	10.6	10.9	3.0	0.8	2.988	0.2
103	ZOQTEE	$[PCP—Ru—PCP(CHCH_2)_2]^{2+}$	1.57	1.60	2.66	2.67	12.3	13.2	12.2	14.2	1.7	0.9	2.981	0.7
			1.58	1.59	2.65	2.69	12.6	15.0	11.4	11.6	8.5	10.0	2.980	1.5
104	RAQXUC	$PCP—Rh(CB_{10}H_{10})$	1.59	1.59	2.72	2.71	13.9	13.7	11.5.	11.9	15.6	10.5	3.030	0.5
105	JASZOS	$Cr(CO)_3—PCP$	1.34	1.34	2.71	2.72	12.8	13.9	14.0	13.4	1.7	1.4	3.050	2.6
106	JASZUY	$(CO)_3Cr—PCP—Cr(CO)_3$	1.33	1.33	2.68	2.68	12.5	14.5	12.5	14.5	0.6	0.6	3.021	0.0
107	JATBAH	$(CO)_3Cr—PCP(4,7-OMe)_2$	1.35	1.36	2.72	2.71	12.0	11.8	13.1	14.2	1.6	1.6	3.026	1.4

* The CSD refcode.[16]

** The dihedral angle between the mean planes of the benzene rings.

*** *Cf.* lit. data.[74]

**** The 3,6-dihydrohexamethyl-1,4-cyclohexadiene ligand.



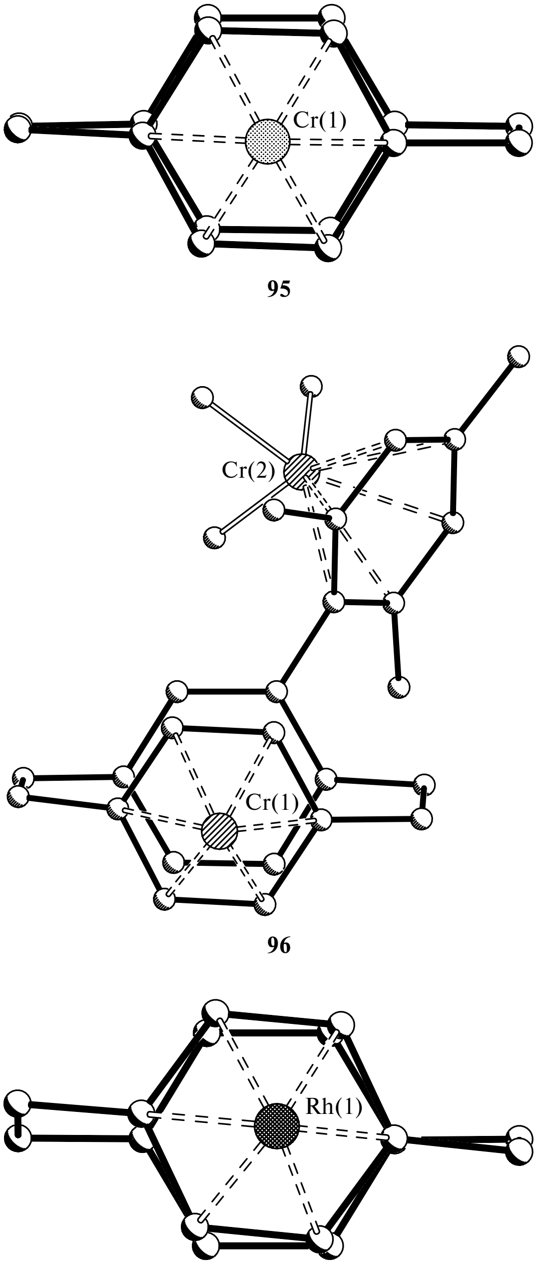
100

Fig. 23. Molecular structure of the (μ_2-η^6,η^6-[2.2]paracyclophane)-bis(η^5-pentamethylcyclopentadienyl)diruthenium complex (**100**), the hydrogen atoms are omitted.

which is characterized by the minimum values of Δ and *P*´ (2.63 and 2.95 Å, respectively). However, this is the only example of molecules, in which both benzene rings are π-coordinated to the ruthenium atoms, which, in turn, are involved in η^5-coordination to the Cp* ligands (Fig. 23).

Finally, the ethylene bridges in complexes **94—104** have similar structures. The distances between the atoms at the bow and stern positions (2.64—2.74 Å) are shortened compared to those in unsubstituted PCP **1**. The torsion angles (τ) in the ethylene bridges vary in a range of 0—11°. The bridging ethylene bond lengths nonsystematically vary in a range of 1.56—1.6 Å. The bond angles at the bridgehead atoms vary within a narrow range of 110.9—112.7°.

The most typical mutual arrangement of the rings is shown in Fig. 24. The maximum difference in the τ_1 and τ_2 torsion angles in molecule **96** is consistent with the shift of the rings parallel to the ethylene bridges. In other complexes, the character of distortions of the skeleton is analogous to that observed in complex **95**, which contains no substituents. A slight twist of the rings with respect to the centroids is observed only in molecule **104**.



95

96

104

Fig. 24. Overlap of the rings in the tricarbonyl-(η^6-[2.2]paracyclophane)chromium (**95**), (4-(η^6-2,4,6-trimethylphenyl)-11,16-η^6-[2.2]paracyclophane)hexacarbonyldichromium (**96**), and (η^6-[2.2]paracyclophane)-(η^5-7-*tert*-butylamino-7-carbaundecaborane)rhodium (**104**) complexes; the ligands additionally coordinated to the metal atoms are omitted.

A comparison of the geometry of the PCP skeleton in the π complexes and the uncoordinated molecules (see Table 1) shows that the benzene rings in the complexes are more closely spaced compared to those in the uncoordinated molecules (the distances Δ and *P*´ in the complexes are smaller; *cf*.: Δ 2.63—2.74 Å and 2.70—2.86 Å; *P*´ 2.95—3.03 Å and 3.00—3.08 Å), whereas the lengths of the ethylene bridges (d_1 and d_2) are somewhat larger (*cf*.: 1.56—1.61 Å and 1.55—1.59 Å).

Three chromium complexes with [2.2]paracyclophane-1,9-dienes, in which the benzene rings are linked by the —CH=CH— bridges, are available in the CSD. The geometric characteristics of complexes **105—107** are given in Table 5. It should be noted that the rings in molecule **106**, in which both benzene rings are coordinated to the chromium atoms, are located at a closer distance compared to that in related compound **105**. An analogous decrease in the distance is observed in the above-described molecule **100**. Otherwise these complexes are no different from chromium complexes **95** and **96**, except for the bridging C—C bond length.

No systematic differences in the lengths of the exocyclic bonds between the atoms at the bow and stern positions and the bridgehead atoms, *viz*., C(1)—C(14), C(2)—C(3), C(11)—C(10), and C(9)—C(6), are observed in the complexes of both types (the lengths vary in a range of 1.49—1.52 Å). The —C=C— double bond is weakened and its length (1.33—1.36 Å) is larger than the lengths typical of the C—CH=CH—C (*cis*) fragment (1.317 Å).[13]

To summarize, the benzene rings retain the C(3),C(6)-boat-like conformation upon the formation of π^6 complexes, the PCP skeleton is "contracted," and the distances between the bow and stern positions and the bottoms of the boats of the benzene rings decrease. The overall conformation of the PCP skeleton remains unchanged. Slight distortions are observed in the structures of compounds containing overcrowded substituents or anions and molecules of a solvent and are, presumably, associated with the intermolecular packing factors.

5. Conclusions

Analysis of the above data allows us to make the following conclusions.

In all the above-considered molecules, the PCP skeleton is scarcely affected by the electronic structure of the substituents (OH, OR, Ar, Alk, S, Hal). The geometric parameters of the substituted rings vary in accordance with the usual influence of electron-donating and electron-withdrawing substituents on the monosubstituted benzene ring (primarily, changes in the *ipso*-angles occur).[75,76] Bond delocalization in the benzene rings and the conformation of the rings (the symmetrical C(3),C(6)-boat) typical of unsubstituted PCP are retained.

The presence of substituents with different effective volumes in molecules of alcohols and different hydrogen bond networks are responsible for the difference in the steric conditions of the molecular packings in the crystals, resulting in substantial nonsystematic quantitative differences in the parameters characterizing the distortion of the PCP skeleton. The τ_1 and τ_2 torsion angles vary from 0.8 to 25.1°. The distances Δ_1 and Δ_2 between the atoms at the bow and stern positions vary in a range of 2.73—2.80 Å. The distances between the aromatic systems also nonsystematically vary in a range of 3.000—3.079 Å. In molecules containing the OH group at position 4 and various proton-acceptor (O or N) substituents at position 5 (*i.e.*, both substituents are on the same side of the boat), the OH group is involved in intramolecular hydrogen bonding with the N or O atoms of the substituent to form the fused H-bonded ring. This leads to "fixation" of the substituent and decreases the parameters characterizing the distortion of the PCP skeleton. For example, the α and β angles vary within a narrower range (7.8—14.5°), whereas an elongation of the C(1)—C(2) bridge (C(3)...C(14), 2.74—2.78 Å) adjacent to the OH group is slightly smaller than that of the C(9)—C(10) bridge (C(6)...C(11), 2.77—2.80 Å) adjacent to the substituent. The distinguishing feature of compounds containing one OAlk substituent at position 4 and various substituents at positions 7 or 5 is that they differ substantially only in the degree of skew of the PCP skeleton (the differences in the torsion angles are as high as 10—15°). These differences are attributable to the packing factors.

The quinoid, semiquinoid, or dihydrogenated benzene rings in [2.2]paracyclophanes are characterized by the geometric parameters typical of the corresponding canonical forms, resulting in substantial deformation of the PCP skeleton.

In quinoid molecules, the absence of C—C-bond delocalization in the benzene ring and the formation of exocyclic double bonds leads to a decrease in repulsion between the π systems in the PCP skeleton and shortening of the distance between the planes of the rings (P', 3.021—3.066 Å). The conformation of the quinoid ring changes substantially and becomes intermediate between the usual C(3),C(6)-boat and the C(4),C(7)-boat, whose bottom is formed by double bonds (the C(3), C(5), C(6), and C(8) atoms); the C—C(=O)—C fragments deviate from the bottom of the boat by 17°. The lower benzene ring is more flattened.

The benzene rings in semiquinoids are located at a distance approximately equal to that in unsubstituted PCP (P' = 3.084—3.100 Å), but these distances are somewhat larger than those in quinones. However, the rings are substantially shifted and twisted, unlike those in unsubstituted PCP. The conformation of the semiquinoid ring substantially changes only in *ortho*-hydrogenated molecules (hydrogenated at position 3), where it approximates the C(6)-half-chair.

Dihydrogenated 4,7-paracyclophanes containing two OH groups (and/or other substituents) at positions 4 and 7 have specific structures associated with the sp^3 hybridization of the C(4) and C(7) atoms. The dihydrogenated ring adopts the C(4),C(7)-boat conformation characterized by large folding angles (α_1 and β_1; aver., 24°). The ethylene bridges are substantially elongated. The C(3)...C(14) and C(6)...C(11) distances are in a range of 2.80—2.83 Å. These distances are the longest of all known [2.2]paracyclophane molecules. The benzene rings are located at a much larger distance compared to those observed in quinoid molecules.

The introduction of substituents into one or both ethylene bridges (C(1)—C(2) and C(9)—C(10)) of [2.2]paracyclophane leads to similar distortions of the PCP skeleton regardless of the nature of the substituent (C, S, Si). One substituent is responsible for strong deformation of the substituted bridge (the τ_1 angle increases to 20—30°). The conformation of the benzene rings, the bridging bond lengths (1.57—1.60 Å), and the distances between the atoms at the bow and stern positions (2.76—2.79 Å) vary only slightly. The distortion of the PCP skeleton is characterized by twist of the rings. The presence of two fluorine atoms in different positions at one of the carbon atoms in each bridge leads to a substantial shortening of the bridging C—C bonds (to 1.54 Å), the skeleton being undistorted. In molecules containing the tetrafluorinated bridges —CF_2—CF_2—, both bridges are strongly puckered (the τ_1 and τ_2 angle vary in a range of 25—30°) and elongated (the distance between the atoms at the bow and stern positions are in a range of 2.81—2.86 Å). The molecules in which the bridges are involved in an aromatic ring (C_{Ar}—C_{Ar} bridges) or contain a double bond (—CH=CH— bridges) differ only in the lengths of the bridging C(1)—C(2) and C(9)—C(10) bonds (1.42—1.44 and 1.31—1.34 Å, respectively), whereas the arrangement of the benzene rings and their conformations remain unchanged.

A change in the bridging bond length is accompanied by a change in the bond angles at the bridgehead atoms, the exocyclic C(Ph)—C bond lengths remaining constant (1.51—1.53 Å). These lengths are somewhat larger than those typical of molecules containing the unsubstituted —CH_2—CH_2— bridges (1.50—1.51 Å). A comparison of the bridging bond lengths (d), the bond angles (ω) at the first and second carbon atoms of the bridges, the degrees of "extension" of the bridge (Δ), and the C_{Ph}—C—C—C_{Ph} torsion angle (τ) (Table 6) shows that there is a rigid correlation between the bond angles and the bond lengths in the planar bridges (the τ angle is close to zero, as in unsubstituted [2.2]paracyclophane), *e.g.*, the bond angle increases as the corresponding bridging bond length decreases. The bridging CF_2—CF_2 bond length is substantially larger than the bridging CF_2—CH_2 bond length and approximates the lengths in monosubstituted bridges, whereas the bridge is, on the contrary, more elongated.

In π complexes, the PCP skeletons have similar more "contracted" structures and the distance between the rings substantially decreases. The coordinated and uncoordinated benzene rings are coplanar and adopt the symmetrical C(3),C(6)-boat conformation, *i.e.*, coordination of one or both rings to the metal atoms has no effect on the conformation of the rings and their mutual arrangement, which remains similar to that in unsubstituted PCP, the distances between the bottoms of the boats being shorter (2.973—3.030 Å). In all complexes, the ethylene bridges are structurally similar, although their length varies nonsystematically within a range of 1.56—1.64 Å. The τ torsion angles vary within a narrow range of 0—11°. The distances between the atoms at the bow and stern positions (2.64—2.74 Å) are shortened compared to those in unsubstituted PCP. In the complexes, there are no systematic differences in the lengths of the exocyclic bonds between the atoms of the benzene rings and the atoms of the bridges, *viz.*, C(1)—C(14), C(2)—C(3), C(11)—C(10), and C(9)—C(6), which vary in a range of 1.49—1.52 Å and are similar to the standard C(sp^2)—C(sp^3) bond length (1.513 Å).[13] The bridging —C=C— double bond in the complexes is weakened and its length (1.33—1.36 Å) is larger than the length typical of the C—CH=CH—C (*cis*) fragment (1.317 Å).[13]

The observed character of distortions of the PCP skeleton in various [2.2]paracyclophanes suggests that the distortion (twist and shift of the benzene rings) of the PCP skeleton is caused primarily by the intramolecular steric (rather than electronic) effects of the substituents. This seems to be reasonable. The distances between the carbon atoms of the benzene rings (2.9—3.1 Å) are substantially smaller than the C...C van der Waals contacts, and the carbon atoms are "held" in the skeleton by the ethylene bridges. The substituents experience usual intramolecular repulsion from the atoms of the PCP skeleton, and the equilibrium conformation of the molecule is achieved due to deformation of the skeleton. Intermolecular contacts are also of importance, because the packing of molecules containing rather flexible fragments in the crystal is determined by the packing steric factors and the occurrence of specific intermolecular interactions (hydrogen bonds, dipole-dipole interactions, *etc.*).

Therefore, [2.2]paracyclophane is simultaneously a rigid and flexible molecular cage.

The rigidity of the PCP skeleton results from the persistence of the C(3),C(6)-boat-like conformation of the benzene rings and the same degree of "extension" of the ethylene bridges. The donor-acceptor properties of the substituents, π-coordination to the metal atoms, and a decrease in the bridging bond lengths have no effect on

Table 6. Selected average characteristics of substituted ethylene bridges

Bridges	d/Å	ω*/deg		Δ/Å	τ/deg
CHR—CH_2	1.58	113.6	113.6	2.79	0
CF_2—CH_2	1.54	115.7	114.5	2.79	3
CF_2—CF_2	1.59	114.4	111.6	2.84	28
C_{Ar}—C_{Ar}	1.43	116.2	118.0	2.81	3
C=C	1.32	119.7	119.1	2.80	1

* The bond angles at the bridgehead carbon atoms.

the conformation of the benzene rings, although the C(3),C(6)-boat conformation is slightly distorted, *viz.*, the folding angles of the boat vary giving rise to more or less flattened symmetrical (both folding angles of the boat have similar values) or unsymmetrical boats.

In quinones and quinoid derivatives of PCP, the conformation of the ring changes substantially and becomes intermediate between the C(3),C(6)- and C(4),C(7)-boats. Hydrogenation of one or two positions of the benzene ring (semiquinoids and dihydrobenzenes, respectively) causes a change in the conformation of the ring. The rings assume a planar structure only as the number of bridges linking the benzene rings increases.

Hence, the benzene rings in paracyclophanes are rather conformationally flexible, as evidenced not only by the fact that [2.2]paracyclophane adopts a boat-like conformation but also by a further distortion of the conformation under the effect of various factors. The bond delocalization in the ring is retained, but the endocyclic angles at the bridgehead C(3) and C(6) atoms decrease with a simultaneous increase in all other angles. Flexibility of the aromatic rings, including the benzene ring, was studied by Shishkin and coworkers. Quantum-chemical calculations demonstrated**[77]** that at room temperature all isolated aromatic molecules (pyridine, pyridazine, pyrimidine, pyrazine, triazines, and benzene) exhibit noticeable conformational flexibility. The transformation of the structure from the planar to nonplanar form (the endocyclic torsion angle is approximately equal to 15°) is accompanied by an increase in the energy by less than 1.5 kcal mol^{-1}. For benzene, this energy is 1.7 kcal mol^{-1}.

The flexibility of the [2.2]paracyclophane skeleton is manifested in a change in the character of distortions of the PCP skeleton (a perpendicular or parallel shift and twist of the benzene rings), resulting in a change in the mutual arrangement of the rings depending on a particular composition of the substituents in the molecules. A distortion of the PCP skeleton can occur due to flexibility of the bridges, which readily assume conformations from planar to substantially twisted (the torsion angles can be as high as 40°). This flexibility of the PCP skeleton indicates that the benzene, quinoid, semiquinoid, and dihydrogenated rings in the PCP skeleton have no effect on each other and behave as isolated systems. Whatever the structure (bond lengths and the conformation) of these rings, the [2.2]paracyclophane skeleton undergoes distortions, *viz.*, the rings are shifted or twisted with respect to each other, due to flexibility of the bridges and their ready adjustment to the shape of the rings. The bridges can also undergo changes to compensate the steric intra- and intermolecular hindrances associated with the molecular packing in the crystals.

Examination of the experimental and theoretical optical spectra of 5-formyl-4-oxy[2.2]paracyclophane and its 4,4′-salen analog (5-CHO—PCP—C=N—C_2H_4—N=C—PCP—5-CHO) demonstrated**[78]** that the π systems in the PCP skeleton are isolated and, in spite of a boat-like distortion of the benzene rings, no mixing of the π—σ orbitals takes place. This is consistent with the results of studies of the transannular interactions in [2.2]paracyclophane**[14]** and [2.2]paracyclophane-4,7-quinone **56**.**[56]**

Precision X-ray diffraction study**[14]** using the multipole refinement made it possible to analyze the experimental electron density distribution ρ(r). These results were compared with the results of quantum-chemical calculations (HF, MP2, and B3LYP). The topological analysis of ρ(r) demonstrated that intramolecular transannular interactions between the aromatic systems are absent and the electron density is accumulated predominantly on the outside of the benzene rings. The lower value of ρ(r) in the ethylene bridges compared to that typical of singles bonds (for example, 1.69 and 1.52 $e\text{Å}^{-3}$ in PCP and ethane, respectively) is indirect evidence that an "indirect" interaction (through the ethylene bridges) between the rings is also absent.

An analogous study**[56]** revealed dynamic disorder of the ethylene bridges in the crystal of **56** (the bridges are "staggered," the C(1)—C(2)—C(9)—C(10) pseudotorsion angle is 11.4°), which does not allow one to perform experimental analysis of ρ(r) in the crystal. Hence, the electronic structure and transannular interactions were analyzed using only data from *ab intio* calculations. The calculated geometric parameters of the molecule agree well with those determined experimentally. Analysis demonstrated that, in spite of the presence of the nonequivalent rings, *viz.*, the π-acceptor quinoid ring and the π-donor benzene ring, the attractive interaction between the rings in molecule **56** is also absent. [2.2]Paracyclophane differs from molecule **56** primarily in that there is a slight accumulation of electron density inside the molecular cavity in **56**.

However, it should be noted that in [2.2]paracyclophane the intramolecular charge transfer occurs in the excited state.**[79]** To estimate the influence of the energies of HOMO and LUMO on the character of intramolecular interactions between the rings, quantum- chemical calculations were carried out for model systems, *viz.*, the radical anion and radical cation of unsubstituted PCP.**[80]** Analysis of the topology of the distribution ρ(r) in the radical anion revealed the critical points (3, −1) in the molecular cavity. These points correspond to the intramolecular charge transfer, whereas interactions between the rings in the radical cation are absent. Since the radical anion serves as a model of donation of the additional electron density to the benzene rings, transannular interactions can occur only in paracyclophane derivatives containing electron-donating substituents. The occurrence of a transannular interaction in the radical anion of [2.2]paracyclophane is manifested in a decrease in the energy of electron affinity of unsubstituted PCP (−0.5 eV) compared to that of benzene.

Accumulation of the electron density on the outside of the benzene rings in [2.2]paracyclophane can be considered as a characteristic feature of this molecular "cage" or the "cage" effect. Apparently, the benzene rings in unsubstituted PCP are stronger electron donors than substituted arenes. This assumption is consistent with the results of experimental and theoretical study[81] of the reactivities of unsubstituted [2.2]paracyclophane and *p*-xylene with respect to $Cr(CO)_6$. It was established that the former compound reacts approximately 25% faster.

These results provide an explanation for the rigidity of the PCP skeleton and the fact that the benzene rings are isolated. Apparently, a redistribution of the bonds in the benzene rings caused either by substituents of different nature or coordination to metal atoms leads to a change in the accumulation of the electron density above the ring and residual electron density in the cavity of the PCP skeleton. It can be assumed that in the complexes containing closely spaced benzene rings, the electron density is "pulled" by metal atoms away from the outside of the ring, resulting in the additional displacement of the electron density from the inner cavity of the skeleton (the rings come closer together). The nature of the metal atom and the ligands coordinated to the metal atoms has no effect on the character of distortions of the PCP skeleton.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 03-03-32214 and 02-07-90322) and the Foundation of the President of the Russian Federation (Federal Program for the Support of Leading Scientific Schools, Project Nos NSh-1060.2003.03 and MK-1209.2003.03).

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Received March 24, 2004;
in revised form July 19, 2004