Unusual Rearrangements of *cis*-4,7-Disubstituted 4,7-Dihydro-4,7-dihydroxy[2.2]paracyclophanes on Dehydration: Stereoselective Formation of Planar Chiral Cyclohexadienones

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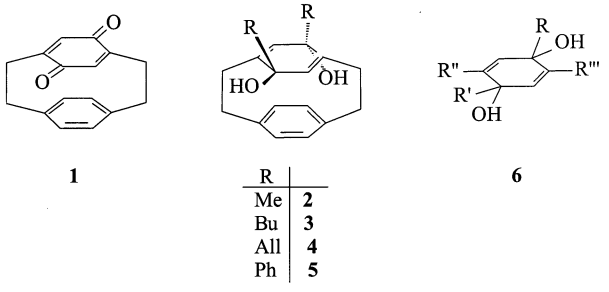
Under acid conditions, *cis*-4,7-disubstituted 4,7-dihydro-4,7-dihydroxy[2.2]paracyclophanes undergo dehydration accompanied by rearrangement, affording cyclohexadienone derivatives as major products and with polysubstituted phenols being formed as minor products. The formation of either an *ortho* or a *para* semiquinoid system, as well as the configuration of the newly formed asymmetric center, depended strictly on the nature of the substituent (alkyl, allyl, or phenyl). The structures of 3,4-dihydro-3,7-dimethyl[2.2]paracyclophane-4-one (**10**), 3,7-diallyl-3,4-dihydro[2.2]paracyclophane-4-one (**12**), and 4,7-dihydro-7,8-diphenyl[2.2]paracyclophane-4-one (**22**) were determined by X-ray structural analysis. [2.2]Paracyclophane-4,7-quinone (**1**) was obtained in optically active form.

Introduction

The synthesis of planar chiral derivatives of [2.2]paracyclophane is currently important, due to the successful use of a number of these compounds as chiral inductors in asymmetric synthesis and catalysis.[1a−1q,2c−2e] To date, however, this class has generally been represented by derivatives of [2.2]paracyclophane with different substitution patterns in the aromatic rings or, much more rarely, bridges.[2a−2e]

Another chiral cyclophane, [2.2]paracyclophane-4,7-quinone (**1**), is itself very attractive as a chiral auxiliary (in asymmetric redox reactions, for example), and also as a starting material for the construction of new planar chiral ligands based on [2.2]paracyclophane. Although racemic **1** was first synthesized as long ago as 1966,[3] chemical investigations of this compound and its derivatives have, to the best of our knowledge, been restricted to the study of donor-acceptor interactions.[4a−4e]

Recently[5] we have found that addition reactions of MeLi, BuLi, All_3B, and PhLi to [2.2]paracyclophane-4,7-quinone occur regio- and stereospecifically, resulting in the corresponding *cis*-4,7-disubstituted 4,7-dihydro-4,7-dihydroxy[2.2]paracyclophanes with *endo* orientation of the hydroxyl groups: namely *cis*-4,7-dimethyl- (**2**), *cis*-4,7-dibutyl- (**3**), *cis*-4,7-diallyl- (**4**), and *cis*-4,7-diphenyl derivatives (**5**) (Scheme 1).



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R	
Me	**2**
Bu	**3**
All	**4**
Ph	**5**

6

Scheme 1

It is known that dihydroxy derivatives of cyclohexa-2,5-diene of type **6** (the closest analogues of the diols **2−5**) undergo acid-promoted dehydration followed by rearrangement into the corresponding polysubstituted phenols.[6−11] As a rule, the rearrangement occurs easily because of the energy gain accompanying aromatization.

Investigating the reactivity of the [2.2]paracyclophanyl diols **2−5** in acid-catalyzed dehydration reactions, we have found that these compounds react fundamentally differently from **6**, and in this paper we want to present the results obtained.

Results and Discussion

Diols **2−4** were dehydrated by heating at reflux in glacial acetic acid. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. We found that dehydration of the

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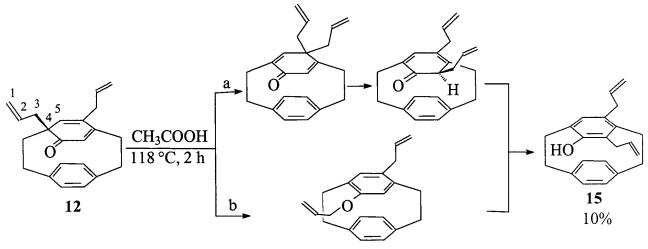
diols **2**–**4** resulted in the formation of two products from each starting compound. The individual compounds **10**–**15** were isolated by preparative chromatography on SiO_2 under an inert atmosphere. However, the expected phenols **13**–**15** were formed only as minor reaction products, whereas the major reaction products **10**–**12** were identified as their structural isomers containing a substituted cyclohexadienone fragment[12] instead of the substituted aromatic ring (see Scheme 2, Table 1).

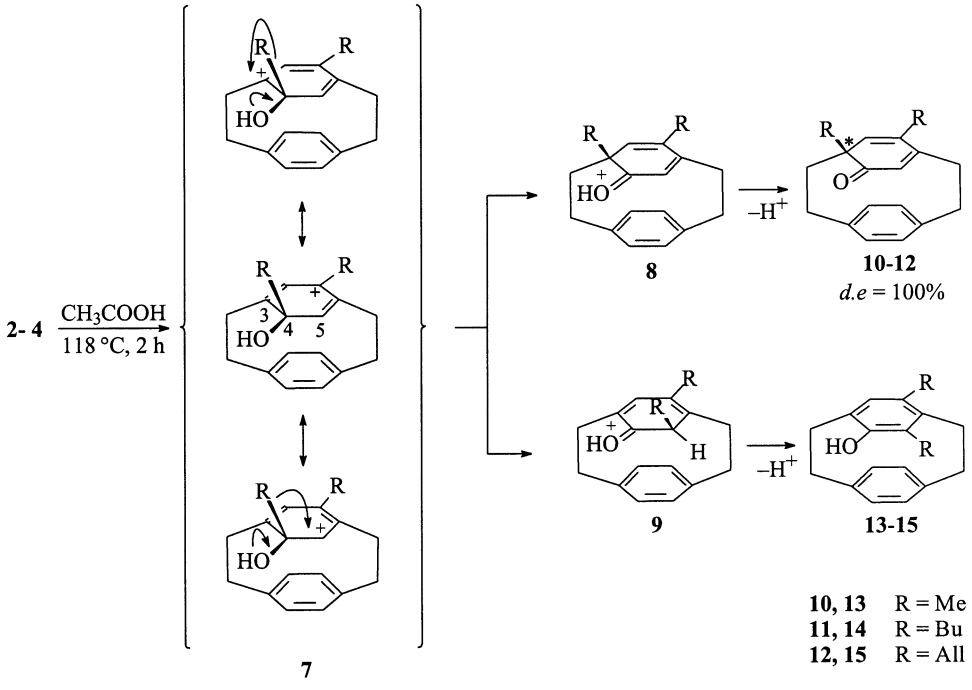
The ratio of the reaction products (cyclohexadienone/phenol) was found to depend on the substituent (Me, Bu, or All) in the starting alcohols **2**–**4**. Thus, dehydration of diols **2** or **3** (containing methyl and butyl substituents) resulted in the formation of **10**/**13** (20:1) and **11**/**14** (10:1), respectively (see Table 1, runs 1 and 2). On the other hand, the dehydration of allyl-substituted diol **4** under the same conditions resulted in the formation of cyclohexadienone **12** and phenol **15** in 2:1 ratio (see Table 1, run 3). We suggest that the increased yield of **15** relative to **13** and **14** could be related to a rearrangement of cyclohexadienone **12** to phenol **15**. Indeed, it was shown in a control experiment that **12** (R = All) in glacial acetic acid at reflux (2 h) underwent a rearrangement to afford phenol **15** in 10% yield



Scheme 3

(Scheme 3), whereas no reverse rearrangement of **15** into **12** occurred under the same conditions. The carbonyl compound **10** with methyl substituents did not undergo any transformation even with an increased reaction time (up to 50 h). Thus, the rearrangement of dienone into phenol was found to be specific to compound **12**, and can be attributed to the well known ability of the allyl group to engage in Claisen- or Cope-type rearrangements.

Since both the cyclohexadienones and the polysubstituted phenols obtained in this study are new classes of [2.2]paracyclophane derivatives, their accurate structural determination was important. The structure of 3,4-dihydro-



Scheme 2

Table 1. Rearrangements of diols **2**–**4**[a]

Run[a] No.	Starting compound	Cyclohexadienone/phenol ratio[b]	Yield of cyclohexadienone,%	Yield of phenol,%
1	**2**	20:1	**10** (75%)	**13** (4%)
2	**3**	10:1	**11** (70%)	**14** (6%)
3	**4**	2:1	**12** (45%)	**15** (22%)

[a] CH_3COOH, T = +118 °C, 2 h. [b] Calculated values are based on the results of ^1H NMR monitoring of the reaction mixture.

3,7-dimethyl[2.2]paracyclophan-4-one (**10**), isolated as a major dehydration product of the diol **2**, was determined on the basis of a series of ^{1}H, ^{13}C, $^{13}C\{^{1}H\}$, and 2D ^{1}H NOESY NMR experiments, and also IR spectroscopy data. Thus, the bands at 1634 and 1656 cm^{-1} in the IR spectrum and the low-field signal at $\delta = 203.30$ ppm in the $^{13}C\{^{1}H\}$ NMR spectrum of **10** unequivocally indicate the presence of a CO group in this compound. These data, taken together with the observation of the signal of a quaternary aliphatic carbon atom at $\delta = 47.73$ ppm, suggest the formation of a cyclohexadienone. Analysis of the interactions in the ^{1}H NOESY spectra (key interactions are shown in Figure 1) points towards the *ortho*-semiquinoid structure of the product.

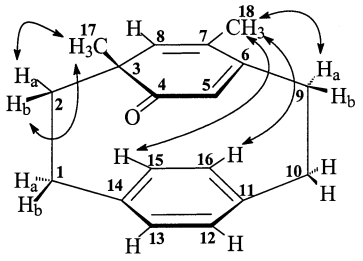


Figure 1. The characteristic interactions in NOESY NMR spectra of **10**

That the first methyl group is located *para* to the CO group is demonstrated by clearly defined interactions between the protons of this substituent with the bridge proton 9-H_a and protons 15-H and 16-H of the aromatic ring. The second methyl group is located *ortho* with respect to the CO group: namely, at the geminal C3 atom. This is evident from the strong interaction between the protons of this substituent with the bridge protons 2-H_a and 2-H_b of the adjacent methylene unit. The structure of compound **10** was also confirmed by single-crystal X-ray diffraction analysis (Figure 2, see a).

3,7-Dibutyl-3,4-dihydro[2.2]paracyclophan-4-one (**11**) and 3,7-diallyl-3,4-dihydro[2.2]paracyclophan-4-one (**12**) were isolated as major dehydration products of diols **3** and **4**, respectively. Their structures were determined by the same approach as employed in the case of **10**. Two bands in the IR spectra (at 1640 and 1660 cm^{-1} for **11** and at 1630 and 1650 cm^{-1} for **12**) are also spectral indications of the presence of the carbonyl groups in these compounds. Like the spectra of **10**, the $^{13}C\{^{1}H\}$ NMR spectra of compounds **11** and **12** exhibit low-field signals for the carbonyl groups, at $\delta = 203.94$ ppm (for **11**) and $\delta = 202.84$ ppm (for **12**), and signals of quaternary carbon atoms at $\delta = 51.87$ ppm (for **11**) and $\delta = 51.71$ ppm (for **12**). The signals of the butyl protons or the allyl $-CH_2-$ groups in the ^{1}H NOESY spectra of compounds **11** and **12** strongly overlap with the signals of the bridge protons of the paracyclophane skeleton. Because of this, we were unable to identify characteristic interactions suitable for unambiguous determination of the positions of these substituents. In principle, alternative possible structures for compounds **11** and **12** – namely, a *para*-semiquinoid structure (both substituents are in geminal positions at C7) and a *ortho*-semiquinoid structure (similar to that of compound **10**) – could be supported by the available spectroscopic data. For this reason, the structure of **12** was mistakenly suggested by us in a preliminary communication[13] to have a *para* arrangement of allyl substituents at the geminal site. In this work, results of ^{1}H-^{13}C HMBC NMR experiments have allowed us to establish unambiguously that only one substituent is located at C7 (*para* relative to the CO group), whereas the second substituent is situated at C3. In addition, careful analysis of the ^{1}H NMR spectra has shown the close resemblance of the

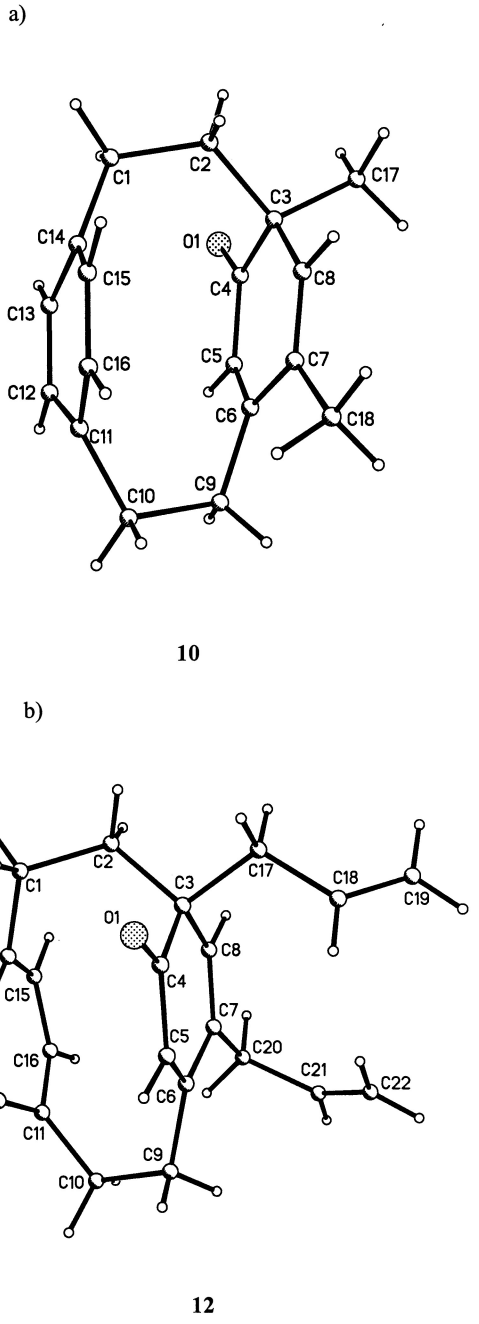


Figure 2. a) Molecular structure of 3,4-dihydro-3,7-dimethyl[2.2]-paracyclophane-4-one (**10**), b) molecular structure of 3,7-diallyl-3,4-dihydro[2.2]paracyclophane-4-one (**12**)

multiplet patterns and chemical shifts of the proton signals of the paracyclophane skeleton in the ^{1}H NMR spectra of compounds **11** and **12** to the corresponding signals in the spectra of compound **10**. Taken together, these results point towards a common *ortho*-semiquinoid structure of the carbonyl compounds **11** and **12**. The structure of compound **12** was finally confirmed by single-crystal X-ray diffraction analysis (Figure 2, see b).

To the best of our knowledge, cyclohexadienones **10**−**12** are the first representatives of paracyclophanes with a C−C bonded substituent at C3. The only example of a stable compound with a substituent at the C3 atom of the paracyclophane skeleton is 3,4-dihydro-3-hydroxy[2.2]paracyclophan-4-one, which is formed on interaction of 4-hydroxy-[2.2]paracyclophane with [Mo(O$_2$)$_2$O]·Py·HMPT.[14]

The structures of the two phenols 4-hydroxy-5,7-dimethyl[2.2]paracyclophane (**13**) and 5,7-diallyl-4-hydroxy[2-.2]paracyclophane (**15**), isolated as minor dehydration products of diols **2** and **4**, respectively, were determined by a series of 1D and 2D homonuclear and heteronuclear NMR experiments. The mutual arrangements of the substituents in the paracyclophane rings were unambiguously established by analysis of the ^{1}H NOESY spectra of **13** and **15** (Figure 3). The characteristic signals of 2-H$_b$ (δ = 3.20 ppm for **13** and δ = 3.05 ppm for **15**) clearly stand out from the signals of the other bridge methylene protons. The signals of the 8-H protons and the OH group exhibit pronounced positive nuclear Overhauser effects (NOEs) with the protons of the methylene group at C2, as well as with the corresponding substituents (methyl or allyl groups) in the other two *ortho* positions. Like those of the semiquinoid compounds **10**−**12**, the ^{1}H NMR spectra of all phenols **13**−**15** exhibit very similar signal multiplicity character and close chemical shifts for the main characteristic groups, allowing us to suggest for **14** a structure similar to that of **13** and **15**.

In contrast to the rearrangements of diols **2**−**4** with alkyl or allyl substituents, no formation of the corresponding phenol was observed in the dehydration of the diol **5**, bearing phenyl substituents, under the same conditions. The reaction resulted in a *para*-semiquinoid compound − 4,7-dihydro-7,8-diphenyl[2.2]paracyclophan-4-one (**22**) − which was isolated as the single product in 80% yield (Scheme 4).

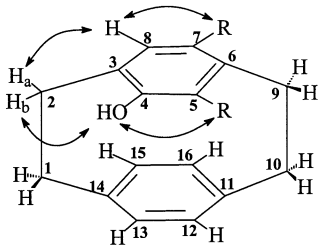


Figure 3. The characteristic interactions in NOESY NMR spectra of **13** and **15**

The presence of the carbonyl group in **22** is supported by characteristic bands at 1612 cm^{-1} and 1642 cm^{-1} in the IR spectrum, together with a low-field signal at δ = 186.69 ppm in ^{13}C NMR spectrum. The characteristic signal at δ = 54.00 ppm indicates a CH−Ph fragment in the molecule. The proton of this fragment showed noticeable NOEs with the *ortho* protons of both phenyl substituents (Figure 4). Taken together, these data allow us to suggest a *para*-semiquinoid structure for compound **22**, and this was

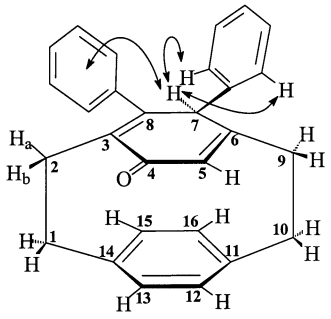
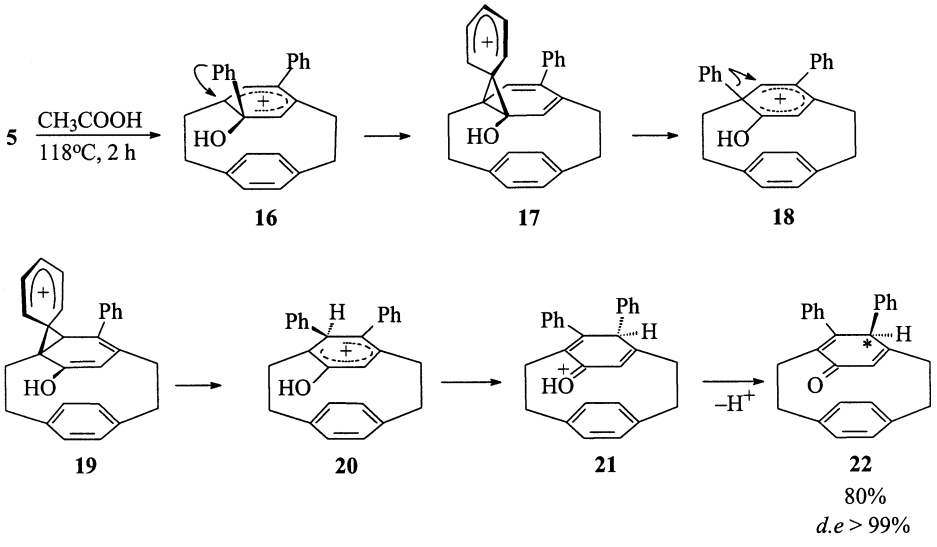
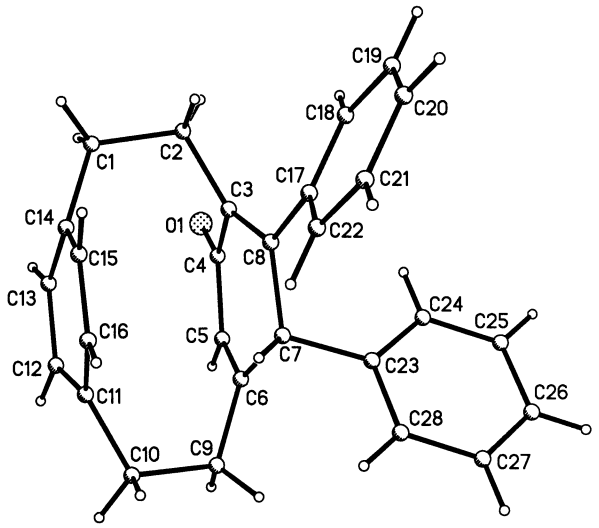


Figure 4. The characteristic interactions in NOE NMR spectra of **22**



Scheme 4

then unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 5).



22

Figure 5. Molecular structure of 4,7-dihydro-7,8-diphenyl[2.2]paracyclophane-4-one (**22**)

Thus, acid dehydration of 4,7-disubstituted 4,7-dihydro-4,7-dihydroxy[2.2]paracyclophanes results in carbonyl compounds with semiquinoid structures as major products. It is known[15] that [2.2]paracyclophanes in super acids (FSO_3H) protonated exclusively at their *ipso* C3 positions, in contrast to methyl-substituted benzenes, which are always protonated at the unsubstituted position. The authors[15] presumed that formation of the cation transforms the π-π repulsion between the two benzene rings into an energetically more favorable charge-transfer interaction. On the other hand, protonation just of the C3 position should result in a reduction in angle strain. We suggest that the carbonyl compounds are produced similarly in this case.

To explain the obtained results we assume that the acid-catalyzed dehydration of diols **2**−**4** results in formation of the cation **7** (Scheme 2). The first possible means of stabilization of **7** is similar to that in the well known dienol-benzene rearrangement[11] and involves the 1,2-migration of the alkyl or allyl substituent from C4 to C5, with the formation of the intermediate cation **9**. Subsequent aromatization of **9** eventually produces phenols **13**−**15**. A more preferable alternative for the transformations of **7** in our case includes the migration of the alkyl substituent in the opposite direction (i.e., from C4 to C3), thus producing the cation **8**. The aromatization of this cation, in analogy to the rearrangements of 1,2,4,6-tetrasubstituted 1,4-dihydroxycyclohexa-2,5-dienes,[10] should cause the migration of the ethylene bridge to C8 with formation of [2.2]metaparacyclophane.[16a−16e] However, this does not take place, and stabilization of **8** proceeds through the removal of the proton, affording the stable dienones **10**−**12** (Scheme 2). In the case of dehydration of the diol **5**, though, neither of the pathways is operative. A suggested pathway for the formation of **22** as shown in Scheme 4 could be imagined. The cation **16** (analogy of **7**), resulting from the dehydration of the diol **5** undergoes a number of successive suprafacial 1,2-migrations of the phenyl substituent from the C4 to the C8 position [**16**→**17** (phenonium ion) → **18** and **18** → **19** (phenonium ion) → **20**] and migration of H atom from C8 to C7 (**20** → **21**). Finally, the cation **21** is stabilized by proton elimination, thus producing the *para*-semiquinoid compound **22**.

It should be noted that both the *ortho*-semiquinoid compounds **10**−**12** and the *para*-semiquinoid derivative **22** each have two elements of chirality: namely, a planar chiral paracyclophanyl fragment and the newly formed asymmetric center. We found that **22** was formed stereospecifically (*de* > 99%) and has a (*Rp*,Sc**) configuration. On the other hand, the specific feature of the geometry of the [2.2]paracyclophane skeleton provides the formation of the *ortho*-semiquinoid compounds **10**−**11** of (*Rp*,Rc**) configuration and cyclohexadienone **12** with allyl-substituted (*Rp*,Sc**) configuration.

Not only the cyclohexadienones **10**−**12**, but also **22** were found to be stable in air, despite the fact that **22** has a hydrogen atom in the geminal C7 position. On the other hand, the polysubstituted phenols **13**−**15** were found to be unstable and quite oxidizable on study.

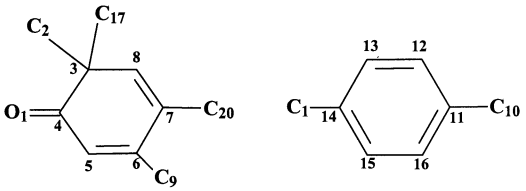
It is worth noting that − as elaborated by us stereospecifically − addition of organolithium reagents to quinone **1**[5] and further rearrangements of the resulting diols could be regarded as attractive routes for the synthesis of a series of enantiopure cyclohexadienols and cyclohexadienones with the aim of the use of these compounds as chiral inductors. This prompted us to synthesize both enantiomers **1**, (−)-(*R*)-**1** (*ee* ≥ 99%) $[\alpha]_D^{25} = -223$ (*c* = 0.166, benzene) and (+)-(*S*)-**1** (*ee* ≥ 98%) $[\alpha]_D^{25} = +211$ (*c* = 0.185, benzene), from the corresponding enantiomers of 4-hydroxy[2.2]paracyclophane[17] by the procedure reported for the synthesis of racemic **1**.[3,5] At present we are engaged in the synthesis of novel (*R*)- and (*S*)-4,7-diaryl-substituted 4,7-dihydro-4,7-dihydroxy[2.2]paracyclophanes (type **5**), in which the aryl substituents have different groups (N, S, O, P-functions etc.) in their *ortho* positions. Any of these substituents in conjunction with a geminal hydroxy group should be able to chelate with metals in the course of asymmetric synthesis and catalysis. In turn, acid-catalyzed rearrangement of these diols should result in optically active 7,8-diaryl-4,7-dihydro[2.2]paracyclophane-4-ones.[18]

X-ray Crystallographic Study of Compounds 10, 12, and 22

Comparative analysis of the results of X-ray investigations of compounds **10**, **12**, and **22** has revealed some specific features of the molecular structure of this class of derivatives of [2.2]paracyclophane.

The crystal structures of compounds **10** and **12** are centrosymmetric and thus contain racemic mixtures of molec-

Table 2. Geometric parameters of molecules **10**, **12**, and **22**



Bond	**10**	**12**	**22**
C4−O1	1.228(2)	1.228(2)	1.205(10) C=O
C3−C4	1.524(2)	1.526(3)	1.510(13)
C3−C8	1.501(2)	1.503(3)	1.349(11) C=C
C3−C2, C6−C9	1.569(2), 1.517(2)	1.574(3), 1.519(3)	1.513(12), 1.497(1)
C4−C5	1.453(2)	1.451(3)	1.452(11)
C5−C6	1.347(2)	1.354(3)	1.335(12) C=C
C6−C7	1.474(2)	1.477(3)	1.512(11)
C8−C7	1.330(2)	1.329(3)	1.530(9)
C3−C17, C7−C20	1.549(2), 1.500(2)	1.564(3), 1.509(3)	1.598(13), 1.491(9)
C14−C15, C14−C13	1.389(2), 1.395(2)	1.393(3), 1.393(3)	1.395(13), 1.383(12)
C11−C12, C11−C16	1.398(2), 1.385(2)	1.394(3), 1.394(3)	1.344(12), 1.427(12)
C12−C13, C15−C16	1.379(2), 1.380(2)	1.379(3), 1.379(3)	1.415(11), 1.395(11)
C11−C10, C1−C14	1.505(2), 1.495(2)	1.504(4), 1.497(3)	1.514(12), 1.519(12)
C1−C2, C9−C10	1.546(3), 1.577(3)	1.549(3), 1.575(3)	1.556(13), 1.598(13)
Ct···Ct	3.037	3.038	2.996

ules of different chirality, in contrast to **22**, which crystallizes in a chiral space group *Cc* ($Z = 4$) and the structure of which contain molecules of the same chirality. The molecular skeletons of **10**, **12**, and **22** are similar despite specific features of **22**, while molecules **10** and **12** are also similar in their crystal structures. The substituted cycle is practically planar (the mean deviation of the atoms is 0.03 Å) and the O1 atom lies in the plane of the cycle. One substituent (the C18 atom in **10** and the C20 atom in **12**) is in the equatorial position (these atoms deviate from the plane of the cycle by 0.160 and 0.138 Å, respectively) while the other substituent (the C17 atom in both **10** and **12**) is in the axial position (the corresponding deviations are 1.268 and 1.412 Å). The unsubstituted ring adopts a boat conformation (C11, C14 − boat). The angles of folding of the rings along the C12···C16 and C13···C15 lines have equal values of 13.0° for **10** and are 12.8 and 12.1°, respectively, for **12**. The geometric parameters of the paracyclophane skeleton in molecules **10** and **12** are also virtually the same (Table 2). In molecule **22** the substituted ring is non-planar (the mean deviation of the atoms is 0.099 Å) and adopts a boat conformation (C3,C6 − boat), typical of paracyclophanes. The atoms that form the ethylene bridges deviate from the "bottom" of the boat (the deviations of the C3 and C6 atoms from the plane passing through the C4, C5, C7, and C8 atoms are 0.232 and 0.215 Å, respectively). The boat is somewhat asymmetric, the angles of folding along the C5···C7 and C4···C8 lines being 17.2 and 18.7°, respectively. The phenyl substituents are arranged in the same manner as in **10** and **12**. One atom, C17, is equatorial (the mean deviation from the plane of the cycle is 0.193 Å) and the second atom, C23, is axial (the deviation is 1.412 Å). Thus, the introduction of the two substituents in positions 3 and 7 ("*meta*" positions) of the cycle (**10** and **12**) has resulted in flattening of the conformation of the cycle, while the introduction of substituents in positions 7 and 8 ("*ortho*" positions) (molecule **22**) gives rise to a boat-like conformation of the cycle, typical of paracyclophanes.

Molecules **10**, **12**, and **22** have somewhat skewed skeletons. The planes of the cycles are nonparallel (the dihedral angles in molecules **10**, **12**, and **22** are 5.5, 5.8, and 4.6°, respectively) and the cycles themselves are shifted with respect to each other. Figure 6 illustrates the superposition of rings (the projections of the molecular skeletons on the plane passing through the C12, C13, C15, and C16 atoms are shown). As can be seen in Figure 6, all semiquinoid molecules are characterized by nearly the same distortion of their skeletons, whereas the molecules of the starting diols **4** and **5** have non-skewed skeletons and parallel rings (*cf.* the superposition of rings in molecule **4** shown in Figure 6).

Conclusion

In this work we have shown that acid-catalyzed dehydration of 4,7-disubstituted 4,7-dihydro-4,7-dihydroxy[2.2]paracyclophanes occurs stereospecifically and results in high yields of stable, planar chiral cyclohexadienones of the [2.2]paracyclophane series with *ortho*-semiquinoid (**10**−**12**) or *para*-semiquinoid (**22**) substructures, whereas the respective phenols are formed only in small amounts. Both enantiomers of [2.2]paracyclophane-4,7-quinone were obtained from the corresponding (*R*)- and (*S*)-4-hydroxy[2.2]-paracyclophane with the aim of investigation of **1** as a chiral inductor as well as its further chiral transformations.

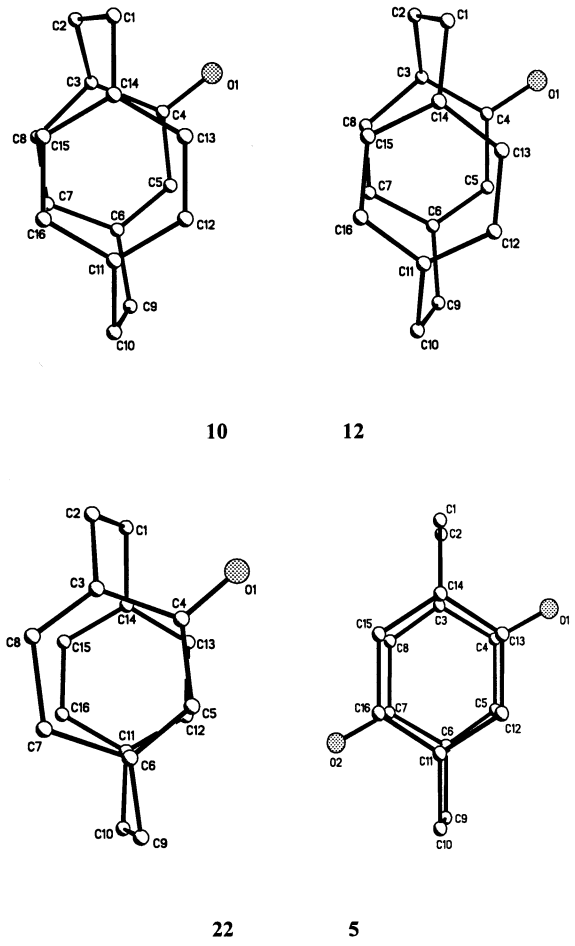


Figure 6. Superposition of rings in molecules **10**, **12**, **22**, and **5** (projections of the molecular skeletons onto the plane passing though the C12,C13,C15,C16 atoms are shown)

Experimental Section

General Remarks: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 spectrometer at 400.13 and 100.61 MHz, respectively, in $CDCl_3$ and [D_6]DMSO. All NMR spectra of compound **22** were recorded in saturated [D_6]DMSO solution at 320 K. Residual signals of the solvent protons with the chemical shifts δ = 7.27 ppm ($CDCl_3$) and 2.5 ppm ([D_6]DMSO) were used as internal standards. Mass spectra were obtained on a Kratos MS 90 mass spectrometer (70 eV) at 200 or 250 °C. TLC analysis was performed with Silufol UV-254 plates (Chemapol), and chromatographic purification and separation of isomers were carried out on Kieselgel 60 silica gel (Merck). Optical rotations: EPO-1.

General Procedure for Rearrangement Reactions: Glacial acetic acid (10 mL) was added to the respective diol (0.4 mmol), and the reaction mixture was heated at reflux for 2 h in a flask fitted with a Dean−Stark trap filled with $MgSO_4$. Acetic acid was removed in vacuo and the reaction mixture was washed with pentane and dried in vacuo. The reaction mixture was chromatographically separated under argon atmosphere with benzene/ethyl acetate (7:1) mixture as eluent.

3,4-Dihydro-3,7-dimethyl[2.2]paracyclophan-4-one (10): Isolated yield 0.076 g (75%). M.p. 91.0−91.5 °C. $C_{18}H_{20}O$ (252.4): calcd. C 85.67, H 7.99; found C 86.01, H 7.90. MS (70 eV): *m*/*z* (%) = 252 $[M]^+$ (35.9), 237 $[M - Me]^+$ (3.8), 209 $[M - Me - CO]^+$ (4.96), 200 $[M - 104]^+$ (2.2), 199 $[M - 104 - H]^+$ (1.7), 172 $[M - 104 - CO]^+$ (9.7), 104 (100). UV (EtOH): λ_{max} (ε) = 201.2 (175000), 230.3 (60000), 349.3 (20000) nm. IR (KBr): $\tilde{\nu}$ = 1634, 1656 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.95 (s, 3 H, 17-H), 1.85 (s, 3 H, 18-H), 1.95 (m, 1 H, 2-Ha), 2.38 (m, 1 H, 9-Hb), 2.40 (m, 1 H, 2-Hb), 2.67 (m, 1 H, 1-Hb), 2.75 (m, 1 H, 9-Ha), 2.84 (m, 1 H, 1-Ha), 3.15 (m, 2 H, 10-Hb, 10-Ha), 5.09 (s, 1 H, 5-H), 5.20 (s, 1 H, 8-H), 6.83 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 12-H), 7.05 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 13-H), 6.75 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 15-H), 7.15 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 16-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.83, 28.35 (C-17, C-18), 30.71, 33.86, 34.57, 42.55, 47.70, 128.68, 128.93, 131.43, 132.13, 133.30, 133.89, 138.99, 139.47, 143.00, 154.98 (C-3), 203.28 (C-4) ppm.

5,7-Dimethyl-4-hydroxy[2.2]paracyclophane (13): Isolated yield 0.004 g (4%). Colorless oil. $C_{18}H_{20}O$ *m*/*z* calcd. 252.1514 $[M]^+$; found 252.1550. MS (70 eV): *m*/*z* (%) = 252 $[M]^+$ (42.82), 237 $[M - Me]^+$ (1.47), 148 $[M - 104]^+$ (100), 120 $[M - CO - 104]^+$ (13.94), 104 $[M - 104]^+$ (47.7). ^{1}H NMR ($CDCl_3$): δ = 1.85 (s, 3 H, 17-H_3), 2.14 (s, 3 H, 18-H_3), 2.58 (m, 1 H, 2-Ha), 3.20 (m, 1 H, 2-Hb), 2.86−3.26 (m, 6 H, all 1-H, 9-H, 10-H), 4.30 (br. s, 1 H, OH), 6.10 (br. s, 1 H, 8-H), 6.43 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 15-H), 6.70 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 12-H), 6.78 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 16-H), 6.83 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 13-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.52 (C-17), 20.36 (C-18), 27.83, 30.09 (C2), 32.76, 33.28, 123.91, 126.91 C-12, 127.78 (C-13), 128.60 (C-16), 129.64, 132.18, 132.45 (C-15), 134.00 (C-8), 138.79, 138.93, 139.04, 150.30 (C-4) ppm.

3,7-Dibutyl-3,4-dihydro[2.2]paracyclophan-4-one (11): Isolated yield 0.094 g (70%). Colorless oil. $C_{24}H_{32}O$ (336.52): calcd. C, 85.66, H 9.58; found C 85.41, H 9.65. MS (70 eV): *m*/*z* (%) = 336 $[M]^+$ (12), 280 $[M - Bu]^+$ (4), 219 $[M - CH_2C_6H_4CH_2]^+$ (13), 189 $[M - CH_2C_6H_4CH_2 - CO - Me]^+$ (9), 177 $[M - CH_2PhCH_2 - Bu + H]^+$ (100). UV (EtOH), λ_{max} (ε) = 205.5 (260000), 209.8 (230000), 230 (150000), 353 (35000) nm. IR (KBr): $\tilde{\nu}$ = 1640, 1660 (C=O) cm^{-1}. ^{1}H NMR($CDCl_3$): δ = 0.7 (t, ^3J = 7.3 Hz, 3 H, 20-H), 0.80−0.95 (m, 2 H, 2 × 19-H), 0.9 (t, ^3J = 7.3, 3 H, 24-H), 1.05 (m, 2 H, 18-H), 1.20−1.50 (m, 4 H, 22-H, 23-H), 1.33, 1.68 (two m, 2 H, 17-H), 1.95 (m, 1 H, 2-Ha), 2.13−2.30 (m, 2 H, 21-H), 2.35 (m, 1 H, 2-Hb), 2.38 (m, 1 H, 9-Hb), 2.69 (m, 1 H, 1-Hb), 2.78 (m, 1 H, 9-Ha), 2.85 (m, 1 H, 1-Ha), 3.15 (m, 2 H, 10-H), 5.10 (s, 1 H, 5-H), 5.20 (s, 1 H, 8-H), 6.74 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 15-H), 6.83 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 12-H), 7.04 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 13-H), 7.08 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 16-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.78 (C-20), 14.08 (C-24), 22.63 (C-23), 23.03 (C-18), 25.64 (C-19), 30.72 (C-1), 31.22 (C-22), 33.02 (C-21), 34.20 (C-10), 34.51 (C-9), 42.75 (C-2), 44.58 (C-17), 51.76 (C-3), 129.22 (C-16), 131.32 (C-13), 131.98 (C-12), 133.25 (C-15), 135.26 (C-5), 135.31 (C-7), 139.18 (C-14), 139.55 C-11, 141.16 (C-8), 154.71 (C-6), 203.94 (C-4) ppm.

5,7-Dibutyl-4-hydroxy[2.2]paracyclophane (14): Isolated yield 0.008 g (6%). Colorless oil. $C_{24}H_{32}O$ *m*/*z*: calcd. 336.2453 $[M]^+$; found 336.2400. MS (70 eV): *m*/*z* (%) = 336 $[M]^+$ (5), 294 $[M - Pr - H]^+$ (17), 280 $[M - Bu]^+$ (2), 232 $[M - CH_2PhCH_2 + H]^+$ (8), 251 $[M - Bu - CO]^+$ (9), 189 $[M - CH_2C_6H_4CH_2 - CO - Me]^+$ (45), 177 $[M - CH_2PhCH_2 - Bu + H]^+$ (39), 104 $[CH_2PhCH_2]^+$ (100). ^{1}H NMR($CDCl_3$): δ = 0.83−3.11 (all m, 26 H, 8 bridge. CH_2, $-C_4H_9$), 3.98 (br. s, 1 H, OH), 6.02 (br. s, 1 H, 8-H), 6.30, 6.59, 6.66, 6.93 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 12-H, 13-H, 15-H, 16-H) ppm.

3,7-Diallyl-3,4-dihydro[2.2]paracyclophan-4-one (12): Isolated yield 0.055 g (45%) m.p. 58.5−59.0 °C. $C_{22}H_{24}O$ (304.43): calcd. C, 86.85, H 8.10, found C 86.80, H 7.95. MS (70 eV): *m/z* (%) = 304 $[M]^+$ (19), 263 $[M - All]^+$ (26.5), 200 $[M - 104]^+$ (2.2), 199 $[M - 104 - H]^+$ (1.7), 172 $[M - 104 - CO]^+$ (9.7), 159 $[M - 104 - All]^+$ (32.7), 131 $[M - 104 - CO - All]^+$ (26.8), 104 (100). UV (EtOH): λ_{max} (ε) = 231 (900), 345 (223) nm. IR (KBr): nu[tilde] = 1630, 1650 (C=O) cm^{-1}. ^1H NMR($CDCl_3$): δ = 1.95 (m, 1 H, 2-Ha), 2.11, 2.33 (two m, 2 H, two 17-H), 2.35 (m, 1 H, 9-Hb), 2.36 (m, 1 H, 2-Hb), 2.70 (m, 1 H, 1-Hb), 2.75 (m, 1 H, 9-Ha), 2.85 (m, 1 H, 1-Ha), 3.05 (m, 2 H, 2 × 20-H), 3.15 (m, 2 H, 2 × 10-H), 4.75 (d, ^3J = 10.4, 1 H, *cis*-19-H), 4.91 (d, ^3J = 17.1 Hz, 1 H, *trans*-19-H), 4.95 (d, ^3J = 10.4 Hz, 1 H, *cis*-22-H), 5.31 (m, 1 H, 18-H), 5.10 (d, ^3J = 17.1 Hz, 1 H, *trans*-22-H), 5.15 (s, 1 H, 5-H), 5.27 (s, 1 H, 8-H), 5.77 (m, 1 H, 21-H), 6.75 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 15-H), 6.85 (d, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 12-H), 7.00 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 13-H), 7.10 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 16-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.63 (C-1), 34.17 (C-10), 34.38 (C-9), 37.47 (C-20), 41.69 (C-2),48.04 (C-17), 51.71 (C-3), 116.69 (C-22), 117.99 (C-19), 129.09 (C-16), 131.47 (C-13), 132.11 C-12, 132.36 (C-18), 133.03 (C-7), 133.31 (C-15), 135.15 (C-5), 135.51 (C-21), 139.08 (C-14), 139.59 (C-11), 141.81 (C-8), 154.50 (C-6), 202.84 (C-4) ppm.

5,7-Diallyl-4-hydroxy[2.2]paracyclophane (15): Isolated yield 0.027 g (22%). Colorless oil. $C_{22}H_{24}O$ *m/z*: calcd. 304.4247 $[M]^+$; found 304.4298. MS (70 eV): *m/z* (%) = 304 $[M]^+$ (12.09), 263 $[M - All]^+$ (1.92), 205 $[M - 2All + H]^+$ (17.18), 172 $[M - 104 - CO]^+$ (13.55), 159 $[M - 104 - All]^+$ (20.95), 104 $[M - 199 - H]^+$ (54.13), 199 (100). IR (KBr): ṽ = 3570 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.50 (m, 1 H, 2-Ha), 2.75−3.40 (m, 10 H, 1-H, 9-H, 10-H, 17-H, 20-H), 3.05 (m, 1 H, 2-Hb), 4.45 (br. s, 1 H, OH), 4.98−5.17 (m, 4 H, 19-H, 22-H), 5.67−5.87 (m, 2 H, 18-H, 21-H), 6.05 (s, 1 H, 8-H), 6.25 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 15-H), 6.50 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 12-H), 6.60 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 16-H), 6.75 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 13-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.48, 29.87 (C-2), 32.70, 33.25, 33.29 and 38.76 (C-17, C-20), 115.25 and 115.73 (C-19, C-22), 124.79, 126.20, 127.94 (C-13), 128.08 (C-12), 129.29 (C-16), 132.09, 132.67 (C-15), 133.92 (C-8), 136.86 and 137.66 (C-18, C-21), 138.04, 138.57, 139.09, 151.08 (C-4) ppm.

4,7-Dihydro-7,8-diphenyl[2.2]paracyclophane-4-one (22): Isolated yield 0.120 g (80%). Decomp. temp. 250−280 °C. $C_{28}H_{24}O$ (376.50): calcd. C 89.33, H 6.43; found C 89.50, H 6.42. MS (70 eV): *m/z* (%) = 376 $[M]^+$ (20), 285 (12.1), 271 $[M - 105]^+$ (78), 257 (42.4), 253 (15.6), 243 $[M - CO - 105]^+$ (39.8), 239 (16.7), 228 (35.8), 215 (24.1), 202 (27.9), 194 (11.1), 181 (22.5), 165 $[M - CO - Ph - H]^+$ (50.7), 128 (44.42). UV (EtOH): λ_{max} (ε) = 228 (210000), 272 (100000), 288 (80000), 330 (40000) nm. IR (KBr): ṽ = 1612, 1642 (C=O) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.44 (m, 1 H, 9-Hb), 2.49 (m, 1 H, 2-Ha), 2.53 (m, 1 H, 9-Ha), 2.69 (m, 1

Table 3. Crystallographic data and refinement parameters for compounds **10**, **12**, and **22**

Compound	**12**	**10**	**22**
Empirical formula	$C_{22}H_{24}O$	$C_{18}H_{20}O$	$C_{28}H_{24}O$
Molecular mass	304.41	252.34	376.47
Symmetry	Monoclinic		
Space group	$P2_1/c$	$P2_1/n$	Cc
Temperature/K	[153] 163	110	110
a [Å]	13.437(3)	6.311(1)	10.865(8)
b [Å]	8.030(2)	26.264(5)	19.164(14)
c [Å]	16.617(3)	8.426(1)	9.315(7)
α [deg]	−	−	−
β [deg]	110.25(3)	105.689(4)	97.53(2)
γ [deg]	−	−	−
V [Å^3]	1682.1(6)	1344.4(4)	1923(2)
Z	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.202	1.247	1.300
Crystal color, crystal shape	colorless, plate		colorless, needle
Crystal dimensions, mm	0.50 × 0.30 × 0.20	0.05 × 0.15 × 0.40	0.30 × 0.20 × 0.10
Diffractometer	Syntex $P2_1$	Bruker SMART′	
Radiation	Mo-K_α (λ = 0.71073)		
Abs.coeff., μ(Mo-K_α), cm^{-1}	0.71	0.75	0.77
Scan type	θ/2θ	φ/ω	
$2\theta_{max}$ [deg]	52	55.12	50.04
Total number of reflections	3586	9290	3646
Number of independent reflections (*R*int)	3322 (0.0163)	3082 (0.0532)	1875 (0.0783)
R_1 calculated against *F* for reflections with $I > 2\sigma(I)$	0.0545 (for 2143 reflections)	0.0466 (for 1677 reflections)	0.0883 (for 1028 reflections)
wR_2 (calculated against F^2 for all reflections)	0.1558	0.0918	0.2278
Number of parameters to be refined	304	252	238
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = 1/3(F_o^2 + 2F_c^2)$		
A	0.1000	0.0296	0.1387
B	0.0000	0.0000	0.0000
GOOF	0.981	0.904	0.905
F(*000*)	656	544	800
CCDC deposition number	194245	194244	194246

H, 1-Ha), 2.72 (m, 1 H, 1-Hb), 3.03 (m, 1 H, 2-Hb), 3.16 (m, 1 H, 10-Hb), 4.35 (s, 1 H, 7-H), 3.43 (m, 1 H, 10-Ha), 5.40 (s, 1 H, 5-H), 6.55 (dd, ^3J = 7.8, ^4J = 1.8, 1 H, 15-H), 6.78 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 13-H), 6.88 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 12-H), 6.95 (d, ^3J = 8.0 Hz, 2 H, 24-H, 28-H), 7.00 (t, ^3J = 8.0 Hz, 1 H, 26-H), 7.05 (t, ^3J = 8.0 Hz, 2 H, 25-H, 27-H), 7.20−7.43 (m, 5 H, 18-H, 19-H, 20-H, 21-H, 22-H), 7.48 (dd, ^3J = 7.8, ^4J = 1.8 Hz, 1 H, 16-H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 26.48, 32.58, 32.91, 33.24, 54.00 (C-7), 126.34 (C-26), 127.82 (2 C, C-24, C-28), 128.11 (2 C, C-25, C-27), 128.19, 129.25 (4 C, (C-18, C-19, C-20, C-21), 129.70 (C-16), 130.61 (C-13), 130.80 (C-15), 132.05 C-12, 132.35 (C-5), 136.07, 136.88, 137.28, 138.07, 138.69, 153.32, 161.55, 186.86 (C-4) ppm.

(−)-(*R*)-[2.2]Paracyclophane-4,7-quinone [(*R*)-1]: Optically active (−)-(*R*)-**1** (*ee* ≥ 99%) was synthesized from optically active (+)-(*R*)-4-hydroxy[2.2]paracyclophane (*ee* ≥ 99%,[17a] 0.680 g, 3.03 mmol) by the procedure reported for the synthesis of racemic **1**.[5] Spectroscopic data are in good agreement with those for racemic **1**.[3,5] Isolated yield (*R*)-**1** 0.505 g (70%). Decomp. temp. 215−248 °C. $C_{16}H_{14}O_2$ (238.29): calcd. C 80.65, H 5.92; found C 80.81, H 5.91. $[\alpha]_D^{25}$ = −223 (*c* = 0.166, benzene).

(+)-(*S*)-[2.2]Paracyclophane-4,7-quinone [(*S*)-1]: Optically active (+)-(*S*)-**1** (*ee* ≥ 98%) was synthesized from optically active (−)-(*S*)-4-hydroxy[2.2]paracyclophane (*ee* ≥ 98%,[17a] 0.500 g, 2.23 mmol) by the procedure reported for the synthesis of racemic **1**.[5] Spectroscopic data are in good agreement with those for racemic **1**.[3,5] Isolated yield (*S*)-**1** 0.378 g (71%). Decomp. temp. 210−238 °C. $C_{16}H_{14}O_2$ (238.29): calcd. C 80.65, H 5.92; found C 80.54, H 5.91. $[\alpha]_D^{25}$ = +211 (*c* = 0.185, benzene).

X-ray Crystallographic Study of Compounds 10, 12, and 22: The principal crystallographic data, the procedures used for collecting experimental data, and the characteristics of structure refinement are listed in Table 3. Single crystals of compounds **10** (*ortho*-semiquinoid), **12**, and **22** (*para*-semiquinoid) suitable for X-ray study were obtained by crystallization from diethyl ether, pentane, and isopropyl alcohol, respectively.

Single-crystal X-ray diffraction experiments for **10** and **22** were carried out with a Bruker SMART 1000 CCD area detector, by use of graphite monochromated Mo-K_α radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure) at 110−140 K. A low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated by use of SAINT software[19] and the SADABS semiempirical method.[20] Single-crystal X-ray diffraction experiments for **12** were carried out with a Syntex P2$_1$ diffractometer (graphite monochromated Mo-K_α radiation, q/2q scans technique) at 163 K. The structures were solved by direct methods and refined by full-matrix, least-squares against F^2_{hkl} in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms in **10** and **12** were located from the difference Fourier syntheses and refined in isotropic approximation. For structure **22**, hydrogen atoms were placed in geometrically calculated positions and included final refinement by the "riding" model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(C_M) or 1.5 U_{eq}(C_{MM}), where U(C_M) and U(C_{MM}) are the equivalent thermal parameters of the methyne and methylene carbon atoms to which corresponding H atoms are bonded, respectively. All calculations were performed on an IBM PC/AT with SHELXTL software.[21] Atomic coordinates, full bond lengths and angles, and thermal parameters are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk].

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[1] [1a] H. J. Reich, K. E. Yelm, *J. Org. Chem.* **1991**, *56*, 5672−5679. [1b] R. Yamada, Y. Higashikawa, Y. Miwa, T. Taga, F. Yoneda, *Tetrahedron: Asymmetry* **1992**, *3*, 1387−1390. [1c] V. Rozenberg, V. Kharitonov, D. Antonov, E. Sergeeva, A. Aleshkin, N. Ikonnikov, S. Orlova, Yu. Belokon′, *Angev. Chem. Int. Ed. Engl.* **1994**, *33*, 91−92. [1d] P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. P. Volante, P. J. Reider, *J. Am. Chem. Soc.* **1997**, *119*, 6207−6208. [1e] S. Banfi, A. Manfredi, F. Montanari, G. Pozzi, S. Quici, *J. Mol. Catalysis A: Chemical* **1996**, *113*, 77−86. [1f] Yu. Belokon′, M. Moscalenko, N. Ikonnikov, L. Yashkina, D. Antonov, E. Vorontsov, V. Rozenberg;, *Tetrahedron: Asymmetry* **1997**, *8*, 3245−3250. [1g] A. H. Vetter, A. Berkessel, *Tetrahedron Letters* **1998**, 1741−1744. [1h] C. Bolm, T. Kuhn, *Synlett* **2000**, 899−901. [1i] D. S. Masterson, D. T. Glatzhofer, *J. Mol. Catalysis A: Chemical* **2000**, *161*, 65−68. [1j] F. Fringuelli, O. Piermatti, F. Pizzo, R. Ruzziconi, *Chem. Lett.* **2000**, 38−39. [1k] V. I. Rozenberg, D. Y. Antonov, R. P. Zhuravsky, E. V. Vorontsov, V. Khrustalev, Z. A. Starikova, N. S. Ikonnikov, Yu. N. Belokon', *Tetrahedron: Asymmetry* **2000**, *11*, 2683−2693. [1l] A. Zanotti-Gerosa, C. Malan, D. Herzberg, *Org. Lett.* **2001**, *3*, 3687−3690. [1m] X.-W. Wu, X.-L. Hou, L.-D. Dai, J. Tao, B.-X. Cao, J. Sun, *Tetrahedron: Asymmetry* **2001**, *12*, 529−532. [1n] S. Tanji, A. Ohno, I. Sato, K. Soal, *Org. Lett.* **2001**, *3*, 287−289. [1o] S. Dahmen, S. Braese, *J. Am. Chem. Soc.* **2002**, *124*, 5940−5941. [1p] A. Cipiciani, F. Fringuelli, O. Piermatti, F. Pizzo, R. Ruzziconi, *J. Org. Chem.* **2002**, *67*, 2665−2670. [1q] R. Ruzziconi, O. Piermatti, G. Ricci, D. Vinci, *Synlett* **2002**, *5*, 747−750.

[2] [2a] M. H. Delton, D. J. Cram, *J. Am. Chem. Soc.* **1970**, *92*, 7623. [2b] H. Delton, D. J. Cram, *J. Am. Chem. Soc.* **1972**, *94*, 2471. [2c] X.-L. Hou, X.-W. Wu, L.-X. Dai, B.-X. Cao, J. Sun, *Chem. Commun.* **2000**, 1195−1196. [2d] Th. Focken, H. Hopf, V. Snieckus, I. Dix, P. G. Jones, *Eur. J. Org. Chem.* **2001**, 2221−2228. [2e] A. Pelter, B. Mootoo, A. Maxwell, A. Reid, *Tetrahedron Letters* **2001**, *42*, 8391−8394.

[3] D. J. Cram, A. C. Day, *J. Org. Chem.* **1966**, *31*, 1227−1232.

[4] [4a] H. A. Staab, W. Rebafka, *Chem. Ber.* **1977**, *110*, 333−3550. [4b] R. Gleiter, W. Scheufer, H. A. Staab, *Chem. Ber.* **1988**, *121*, 1257−1264. [4c] A. K. Wisor, L. Czuchajowski, *Theor. Chim. Acta* **1988**, *74*, 445−461. [4d] H. A. Staab, G. Knaus, H.-E. Henke, C. Krieger, *Chem. Ber.* **1983**, *116*, 2785−2807. [4e] H. A. Staab, R. Reimann-Haas, P. Ulrich, C. Krieger, *Chem. Ber.* **1983**, *116*, 2808−2826.

[5] N. V. Vorontsova, V. I. Rozenberg, E. V. Vorontsov, D. Y. Antonov, Z. A. Starikova, Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.* **2002**, *8*, 1369−1375 [*Russ. Chem. Bull. Int. Ed.* (Engl. Transl.)] **2002**, 8, 1483−1490.

[6] B. M. Mikhajlov, G. S. Ter-Sarkisyan, N. A. Nikolaeva, *Doklady Akad. Nauk SSSR* **1968**, 547 (in Russian).

[7] G. S. Ter-Sarkisyan, N. A. Nikolaeva, V. G. Kiselev, B. M. Mikhajlov, *Zh. Obshch. Khim.* [*J. Gen. Chem. USSR*] **1971**, 41, 152 (in Russian).

[8] H. M. Crowford, M. Lumpkin, M. McDonald, *J. Am. Chem. Soc.* **1952**, *74*, 4087.

[9] E. Schinzel, F. Wessely, *Monatsch.* **1955**, *86*, 912−923.

[10] A. Rieker, G. Henes, *Tetrahedron Letters* **1968**, *34*, 3775−3778.

[11] F. Alonso, M. Yus, *Tetrahedron* **1992**, *48*, 2709.

[12] Compounds with a diene six-membered ring, exocyclic double bond, and a saturated geminal site are also referred to as semiquinoid compounds, see: V. I. Rozenberg, V. A Nikanorov, V. I. Bakhmutov, O. A. Reutov, *J. Organomet. Chem.* **1986**, 351−362.

[13] N. V. Vorontsova, V. I. Rozenberg, E. V. Vorontsov, D. Yu. Antonov, Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.* **2000**, *6*, 1138−1139 [*Russ. Chem. Bull.,* **2000**, *6*, 1133−1134. (Engl. Transl.)].
[14] K. Krohn, H. Rieger, H. Hopf, D. Barrett, P. G. Jones, D. Doring, *Chem. Ber.* **1990**, *123*, 1729−1732.
[15] H. Hopf, J.-H. Shin, H. Volz, *Angew. Chem.* **1987**, *99*, 594−595, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 564−565.
[16] The rearrangement of [2.2]paracyclophane into [2.2]metaparacyclophane is well known for different reactions with participation of the C3 atom of the [2.2]paracyclophane skeleton; see: [16a] D. J. Cram, J. M. Cram, *Acc. Chem. Res.* **1971**, *4*, 204. [16b] J. Cram, R. C. Helgeson, D. Lock, L. A. Singer, *J. Am. Chem. Soc.* **1966**, *88*, 1324. [16c] M. H. Delton, R. E. Gilman, D. J. Cram, *J. Am. Chem. Soc.* **1971**, *93*, 2329. [16d] V. A. Nikanorov, V. I. Rozenberg, V. G. Kharitonov, D. Yu. Antonov, V. V. Mikul′shina, M. V. Galakhov, D. P. Krut′ko, N. S. Kopelev, V. N. Guryshev, V. P. Yur′ev, O. A. Reutov, *Doklady Akad. Nauk SSSR.* **1990**, *315*, 1388−1392 [*Doklady Chem.* **1990**, *315* (Engl. Transl.)]. At the same time, however, there there are some processes where CH_3 migration in paracyclophane involves C3 as an intermediate position without rearrangement, see: [16e] J. Kleinschroth, S. El-tamany, H. Hopf, *Tetrahedron Lett.* **1982**, 3345−3348.
[17] [17a] V. Rozenberg, T. Danilova, E. Sergeeva, E. Vorontsov, Z. Starikova, A. Korlyukov, H. Hopf, *Eur. J. Org. Chem.* **2002**, *3*, 468−477. [17b] A. Cipiciani, F. Bellezza, F. Fringuelli, M. G. Silvestrini, *Tetrahedron: Asymmetry* **2001**, *12*, 2277−2281. [17c] A. Cipiciani, F. Fringuelli, V. Mancini, O. Piermatti, F. Pizzo, R. Ruzziconi, *J. Org. Chem.* **1997**, *62*, 3744−3747.
[18] N. V. Vorontsova, V. I. Rozenberg, E. V. Vorontsov, Z. A. Starikova, unpublished results.
[19] *SMART V5.051* and *SAINT V5.00*, Area detector control and integration software, Bruker AXS Inc., Madison,WI-53719, USA, **1998**.
[20] G. M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, WI-53719, USA, **1997**.
[21] G. M. Sheldrick, *SHELXTL-97, Version 5.10*, Bruker AXS Inc., Madison, WI-53719, USA (Bruker SHELXTL), **1997**.

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