Diastereomers Composed of Two Planar-Chiral Subunits: Bis([2.2]paracyclophan-4-yl)methane and Analogues

Ludger Ernst*[a] and Lars Wittkowski[a]

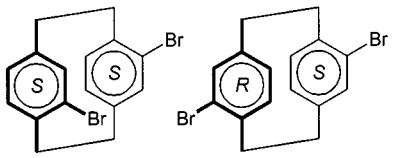
Dedicated to Professor Wolfgang Lüttke on the occasion of his 80th birthday

Keywords: Planar chirality / Cyclophanes / Configuration determination / NMR spectroscopy / Diastereomers

A series of compounds Q_2Z was prepared, where Q = [2.2]-paracyclophan-4-yl and Z = C(=O) (**4**), CH_2 (**5**), $SiMe_2$ (**6**), S (**7**), P(=O)OMe (**8**), and C(=O)C(=O) (**9**). Because of the planar chirality of Q, these compounds occur as *meso*- (**m**) and chiral (**c**) diastereomers, which were formed in equal amounts. They were separated in the cases of **4**–**7** and enriched in the case of **9** (diastereomeric ratio ca. 7:3). Compound **8** possesses a pseudoasymmetric phosphorus centre and occurs as one *chiral* (**8c**) and two *meso* diastereomers ($\mathbf{8m}_1$, $\mathbf{8m}_2$), all three of which were isolated separately. The configurations of **5m/5c**, **6m/6c**, and **8c** were directly determined by NMR spectroscopy, that of **4m/4c** indirectly by reducing the separated compounds to **5m** and **5c**, respectively, and that of **7m** by X-ray diffraction. The favoured conformations of **4**–**8** were studied by molecular mechanics computations by using the MM3(94) program. An attempt was made to rationalize some chemical shift differences between diastereomers on the basis of the conformers predicted.

Introduction

The possible elements of chirality are centres, axes and planes of chirality. If a diastereomer contains two constitutionally equal elements of chirality, *C*, it is either chiral, when the sense of chirality of the two elements is equal (C_RC_R or C_SC_S), or it possesses the optically inactive, symmetrical *meso* configuration, when the two elements are of opposite chirality and thus cancel (C_RC_S). By far the most common diastereomers with two constitutionally equal elements of chirality are those with two chirality centres, the tartaric acids being *the* classical case. Already in 1853, Pasteur converted (+)-tartaric acid into (±)-tartaric acid ("racemic acid") and *meso*-tartaric acid by heating.[1] Later, Le Bel and van't Hoff explained the optical inactivity of *meso*-tartaric acid by intramolecular cancellation.[2] Diastereomers with two constitutionally equal chirality axes have also been known for a long time. Suitably substituted terphenyls are representative examples, which were first prepared by Adams et al. in 1930.[3] These can occur as *cis* (chiral) and *trans* (*meso*) atropisomers or vice versa. We are interested in the third group, viz. in diastereomers containing two constitutionally equal groups of planar chirality. Among molecules with planar chirality, the cyclophanes are the most important[4a] and two constitutionally equal planes of chirality ("CEPC") can be present either in the same cyclophane unit or in two separate such units. A simple example of the first possibility is given by the pseudo-*ortho* and pseudo-*para* stereoisomers of 4,12-dibromo[2.2]-paracyclophane:[5] the pseudo-*ortho* isomer contains two CEPCs of equal configuration[6] (*S*,*S* isomer shown in **1**, Scheme 1) whereas they are of the opposite configuration in the pseudo-*para* isomer (*R*,*S*, **2**) which is therefore achiral. More complex cases are the diastereomeric [2.2](1,5)naphthalenophanes[7] or the recent cyclobis(paraquat-1,5-naphthalene) tetracations.[8] Examples with two CEPCs present in separate cyclophane units could have two chiral cyclophanyl groups, e.g. [2.2]paracyclophan-4-yl (abbreviated as Q), attached to a common framework Z in a symmetrical fashion. We are interested in this class of compounds Q_2Z, and particularly in the different NMR spectra of chiral ($Q^R{}_2Z/Q^S{}_2Z$) and *meso* (Q^RZQ^S) diastereomers (Scheme 2) and the reasons for these differences.



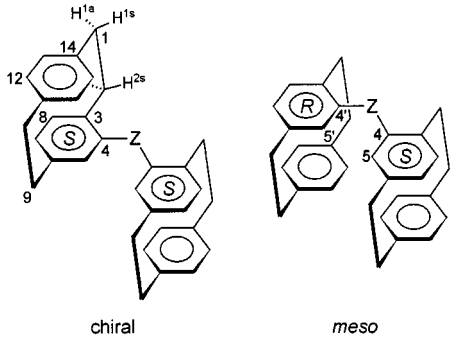
1 2

Scheme 1. Two constitutionally equal planes of chirality within the same paracyclophane unit, of the same (**1**) or the opposite (**2**) sense of chirality

The simplest molecule comprising two [2.2]paracyclophanyl groups is the "dimer" Q_2, bi([2.2]paracyclophan-4-yl) (**3**), which has been prepared by Kuś.[9a] No information as to its diastereomeric uniformity or configuration was given originally. Very recently, an X-ray diffraction study showed[9b] that the crystals isolated contained the *meso* diastereomer but it is not clear whether the chiral diastereomer was also formed in the synthesis. Our numerous attempts to repeat the synthesis of **3** in order to investigate its NMR properties more closely were unsuccessful. Instead, we addressed our attention to the series of molecules **4**−**9**, in

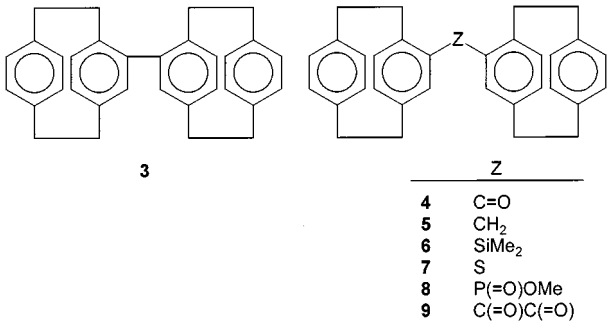
[a] Institut für Organische Chemie der Technischen Universität Braunschweig,
Hagenring 30, D-38106 Braunschweig, Germany
Fax: (internat.) + 49(0)531/391-5387
E-mail: L.Ernst@tu-bs.de

  1434−193X/99/0707−1653 $ 17.50+.50/0



Scheme 2. Chiral and *meso* diastereomers of Q_2Z-type compounds (Q = [2.2]paracyclophan-4-yl; Z = central atom or group); the (*S*,*S*) enantiomer is shown for the chiral diastereomer

which two [2.2]paracyclophan-4-yl moieties are attached to a common group [CO, CH_2, $SiMe_2$, P(=O)OMe, COCO] or atom (S), see Scheme 3.



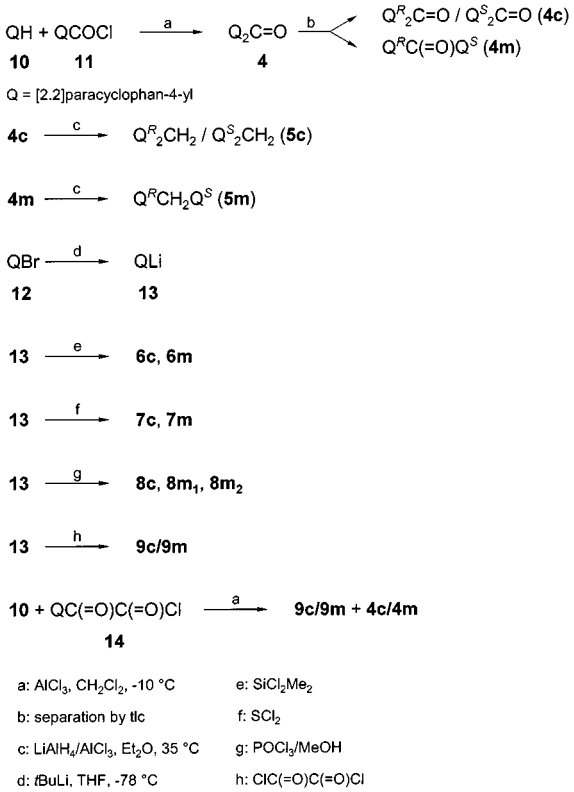
Scheme 3

Results and Discussion

Synthesis, Separation, and Assignment of the Diastereomers

An overview of the procedures used to prepare the desired products **4**−**9** is given in Scheme 4.

Bis([2.2]paracyclophan-4-yl) ketone (**4**) was obtained in 79% yield by Friedel−Crafts acylation of [2.2]paracyclophane (**10**) with its carboxylic acid chloride **11**.[11] The NMR spectra of the raw product showed that a 1:1 mixture of the *meso* (**4m**) and chiral (**4c**) diastereomers had been formed; these isomers were separated by TLC. Due to the lack of suitable indicator groups, the configurational assignment of the diastereomers by NMR is not feasible at this stage. The diastereomeric ketones were separately reduced with $LiAlH_4/AlCl_3$ in quantitative yield to the corresponding methanes **5m** and **5c**, respectively. A large excess of $LiAlH_4$ was necessary to avoid formation of the alcohols. The stereoisomeric hydrocarbons are easily identified by ^1H NMR (Figure 1): In **5c**, the two paracyclophanyl groups are homochiral, and hence the molecule possesses a C_2 axis which passes through the central CH_2 group and causes chemical equivalence of its hydrogen atoms. These give rise to a singlet at δ = 3.58. In the *meso* compound **5m**, the two C−H bonds of the central CH_2 group lie in the plane of



Scheme 4. Synthesis of **4**−**9**

symmetry which transforms the heterochiral paracyclophanyl groups into each other. The hydrogen atoms themselves, however, are not related by symmetry and give an AX spectrum (δ = 3.85, 3.27; $|J|$ = 15.9 Hz) with surprisingly different chemical shifts, which are nearly equidistant to high and low frequencies from the chemical shift of **5c**. The configurational assignment of hydrocarbons **5c** and **5m** also clarifies the configuration of the precursor ketones **4c** and **4m** because the paracyclophanyl groups cannot racemize under the conditions applied in reducing **4** to **5**. Moreover, the separation of the diastereomers at the ketone stage is advantageous, because the hydrocarbons **5m** and **5c** show very similar chromatographic behaviour whereas the ketones differ substantially. On the other hand, the ketones show little difference in solubility and have similar melting points (**4c**: 221°C; **4m**: 230°C), whereas the *meso* hydrocarbon is better soluble in CH_2Cl_2 or $CHCl_3$ than its chiral counterpart. The melting points of the hydrocarbons also differ more than those of the ketones (**5c**: 272°C; **5m**: 228°C).

The remaining products Q_2Z, **6**−**9**, were all prepared from 4-bromo[2.2]paracyclophane (**12**). While **12** is a well-known compound,[5] carefully controlled conditions in the bromination of **10** (see Experimental Section) allowed us to obtain an improved yield of 99% and a product of 98% purity, which was deemed sufficient for **12** serving as a starting material. Bromo compound **12** was lithiated with *tert*-butyllithium at −78°C in tetrahydrofuran and the lithio derivative **13** was quenched with dichlorodimethylsilane, sulfur dichloride, phosphoryl chloride/MeOH, and oxalyl

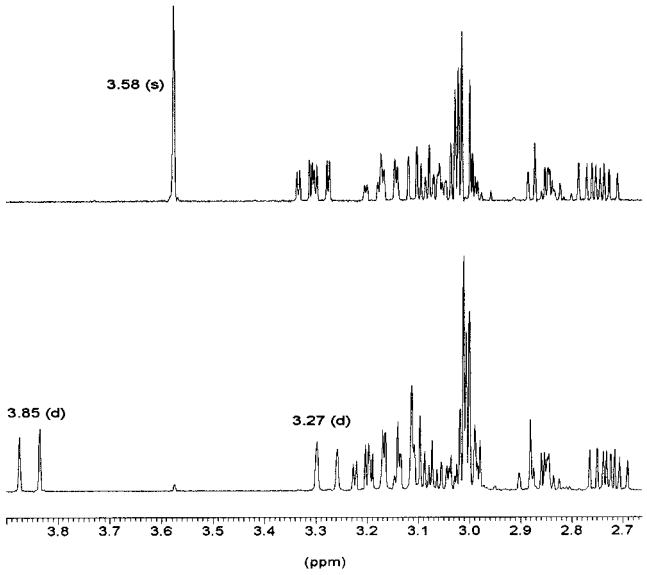


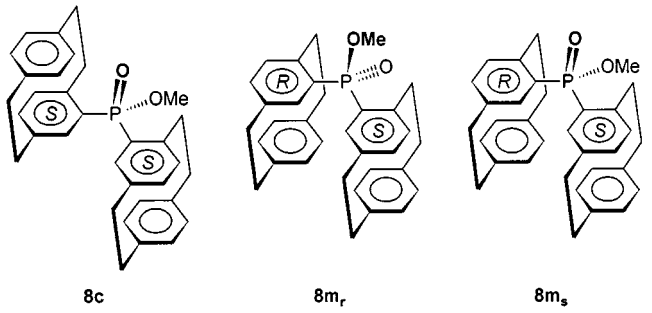
Figure 1. Aliphatic region of the 400-MHz ^{1}H-NMR spectra of the chiral (**5c**, top) and the *meso* (**5m**, bottom) diastereomer of bis([2.2]paracyclophan-4-yl)methane

chloride to furnish the products Q_2SiMe_2 (**6**), Q_2S (**7**), $Q_2P(=O)OMe$ (**8**), and $QC(=O)C(=O)Q$ (**9**), respectively. In the raw product, the diastereomers of **6** (**6c** and **6m**) are present in equal amounts. They are separated by fractional crystallization and can be assigned by ^{13}C NMR or, in analogy to **5c/5m**, by ^{1}H NMR by means of the respective chemical equivalence (**6c**: $\delta_C = 1.09$; $\delta_H = 0.79$) and non-equivalence (**6m**: $\delta_C = 1.86, 0.56$; $\delta_H = 0.79, 0.57$) of the methyl signals. In contrast to the hydrocarbons **5**, the *meso* diastereomer is the less soluble of the silanes **6** and has the higher melting point (**6m**: 254°C; **6c**: 180°C).

As in the case of the ketones **4**, no NMR-active "handle" is present in the sulfides **7** to assign the diastereomers, which are formed in equal proportions according to analytical HPLC. However, crystals suitable for X-ray diffraction were obtained of the better soluble sulfide, which turned out to have the *meso* configuration.[12]

The reaction of **13** with $POCl_3$ results only in a twofold replacement of chlorine by Q, probably because of the steric strain that would result from the formation of $P(=O)Q_3$. After workup with methanol, three stereoisomeric products $PQ_2(=O)OMe$ can be isolated, viz. a (racemic) chiral product, $PQ^R{}_2(=O)OMe/PQ^S{}_2(=O)OMe$ (**8c**), and two different products of a *meso* configuration, $PQ^RQ^S(=O)OMe$ (**8m$_1$** and **8m$_2$**). Being connected to four different ligands, the phosphorus atom in **8m$_1$** and **8m$_2$** is stereogenic yet only "pseudoasymmetric" because the ligands Q^R and Q^S are enantiomorphic (Scheme 5). The stereochemical situation in **8** is therefore analogous to the textbook example of 2,3,4-trihydroxyglutaric acid,[4b] only with planar instead of central chirality of the enantiomorphic ligands.

The chiral diastereomer, **8c**, can be distinguished from the *meso* diastereomers because its two homomorphic ligands Q are diastereotopic and thus give rise to 32 ^{13}C-NMR signals for the paracyclophane moieties. Each *meso*



Scheme 5. Configurations of the diastereomers of **8**; the (*S*,*S*) enantiomer is shown for the chiral diastereomer **8c**; the two *meso* diastereomers are **8m$_r$** and **8m$_s$** with (*r*) and (*s*) configuration, respectively, of the pseudoasymmetric phosphorus atom

diastereomer, on the other hand, shows only 16 paracyclophane lines in the ^{13}C-NMR spectrum as a consequence of the intramolecular plane of symmetry. Unfortunately, the NMR spectra do not allow the individual assignment of the *r* and *s* configuration of the phosphorus centre to **8m$_1$** and **8m$_2$**. Single crystals suitable for X-ray diffraction were not obtained either, so the absolute configurations of **8m$_1$** and **8m$_2$** must be left open.

The ^{31}P-NMR spectrum of the raw product showed that the formation of **8** was not diastereoselective: **8c**, **8m$_1$** and **8m$_2$** had been formed in the statistical ratio of 2:1:1. The separation of the diastereomers was achieved by column chromatography which gave a mixed fraction of **8c** and **8m$_1$** and a second fraction of pure **8m$_2$** (m.p. 196°C). Fractional crystallization from MeOH of the mixed fraction furnished less soluble **8c** (m.p. 254°C) and better soluble **8m$_1$** (m.p. 218°C).

"Paracyclophanil" (**9**), a known compound,[10] was synthesized by Friedel–Crafts acylation of paracyclophane with Q(C=O)COCl (**14**),[11] but the reaction gave only 22% of **9m/9c** in addition to the main product **4m/4c** (65%), which results from decarbonylation of the acid chloride before it reacts. Alternatively, **9m/9c** was prepared in somewhat higher yield (31%) from **13** and oxalyl chloride. The NMR spectra of the raw products were too complex to judge the diastereoselectivities of the preparations, but in view of the other results, diastereoselectivity would not be expected. The diastereomers **9m** and **9c** are difficult to separate. We could enrich one diastereomer by TLC to a ratio of 7:3. The absence of suitable NMR indicator groups and the lack of a pure crystalline product prevented the diastereomeric assignment of the **9m/9c** mixture. The smallness of the differences between the properties of **9m** and **9c** is certainly due to the increased distance between the chiral subunits in **9** relative to **4**–**8**. No further attempts were undertaken to characterize **9** and the remaining discussion is limited to **4**–**8**.

Conformational Analysis of the Diastereomers of 4–8

The preferred conformations of the diastereomers of **4**–**8** were studied using Allinger's program MM3(94).[13] The most significant internal coordinates describing the confor-

mations of the Q_2Z molecules are the torsional angles about the two Q−Z bonds. We define Θ_1 as the torsional angle C5−C4−Z−C4′ and Θ_2 as C4−Z−C4′−C5′. The Θ_1,Θ_2 combinations corresponding to minima of the conformational energy were searched by using both the stochastic search method according to Saunders,[14] which is implemented in MM3(94), and the dihedral driver method. In the latter approach, Θ_1 and Θ_2 were incremented independently from −180° to +180° in steps of 10°. For the *meso* compounds the energy surface $E(\Theta_1,\Theta_2)$ is symmetrical with respect to the line $\Theta_1 = -\Theta_2$, i.e. for each conformation with $\Theta_1 = x$, $\Theta_2 = y$ there exists an enantiomeric conformation with $\Theta_1 = -y$, $\Theta_2 = -x$. For the chiral compounds the energy surface is symmetrical with respect to the line $\Theta_1 = \Theta_2$ and each conformation with $\Theta_1 = x$, $\Theta_2 = y$ is accompanied by an identical conformation with $\Theta_1 = y$, $\Theta_2 = x$ and, of course, the conformations of the (*S*,*S*) isomers with $\Theta_1 = x$, $\Theta_2 = y$ are isoenergetic to those of the (*R*,*R*) isomers with $\Theta_1 = -x$, $\Theta_2 = -y$ and $\Theta_1 = -y$, $\Theta_2 = -x$.

Table 1 gives the Θ_1/Θ_2 coordinates and the relative steric energies E_{st} of the lowest energy ($E_{st} = 0$) and the second lowest energy conformations of the diastereomers of **4**−**8**. When the coordinates are visualized graphically (Figure 2) one recognizes that the energy minima are confined to a few relatively narrow Θ_1/Θ_2 regions. The MM3 computations predict that the lowest energy conformation for all *meso* compounds lies in region A (Figure 2a) with torsional coordinates $\Theta_1 = 37\pm27°$, $\Theta_2 = -131\pm19°$. The second lowest minima lie in region B ($\Theta_1 = -15\pm5°$, $\Theta_2 = -69\pm20°$) for the compounds which have only lone pairs or hydrogen atoms as ligand of the central atom Z (**7m**, **5m**) or in which Z is sp^2-hybridized (**4m**). Carbon or oxygen ligands on an sp^3-Z centre (**6m**, $\mathbf{8m_r}$, $\mathbf{8m_s}$[15]) shift the second lowest energy minimum to region C ($\Theta_1 = -105\pm5°$, $\Theta_2 = -110\pm5°$). However, while the second lowest energy minima are predicted to be substantially less stable (ΔE = 1.7−5.1 kcal mol^{-1}) than the lowest energy minima for **4m**, **5m**, $\mathbf{8m_r}$, $\mathbf{8m_s}$, they are of comparable stability (ΔE = 0.4−0.7 kcal mol^{-1}) for **6m** and **7m**.

For the chiral diastereomers of **4**−**8**, MM3 predicts that all compounds possess their lowest-energy conformational minimum in region D (Figure 2b) in which Θ_1 and Θ_2 have similar values [$\Theta_1 = 149\pm19°$, $\Theta_2 = 135\pm15°$: The (*S*,*S*) diastereomers were computed]. These conformers thus lie close to the symmetry line and not far from their counterparts with Θ_1 and Θ_2 interchanged. The second minimum energy region E is characterized by torsional angles $\Theta_1 = 60\pm20°$, $\Theta_2 = 35\pm15°$, also close to a symmetrical arrangement. Only for compound **4c** is conformer **E** estimated to be of much higher energy than **D** (ΔE = 5.2 kcal mol^{-1}). In the other chiral diastereomers conformer **E** is of the same energy as **D** (**7c**) or is only slightly less stable (**5c**, **6c**, **8c**; ΔE = 0.4−0.9 kcal mol^{-1}). The computed energy minima are relatively shallow, i. e. the conformers are not very well defined and are expected to undergo rather large torsional motions. For instance, the calculations for (*S*,*S*)-**4c** indicate that the energy of the minimum conformation with $\Theta_1 = 150°$, $\Theta_2 = 143°$ is raised by only 0.3 kcal/mol when Θ_1 is changed by ±10° (the optimum value of Θ_2 is changed concurrently by ca. 3.5°).

Table 1. Conformational energies E_{st} computed by MM3(94) for the lowest and second lowest energy minima of the *meso* and chiral diastereomers of **4**−**8**[a]

Compound	Θ_1 [°]	Θ_2 [°]	E_{st} [kcal mol^{-1}]	Type of conformation[b]
4m	10	−131	0.0	A
	−20	−68	5.1	B
5m	40	−112	0.0	A
	−10	−89	1.7	B
6m	64	−140	0.0	A
	−110	−110	0.4	C
7m	20	−140	0.0	A
	−10	−49	0.7	B
$\mathbf{8m_r}$	29	−150	0.0	A
	−110	−105	2.8	C
$\mathbf{8m_s}$	62	−140	0.0	A
	−100	−114	4.9	C
4c	150	143	0.0	D
	80	20	5.2	E
5c	130	120	0.0	D
	53	30	0.9	E
6c	160	140	0.0	D
	52	30	0.6	E
7c	167	150	0.0	D
	40	30	0.0	E
8c	160	121	0.0	D
	64	50	0.4	E

[a] In the *meso* compounds Θ_1 and Θ_2 refer to the C4−Z bond of the (*S*)- and (*R*)-paracyclophane moiety, respectively. In the chiral compounds Θ_1 and Θ_2 are equivalent. The values given are for the (*S*,*S*) diastereomers. − [b] Type of conformation as defined by regions A−E in Figure 2.

For some of the diastereomers, X-ray structure analyses have been carried out[12] (see ref.[16] for **6c**/**6m**) and it is of interest to note that, apart from **6c**, the energy minimum in the solid state (symbol * in Figures 2a and 2b) in all cases corresponds to the lowest or second lowest energy conformation computed by MM3 (for the gas phase).

NMR Spectra of the Diastereomers of Compounds 4−8

The ^{1}H- and ^{13}C-NMR spectra of the aromatic parts of the diastereomers of **4**−**8** could be assigned by standard techniques (H,H-COSY, C,H-HETCOR, C,H-COLOC and, in part, ^{1}H{^{1}H}-NOE difference spectra). The same was true for the ^{13}C spectra of the cyclophane bridges. The ^{1}H spectra of the bridges could be analysed fully in some cases (C1−C2 bridges in **4m**, **5m**, **5c**, **6m**, **7m**, **7c**, C9−C10 bridge in **4m**) but not in the remaining ones because there was too much overlap and second-order character in the one-dimensional spectra at the available measuring frequency of 400 MHz. When the analysis was possible, the results bore great resemblance to those obtained previously for a series of other simple 4-monosubstituted [2.2]paracyclophanes[17] and need not be discussed again. The main interest in the NMR data lies in the chemical shift differences between the chiral and the *meso* diastereomers. Table

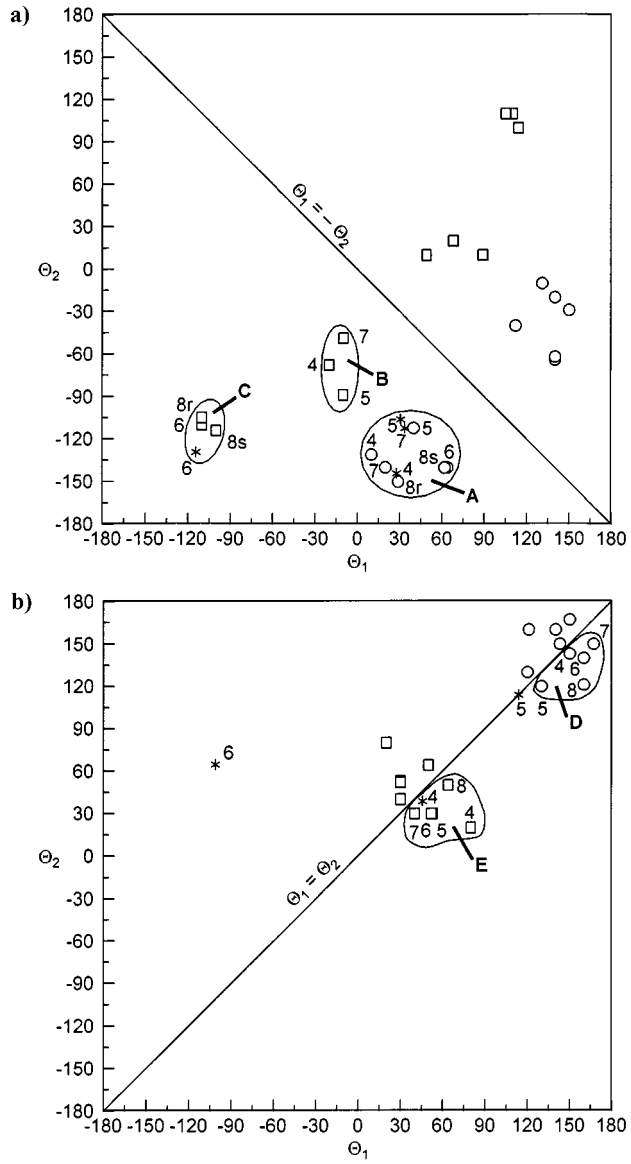


Figure 2. Lowest (circles) and second lowest (squares) energy minima and associated torsional angles Θ_1, Θ_2 for **4**−**8** as computed by MM3(94): **a)** *meso* diastereomers; **b)** chiral diastereomers (*S*,*S*); minimum energy regions are labelled A−E and are only indicated on one side of the symmetry line; an asterisk indicates the preferred conformation found in the solid state

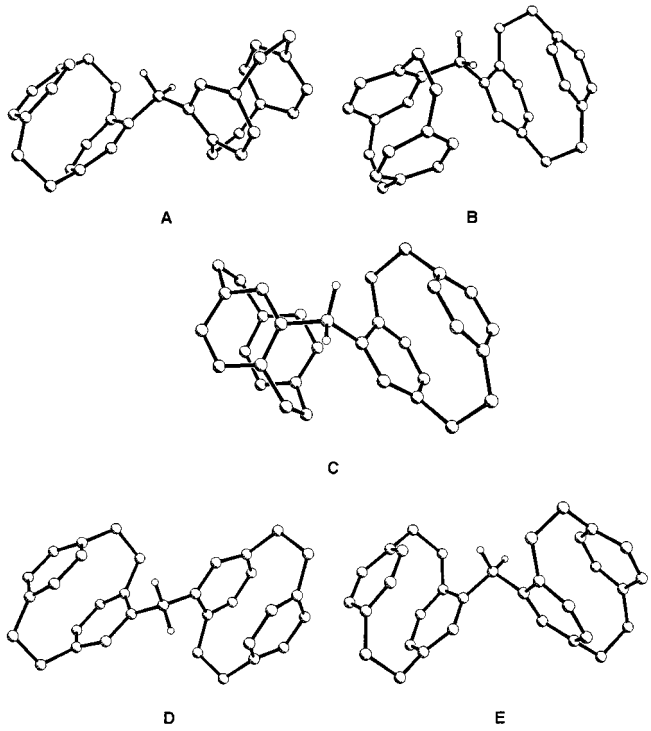


Figure 3. View of the conformers corresponding to the minimum energy regions **A**−**C** (*meso* diastereomers) and **D**−**E** (chiral diastereomers); the geometries were produced by taking a *meso*- and a chiral Q_2Z model with [2.2]paracyclophane moieties of D_{2h} symmetry and setting the torsional angles Θ_1 and Θ_2 to the following values: **A**: 37°/−131°; **B**: −15°/−69°; **C**: −105°/−110°; **D**: 149°/135°; **E**: 60°/35°; the hydrogen atoms are omitted for clarity; the small ligands to the central atom are included to make recognition of the orientation of the molecules easier; these ligands represent hydrogen atoms, lone pairs, methyl groups or oxygen-containing ligands or the bisector of their angle with the central atom may indicate the direction of the C=O double bond in the ketones; the *meso* diastereomers **A**−**C** are plotted with the (*S*)-paracyclophanyl unit on the left-hand side

2 contains the largest ^{1}H- and ^{13}C-shift differences between corresponding nuclei in the pairs of diastereomers **4**−**7** (*meso* minus chiral), in the two *meso* diastereomers of **8** and between the diastereotopic ligands of the chiral diastereomer **8c**. Generally, these shift differences are rather small: less than 0.5 ppm in the ^{1}H and less than 1.9 ppm in the ^{13}C NMR spectra. Only a minor part of the ^{13}C shift differences is probably due to effects of the magnetic anisotropies of the Z or the paracyclophanyl groups;[18] the major part is expected to be caused by the different steric interactions in the preferred conformations of the diastereomers. A detailed interpretation is hampered by the smallness of the effects.

We attempted a qualitative interpretation of the three ^{13}C chemical shifts of the $SiCH_3$ groups in **6m** (δ = 1.86 and 0.56) and **6c** (δ = 1.09) making use of the assumed linear dependence of γ effects upon torsional angles.[19] We considered conformers **A** and **C** for **6m** and **D** and **E** for **6c** as computed with MM3. Taking the four torsional angles between the $SiCH_3$ carbon atoms and the hydrogen-bearing *ortho*-carbon atoms C5 and C5′, H_3C−Si−C4−*C5* and H_3C−Si−C4′−*C5′*, respectively, assuming decreasing shielding with increasing torsional angles, and weighting the conformers according to their computed steric energies, one expects the equivalent methyl carbon nuclei of **6c** to possess a chemical shift in between those of the two methyl carbon atoms of **6m** as found experimentally. According to this treatment, the (*pro*-*R*)-CH_3 carbon nucleus in **6m** should be shielded relative to its (*pro*-*S*) counterpart. This relative shielding can be traced back to the close contact of the (*pro*-*R*)-methyl carbon atom in conformer **A** with the C5−H fragment of the (*R*)-paracyclophanyl ligand and a somewhat larger distance from the analogous fragment in the (*S*) ligand. The shielding of the $SiCH_3$ carbon atoms in **6c** relative to that of (*pro*-*S*)-CH_3 in **6m** may be explained by contacts in conformer **D** of one methyl group with the C5−H fragment of one paracyclophanyl ligand and of the

Table 2. Differences in chemical shifts [ppm] or coupling constants [Hz] within pairs of diastereomers

Nucleus	Shift difference	Nucleus	Shift difference	Nucleus	Shift difference
	δ(**4m**) − δ(**4c**)		δ(**5m**) − δ(**5c**)		δ(**6m**) − δ(**6c**)
1-H_s	+0.30	CH_2(a)[a]	+0.27	2-H_a	+0.22
2-H_s	+0.46	CH_2(b)	−0.31	15-H	+0.18
5-H	−0.44	other H	≤ |0.13|	$SiMe_2$(b)[b]	−0.22
other H	≤ |0.16|			other H	≤ |0.12|
C-4	−0.98	all C	≤ |0.36|	C-4	−0.65
C-5	+0.50			$SiMe_2$(a)[c]	+0.77
C-6	−0.50			$SiMe_2$(b)	−0.53
other C	≤ |0.38|			other C	≤ |0.39|
	δ(**7m**) − δ(**7c**)		δ(**8m$_1$**) − δ(**8m$_2$**)		δ(**8c**) − δ(**8c′**)[d]
all H	≤ |0.13|	15-H	+0.40	C-3	+1.07
C-3	−1.01	other H	≤ |0.15|	C-4	−1.85
C-4	−0.81	C-2	−0.80	C-14	+0.67
C-5	−0.76	$POCH_3$	−0.41	C-15	+1.07
other C	≤ |0.42|	other C	≤ |0.26|	other C	≤ |0.46|
		P	−3.19		
			J_{PX}(**8m$_1$**) − J_{PX}(**8m$_2$**)		J_{PC}(**8c**) − J_{PC}(**8c′**)
		$POCH_3$	−1.2	C-3	+3.0
		C-3	+2.0	C-4	−2.0
		C-5	−2.4	C-5	−4.2
		other C	≤ |0.9|	C-6	−1.9
				other C	≤ |1.2|

[a] Less shielded methylene proton. − [b] More highly shielded SiMe protons. − [c] Less shielded SiMe carbon atom. −[d] Difference between the diastereotopic paracyclophanyl groups in **8c**

other methyl group with the analogous fragment of the other ligand. The (*pro-S*)-methyl group in **6m** experiences an arrangement leading to substantial shielding only with the C5−H fragment of the (*S*)-paracyclophanyl ligand in conformer **C**. But its importance is diminished by the low population calculated for this conformer. In accordance with the preceding discussion we assign, with due reservation, δ_C = 1.86 and 0.56 − and from the C,H-HETCOR spectrum also δ_H = 0.79 and 0.57 − to the (*pro-S*)- and (*pro-R*)-$SiCH_3$ groups, respectively.

Other ^{13}C chemical shift differences within the pairs of diastereomers are difficult to interpret. It is evident, however, that the nuclei affected most are C-4, the connection point of the ligand to the central atom Z, and carbon nuclei in the vicinity of C-4. Generally speaking, the shift changes of C-4 and its neighbours may be supposed to reflect mainly the different steric situation that is created when the configuration of one paracyclophanyl group is inverted. It is also noteworthy that the chemical shifts of C-4 and C-4′ in the two diastereotopic paracyclophanyl ligands of **8c** differ distinctly more (|Δδ| = 1.85) than any of the shifts of analogous carbon atoms in the pairs of diastereomers. Finally, we note the distinct ^{31}P chemical shifts of the three diastereomers of **8** and also some differences in J_{PC} coupling constants involving carbon atoms in the vicinity of C-4. The larger and smaller magnitudes of $J_{P,C\text{-}3}$ and $J_{P,C\text{-}5}$, respectively, in **8m$_1$** relative to **8m$_2$** indicate the influence upon these geminal couplings of the orientation of the ligands (=O, $-OCH_3$) bound to the central phosphorus atom. This may be compared with the well-known dependence of $^2J_{PC}$ couplings on the phosphorus lone pair orientation in compounds containing trivalent phosphorus.[20] Even larger differences are observed for these coupling constants between the diastereotopic phane ligands in **8c**.

The largest ^1H chemical shift differences between diastereomers are observed for protons 1-H_s, 2-H_s, 5-H in **4m/4c** and for the central methylene group in **5m/5c**. As the differences in **4m/4c** are larger than in all other pairs of compounds it is tempting to attribute them to the effects of the carbonyl group. Inspection of the calculated conformers with the aid of Dreiding models and consideration of the magnetic anisotropy of the C=O group as discussed by Karabatsos et al.[21] suggest − in a very qualitative manner − that 5-H should be shielded in **4m** (averaged over the two possible conformers **A**) relative to **4c** (conformer **D**) and suggest the opposite for 1-H_s and 2-H_s. This is indeed what we found experimentally (Table 2). We also tried to rationalize the relative chemical shifts of the methylene protons in **5m** and **5c** by applying the ring current model of aromatic systems.[22] For this purpose, Cartesian coordinates were calculated with HYPERCHEM[23] for **5m** and **5c** assuming local D_{2h} symmetry for all [2.2]paracyclophane fragments to keep the problem relatively simple. Conformers **A** and **B** of **5m** and **D** and **E** of **5c** were created by setting the torsional angles Θ_1 and Θ_2 to the values predicted by MM3. The best planes were then calculated[24] for the non-bridgehead carbon atoms of all aromatic rings. For each conformer the distances *d* of the methylene protons from the centres of the four aromatic rings were computed together with the vertical displacements *z* of these protons from the best planes mentioned. The values of *d* and *z* furnished ρ, the component of *d* in the aromatic plane. Both *z* and ρ were expressed in units of benzene ring radii (139 pm). The combined contributions of the ring currents of the four aromatic rings in each conformer were obtained by adding the individual current shieldings from the tables of Johnson and Bovey[25] and of Haigh and Mallion[26] (assuming the latter authors′ parameter φ to be 0°). Disappointingly, however,

neither the Johnson−Bovey nor the Haigh−Mallion approach resulted in relative chemical shifts of the methylene protons that were comparable with the experimental findings. When the methylene proton chemical shifts are referenced to the the CH_2 signal of **5c**, the experimental shifts are $\delta_{rel} = +0.27$ (H_a in **5m**), ±0.00 (**5c**), −0.31 (H_b in **5m**) while the estimated ring current effects lead to $\delta_{rel} = +0.013$ (*pro-R*-H in **5m**), ±0.000 (**5c**), −0.049 (*pro-S*-H in **5m**) [Johnson−Bovey tables] and, respectively, $\delta_{rel} = \pm 0.000$ (**5c**), −0.016 (*pro-S*-H in **5m**), −0.035 (*pro-R*-H in **5m**) [Haigh−Mallion tables]. Several explanations for these discrepancies offer themselves. Either ring current effects are not the determining factor of the relative methylene proton chemical shifts and these are rather governed by other, e.g. steric, effects or the preferred conformations of **5m** and/or **5c** are not those predicted by the force-field calculations or the simplifying assumptions made in estimating the ring current effects (D_{2h} symmetry of the paracyclophane fragments, i.e. neglecting torsions of the benzene rings about the normals through their centres) are severe enough to falsify the results of the calculations.

Conclusion

We have synthesized a series of molecules possessing two planar chiral [2.2]paracyclophane ligands connected to a central atom or group. These molecules are formed unselectively as *meso* and chiral diastereomers. With one exception, the properties of the diastereomers are different enough to allow separation by crystallization or chromatography. Assignment of the configurations was achieved mainly, directly or indirectly, from the symmetry of the NMR spectra of the central groups. The relatively small ^{1}H-NMR chemical shift differences between the diastereomers could not be rationalized by considering the expected aromatic ring-current effects in the preferred conformations predicted by MM3. Only a few larger shift differences between some protons of the diastereomeric ketones seem to be correlated with the favoured orientations of these nuclei with respect to the carbonyl group.

Experimental Section

General Remarks: [2.2]Paracyclophane was obtained from Comelec, La-Chaux-de-Fonds, Switzerland. The *tert*-butyllithium solutions were analysed quantitatively by double titration according to Gilman.[27] − Melting points are not corrected. − Elemental analyses: Institute of Pharmaceutical Chemistry and Institute of Inorganic and Analytical Chemistry of the Technical University of Braunschweig. − EI MS: Finnigan MAT 8430, 70 eV. High-resolution mass determinations by peak matching, resolution: 10000. − UV/Vis: Hewlett-Packard 8452 diode array spectrometer. − IR: Nicolet 320 FT-IR spectrometer (KBr pellets). − NMR (ca. 296 K): Bruker AM-400 at 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C), Bruker AC-200 at 81.0 MHz (^{31}P), solvent $CDCl_3$. Chemical shift referencing: internal TMS (^{1}H), $CDCl_3$ (^{13}C, δ = 77.05), Ξ = 40.480716 (^{31}P). The latter value was determined for ext. H_3PO_4 in $CDCl_3$ with 0.05% TMS (v/v). Multiplicities given with the ^{13}C spectra refer to splittings that would be caused by ^1J(C,H) coupling and were determined by DEPT-135 experiments.[28a] Other assignment techniques used: NOE difference spectra:[28b] saturation times 6 s, irradiation power levels 40−42 dB below 0.2 W (nominal), irradiation either at a single frequency or at multiple frequencies per multiplet,[28c] depending on the selectivity required. H,H-COSY[28d] experiments and variant optimized for small long-range couplings (COSY-LR):[28e] relaxation delay 0.4−0.8 s, delay for the evolution of small couplings 80 ms. C,H-HETCOR:[28f] with suppression of H,H coupling in F_1,[29] relaxation delay 0.4 s, polarization transfer and refocussing delays both 3.23 ms for the aromatic carbon atoms, 3.45−4.00 ms and 1.72−2.00 ms respectively, for the aliphatic carbon atoms. C,H-COLOC:[28g] relaxation delay 0.8 s, polarization transfer and refocussing delay 30 and 37.5 ms, respectively. For all 2D experiments digital resolutions were chosen to be good enough to permit the separation of close chemical shifts in both dimensions. Iterative analyses of spin systems were carried out with LCN387[30] on a personal computer. A number of relative signs of J_{PC} and J_{PH} coupling constants was deduced from the shape of the cross-peaks[31] in the C,H-HETCOR or C,H-COLOC spectra of the diastereomers of **8**. − Molecular mechanics computations were carried out with a Silicon Graphics Indigo2 machine using Allinger's program MM3(94).[13] The input files were generated with the Spartan 4.0 software from Wavefunction, Inc. Parameters not contained explicitly in MM3(94) were approximated by the automatic parameter estimation module provided with this program. This concerned the sulfur- and phosphorus-containing molecules **7** and **8**.

***meso*- and Chiral Bis([2.2]paracyclophan-4-yl)methanone (4m/4c):** In a Schlenk flask under N_2 [2.2]paracyclophane (**10**; 400 mg, 1.92 mmol) and [2.2]paracyclophane-4-carbonyl chloride[11] (**11**; 650 mg, 2.4 mmol) were dissolved in CH_2Cl_2 (40 mL) and cooled to −10°C. Finely ground $AlCl_3$ (320 mg, 2.4 mmol) was added in small portions while the solution turned dark red. The reaction was completed without cooling overnight. Hydrolysis with ice water (20 mL), extraction with CH_2Cl_2, drying of the organic phase with $MgSO_4$, and removal of the solvent in vacuo gave a mixture of **4m/4c** and [2.2]paracyclophane. By dry column flash chromatography **10** was first eluted with petroleum ether and then **4m/4c** with petroleum ether/CH_2Cl_2 (1:1). Yield 669 mg (79%), diastereomer ratio 1:1 according to the ^{1}H-NMR spectrum. The diastereomers can be separated by TLC (SiO_2; petroleum ether/CH_2Cl_2, 1:1) and are recrystallized from CH_2Cl_2/2-propanol. Their configurations are determined by ^{1}H NMR after converting them to **5m** and **5c**, respectively.

***meso* Diastereomer 4m:** M.p. 230°C. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 206 nm, sh (4.69), 210 sh (4.67), 218 sh (4.58), 244 sh (4.01), 296 (3.89)− IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2851 (m), 1645 (vs), 1269 (m), 807 (m). − ^{1}H NMR ($CDCl_3$): δ = 6.67 (dd, 15-H), 6.61 (dd, 7-H), 6.53 (dd, 13-H), 6.499 (d, 8-H), 6.496 (dd, 12-H), 6.30 (d, 5-H), 6.23 (dd, 16-H), 3.54 (ddd, 2-H_s), 3.31 (ddd, 1-H_s), 3.10 (ddd, 1-H_a), 3.06 (m_c, 9-H_a), 3.02 (m_c, 10-H_s), 2.91 (m_c, 10-H_a), 2.83 (m_c, 2-H_a), 2.79 (m_c, 9-H_s); $J_{5,7}$ = 2.0 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.8, $J_{12,16}$ = 2.0, $J_{13,15}$ = 2.0, $J_{15,16}$ = 7.9, $J_{1a,1s}$ = −12.7, $J_{1a,2a}$ = 10.3, $J_{1a,2s}$ = 1.8, $J_{1s,2a}$ = 6.0, $J_{1s,2s}$ = 10.3, $J_{2a,2s}$ = −12.7, $J_{9a,9s}$ = −13.2, $J_{9a,10a}$ = 10.6, $J_{9a,10s}$ = 3.0, $J_{9s,10a}$ = 5.3, $J_{9s,10s}$ = 10.6, $J_{10a,10s}$ = −13.3. − ^{13}C NMR ($CDCl_3$): δ = 197.49 (s, C-17), 141.78 (s, C-3), 140.02 (s, C-14), 139.15 (s, C-11), 139.09 (s, C-6), 138.20 (s, C-4), 135.84 (d, C-7), 135.69 (d, C-8), 134.75 (d, C-5), 132.68 (d, C-13), 132.51 (d, C-16), 132.44 (d, C-12), 130.98 (d, C-15), 35.52 (t, C-2), 35.48 (t, C-1), 35.09 (t, C-10), 34.91 (t, C-9). − MS (70 eV); *m/z* (%): 442 (100) [M$^+$], 338 (41), 233 (30), 219 (23),

191 (18), 104 (20). − $C_{33}H_{30}O$ (442.6): calcd. C 89.55, H 6.83; found C 89.37, H 6.97.

Chiral Diastereomer 4c: M.p. 221°C. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 204 nm, sh (4.69), 210 sh (4.65), 220 sh (4.56), 242 sh (4.05), 294 (3.89). − IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1} (s), 2851 (m), 1652 (vs), 1262 (m), 803 (m). − ^1H NMR ($CDCl_3$): δ = 6.74 (d, 5-H), 6.65 (dd, 7-H), 6.61 (d, 15-H), 6.49 (m_c, 2 H, 12-H, 13-H), 6.47 (d, 8-H), 6.35 (d, 16-H), 3.12 (m_c, 9-H_a), 3.08 (m_c, 2-H_s), 3.09 (m_c, 10-H_s), 3.01 (m_c, 2 H, 1-H_a, 1-H_s), 2.96 (m_c, 10-H_a), 2.91 (m_c, 9-H_s), 2.67 (ddd, 2-H_a); $J_{5,7}$ = 2.0 Hz, $J_{7,8}$ = 7.8 (assumed value for the purpose of analysis), $J_{12,13}$ = 7.8, $J_{12,16}$ = 2.1, $J_{13,15}$ = 2.1, $J_{15,16}$ = 8.0. − ^{13}C NMR ($CDCl_3$): δ = 197.11 (s, C-17), 141.58 (s, C-3), 139.68 (s, C-14), 139.59 (s, C-6), 139.25 (s, C-11), 139.18 (s, C-4), 135.84 (d, C-7), 135.50 (d, C-8), 134.25 (d, C-5), 132.59 (d, C-13), 132.49 (d, C-12), 132.40 (d, C-16), 131.14 (d, C-15), 35.59 (t, 2 C, C-1, C-2), 35.19 (t, C-10), 35.03 (t, C-9). − MS (70 eV); *m/z* (%): 442 (100) [M^+], 337 (40), 233 (40), 219 (38), 191 (28), 104 (32). − $C_{33}H_{30}O$ (442.6): calcd. C 89.55, H 6.83; found C 89.49, H 6.76.

***meso*-Bis([2.2]paracyclophan-4-yl)methane (5m):** According to the general procedure of ref.[32], $LiAlH_4$ (15 mg, 0.40 mmol), finely ground $AlCl_3$ (105.5 mg, 0.79 mmol) and diethyl ether (25 mL, absolute) were stirred at room temp. and **4m** (100 mg, 0.23 mmol) was added. The mixture was refluxed for 1 h. Excess $LiAlH_4$ was destroyed by adding ethyl acetate and the mixture poured into dilute H_2SO_4. Extraction with CH_2Cl_2, drying of the organic phase with $MgSO_4$, and distilling off the solvents furnished the raw product which was freed from impurities by dry column flash chromatography (SiO_2; petroleum ether/CH_2Cl_2, 1:1). Recrystallization from CH_2Cl_2/2-propanol (slow diffusion method) gave 96 mg (99%) of **5m**, m.p. 228°C. The solubility of **5m** in CH_2Cl_2 or $CHCl_3$ was better than that of **5c**. − UV (CH_3CN): λ_{max} (lg ε) = 210 nm, sh (4.50), 228 sh (4.56), 242 sh (4.01). − IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (s), 2849 (m), 1592 (w), 1411 (w), 797 (w), 716 (m). − ^1H NMR ($CDCl_3$): δ = 6.85 (dd, 15-H), 6.53 (dd, 12-H), 6.46 (dd, 13-H), 6.40 (dd, 7-H), 6.36 ("d", 2 H, 8-H, 16-H), 5.94 (d, 5-H), 3.85 (d, 17-H), 3.27 (d, 17-H), 3.18 (ddd, 2-H_s), 3.12 (m_c, 1-H_a), 3.07 (m_c, 1-H_s), 3.05−2.97 (m, 3 H, 9-H_a, 10-H_a, 10-H_s), 2.85 (m_c, 9-H_s), 2.71 (ddd, 2-H_a); $J_{5,7}$ = 1.8 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.8, $J_{12,16}$ = 1.9, $J_{13,15}$ = 1.9, $J_{15,16}$ = 7.9, $J_{17,17'}$ = −15.9, $J_{1a,1s}$ = −13.3, $J_{1a,2a}$ = 10.8, $J_{1a,2s}$ = 2.0, $J_{1s,2a}$ = 6.1, $J_{1s,2s}$ = 10.3, $J_{2a,2s}$ = −13.6. − ^{13}C NMR ($CDCl_3$): δ = 139.67 (s, C-6), 139.63 (s, C-4), 139.55 (s, C-11), 139.34 (s, C-14), 137.98 (s, C-3), 135.06 (d, C-5), 134.61 (d, C-8), 133.28 (d, C-12), 133.24 (d, C-13), 132.12 (d, C-16), 130.51 (d, C-7), 128.11 (d, C-15), 38.83 (t, C-17), 35.28 (t, C-10), 35.00 (t, C-9), 34.21 (t, C-1), 33.51 (t, C-2). − MS (70 eV); *m/z* (%): 428 (100) [M^+], 323 (72), 309 (45), 219 (44), 205 (92), 191 (45), 104 (18). − $C_{33}H_{32}$ (428.6): calcd. C 92.47, H 7.53; found C 92.68, H 7.47.

Chiral Bis([2.2]paracyclophan-4-yl)methane (5c): Prepared from **4c** (100 mg, 0.23 mmol) in the same way as the diastereomer. Yield 96 mg (99%), m.p. 272°C. − UV (CH_3CN): λ_{max} (lg ε) = 212 nm, sh (4.47), 228 sh (4.55), 240 sh (4.08). − IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1} (s), 2850 (m), 1588 (w), 1412 (w), 796 (w), 722 (m). − ^1H NMR ($CDCl_3$): δ = 6.88 (dd, 15-H), 6.55 (dd, 12-H), 6.49 (dd, 13-H), 6.43 (dd, 16-H), 6.39 (dd, 7-H), 6.37 (d, 8-H), 6.01 (d, 5-H), 3.58 (s, 2 H, 17-H, 17-H′), 3.31 (ddd, 2-H_s), 3.17 (m_c, 1-H_a), 3.09 (ddd, 1-H_s), 3.01 (m_c, 3 H, 9-H_a, 10-H_a, 10-H_s), 2.85 (m_c, 9-H_s), 2.75 (ddd, 2-H_a); $J_{5,7}$ = 1.8 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.8, $J_{12,16}$ = 2.0, $J_{13,15}$ = 2.0, $J_{15,16}$ = 7.9, $J_{1a,1s}$ = −13.3, $J_{1a,2a}$ = 10.6, $J_{1a,2s}$ = 1.9, $J_{1s,2a}$ = 6.5, $J_{1s,2s}$ = 10.1, $J_{2a,2s}$ = −13.6. − ^{13}C NMR ($CDCl_3$): δ = 139.81 (s, C-4), 139.59 (s, C-11), 139.57 (s, C-6), 139.44 (s, C-14), 138.18 (s, C-3), 135.28 (d, C-5), 134.90 (d, C-8), 133.37 (d, C-12), 133.26 (d, C-13), 131.98 (d, C-16), 130.39 (d, C-7), 128.23 (d, C-15), 38.99 (t, C-17), 35.36 (t, C-10), 35.01 (t, C-9), 34.36 (t, C-1), 33.87 (t, C-2). − MS (70 eV); *m/z* (%): 428 (100) [M^+], 323 (75), 309 (45), 219 (46), 205 (94), 191 (48), 104 (22). − $C_{33}H_{32}$ (428.6): calcd. C 92.47, H 7.53; found C 92.39, H 7.53.

4-Bromo[2.2]paracyclophane (12):[5] In a 100-mL three-necked flask 2 mL of a solution of Br_2 (1.59 g, 9.9 mmol) in CCl_4 (15 mL) was added to iron powder (12 mg, 0.2 mmol) and stirred for 15 min at room temp. The suspension was diluted with CH_2Cl_2 (45 mL) and **10** (2.00 g, 9.6 mmol) was added. When **10** had dissolved the remaining Br_2 solution was slowly added dropwise and the mixture was stirred for 2 h. The dark-red reaction mixture was then washed twice with a saturated aqueous $NaHSO_3$ solution. This decolourized the organic phase which was separated and dried with anhydrous $MgSO_4$. Removal of the solvent and sublimation of the residue at 130°C/0.7 Torr yielded 2.74 g (99%) of **12** as a colourless solid, m.p. 134°C (ref.[5] 136−138°C; 82%). The ^1H- and ^{13}C-NMR spectra agree well with those of ref.[17] Analytical HPLC (RP-18, MeOH/H_2O, 90:10) showed a total of 2% impurities to be present, viz. **2**,[5] **10**, and **1**.[5] The former two impurities could be removed by TLC (eluent: *n*-hexane/CH_2Cl_2 mixtures), the latter by zone sublimation. This was considered unnecessary for using **12** as a starting material.

Preparation of a Solution of 4-Lithio[2.2]paracyclophane (13): To absolute THF (7 mL) at −78°C in a dry Schlenk flask under N_2 *tert*-butyllithium (2.03 mL of a 1.37 M solution in pentane, 2.79 mmol) was added through a septum. Then, a solution of **12** (500 mg, 1.74 mmol) in abs. THF (3 mL) was added dropwise with stirring over a period of 15 min. Stirring was continued for 2 h at −78°C while the colour of the solution changed from yellow to gold. This solution was used in the preparation of **6**−**9** as described below.

***meso*- and Chiral Dimethylbis([2.2]paracyclophan-4-yl)silane (6m/6c):** To a solution of **13** in THF, prepared from **12** (500 mg, 1.74 mmol) as described above, dichlorodimethylsilane (80.9 mg, 0.63 mmol, distilled from CaH_2) was added at −78°C and the solution was left overnight to reach room temp. The colourless, slightly turbid solution was mixed with water (5 mL) and stirred for 10 min. The solution was extracted with CH_2Cl_2, the organic phase dried with anhydrous $MgSO_4$, and the solvent removed in vacuo. The raw product was purified by flash column chromatography (SiO_2; *n*-hexane/CH_2Cl_2, 10:1). Yield 212 mg (72%) of a 1:1 diastereomeric mixture (**6m/6c**). The diastereomers could be distinguished by analytical HPLC (RP-18; CH_3CN/H_2O, 90:10). To separate the diastereomers by fractional crystallization the mixture was dissolved in CH_2Cl_2 and an equal volume of 2-propanol was added. At 70°C enough CH_2Cl_2 was distilled off to cause the solution to become cloudy. CH_2Cl_2 was then added to just dissolve the solid formed and the solution was kept in the refrigerator for crystallization. Repetition of the procedure with the solid and the mother liquor furnished four fractions. The *meso* diastereomer was obtained from the least soluble and the chiral pair of enantiomers from the most soluble fraction. Colourless single crystals for X-ray diffraction were obtained by recrystallising from CH_2Cl_2/2-propanol (**6m**) and from *n*-hexane (**6c**), respectively.

***meso* Diastereomer 6m:** M.p. 254°C, less soluble in $CHCl_3$ or CH_2Cl_2. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 210 nm, sh (4.56), 230 (4.50), 256 sh (3.86). − IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1} (s), 2850 (m), 1499 (w), 1245 (m), 806 (s), 726 (m). − ^1H NMR ($CDCl_3$): δ = 6.77 (d, 5-H), 6.55 (dd, 12-H), 6.52 (dd, 13-H), 6.42 (dd, 7-H), 6.33 (d, 8-H), 6.26 (dd, 16-H), 6.19 (dd, 15-H), 3.19 (m, 9-H_a), 3.16 (m, 10-H_s), 3.07 (m, 2-H_s), 3.01 (m, 2-H_a), 2.97 (m, 10-H_a), 2.94 (m, 9-

H_s), 2.89 (m, 1-H_a), 2.71 (ddd, 1-H_s), 0.79 (s, 3 H, 17-H), 0.57 (s, 3 H, 17-H′); $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.7, $J_{12,16}$ = 2.0, $J_{13,15}$ = 1.9, $J_{15,16}$ = 7.9, $J_{1a,1s}$ = −13.1, $J_{1a,2a}$ = 10.8, $J_{1a,2s}$ = 3.3, $J_{1s,2a}$ = 4.4, $J_{1s,2s}$ = 10.5, $J_{2a,2s}$ = −13.2; NOE measurements (saturated signal → enhanced signal): 5-H → 1-H_s, 16-H, 17-H, 17-H′; 17-H → 1-H_s, 2-H_s, 5-H, 15-H; 17-H′ → 5-H, (15-H, weak). − ^{13}C NMR ($CDCl_3$): δ = 146.56 (s, C-3), 139.61 (s, C-11), 139.22 (s, C-14), 138.23 (s, C-6), 137.76 (d, C-5), 137.22 (s, C-4), 134.60 (d, C-7), 134.17 (d, C-8), 133.26 (d, C-15), 132.63 (d, C-16), 132.24 (d, C-12, C-13), 36.21 (t, C-2), 35.49 (t, C-9), 35.43 (t, C-1, C-10), 1.86 (q, C-17), 0.56 (t, C-17′). − MS (70 eV); *m*/*z* (%): 472 (100) [M^+], 457 (68), 368 (40), 353 (85), 263 (37), 249 (48), 191 (58), 104 (60). − X-ray structural analysis: ref.[16] − $C_{34}H_{36}Si$ (472.7): calcd. C 86.38, H 7.68; found C 85.83, H 7.61.

Chiral Diastereomer 6c: M.p. 180°C, better soluble in CH_2Cl_2 or $CHCl_3$. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 208 nm, sh (4.40), 228 (4.31), 250 sh (3.76). − IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1} (s), 2850 (m), 1410 (w), 1245 (s), 1095 (m), 984 (m), 808 (s), 722 (s). − ^{1}H NMR ($CDCl_3$): δ = 6.80 (d, 5-H), 6.52 (dd, 12-H), 6.49 (dd, 13-H), 6.40 (dd, 7-H), 6.29 (d, 8-H), 6.25 (dd, 16-H), 6.01 (dd, 15-H), 3.15, 3.13 (m, 2 H, 9-H_a, 10-H_s), 2.99, 2.97 (m, 2 H, 10-H_a, 9-H_s), 2.83 (m, 1-H_s), 2.79 (m, 2-H_a), 2.77, 2.74 (m, 2 H, 1-H_s, 2-H_s), 0.79 (s, 6 H, 17-H), assignments of the 1- and 2-H signals are not final; $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.6, $J_{12,13}$ = 7.7, $J_{12,16}$ = 2.0, $J_{13,15}$ = 2.0, $J_{15,16}$ = 7.9; NOE measurements: (saturated signal → enhanced signal): 5-H → 9-H_s, 16-H, 17-H; 17-H → 5-H, 15-H. − ^{13}C NMR ($CDCl_3$): δ = 146.34 (s, C-3), 139.49 (s, C-11), 139.29 (s, C-14), 137.87 (s, C-4), 137.84 (s, C-6), 137.59 (d, C-5), 134.50 (d, C-7), 134.09 (d, C-8), 133.11 (d, C-15), 132.60 (d, C-16), 132.33 (d, C-13), 132.20 (d, C-12), 35.95 (t, C-2), 35.62 (t, C-1), 35.45 (t, C-9, C-10), 1.09 (q, 2 C, C-17). − MS (70 eV); *m*/*z* (%): 472 (100) [M^+], 457 (57), 368 (40), 353 (91), 263 (44), 249 (60), 191 (64), 104 (65). − X-ray structural analysis: ref.[16] − $C_{34}H_{36}Si$ (472.7): calcd. C 86.38, H 7.68; found C 85.72, H 7.57.

***meso* and Chiral Bis([2.2]paracyclophan-4-yl) Sulfide (7m/7c):** To a solution of **13** in THF, prepared from **12** (1.00 g, 3.48 mmol) as described above, sulfur dichloride (143.4 mg, 1.39 mmol, distilled from PCl_3, b.p. 58°C) was added at −78°C and the solution was left overnight to reach room temp. The greyish suspension was mixed with water (5 mL) and stirred for 10 min. The solvent was removed in vacuo, the remaining solid dissolved in CH_2Cl_2 and adsorbed on silica gel. Flash column chromatography (SiO_2; *n*-hexane/CH_2Cl_2, 5:1) furnished a 1:1 mixture of the diastereomers **7m/7c** containing ca. 5% of disulfides as side products, yield 278 mg, 45%. To separate the stereoisomers, four fractions were prepared as described for **6m/6c**. The solvent was removed from the most soluble fraction and the residue recrystallized from boiling 2-propanol. The resulting solid consisted of sulfide and the disulfides whereas the supernatant was free of disulfides. The solvent of this supernatant was distilled off in vacuo and the remaing solid recrystallized again from 2-propanol. This gave colourless fibrous single crystals suitable for X-ray structure determination, according to which the better soluble sulfide is the *meso* diastereomer **7m**.[12] The least soluble sulfide fraction was dissolved in CH_2Cl_2 and the chiral diastereomer **7c** was precipitated as a colourless solid by cautious addition of an upper layer of 2-propanol.

***meso* Diastereomer 7m:** M.p. 220°C, better soluble in CH_2Cl_2 or $CHCl_3$. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 222 nm, sh (4.44), 242 sh (4.11), 254 sh (3.90). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2849 (m), 1581 (w), 848 (w), 718 (m). − ^{1}H NMR ($CDCl_3$): δ = 7.09 (dd, 15-H), 6.51 (dd, 12-H), 6.46 (dd, 13-H), 6.44 (dd, 7-H), 6.41 (d, 8-H), 6.27 (dd, 16-H), 6.21 (d, 5-H), 3.33 (ddd, 2-H_s), 3.25 (ddd, 1-H_s), 3.03 (ddd, 1-H_a), 3.06−2.94 (m, 3 H, 9-H_a, 10-H_a,H_s), 2.82 (m_c, 9-H_s), 2.70 (ddd, 2-H_a); $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.8, $J_{12,16}$ = 2.0, $J_{13,15}$ = 2.0, $J_{15,16}$ = 7.8, $J_{1a,1s}$ = −13.1, $J_{1a,2a}$ = 10.6, $J_{1a,2s}$ = 2.1, $J_{1s,2a}$ = 5.8, $J_{1s,2s}$ = 10.2, $J_{2a,2s}$ = −13.5. − ^{13}C NMR ($CDCl_3$): δ = 140.61 (s, C-6), 140.19 (s, C-3), 139.47 (s, C-14), 139.21 (s, C-11), 135.99 (s, C-4), 135.57 (d, C-5), 134.91 (d, C-8), 133.26 (d, C-13), 132.76 (d, C-12), 132.04 (d, C-16), 131.45 (d, C-7), 128.96 (d, C-15), 35.32 (t, C-10), 34.98 (t, C-9), 34.31 (t, C-2), 33.79 (t, C-1). − MS (70 eV); *m*/*z* (%): 446 (100) [M^+], 342 (52), 328 (62), 237 (35), 223 (63), 104 (20). − $C_{32}H_{30}S$ (446.7): calcd. C 86.05, H 6.77, S 7.18; found C 85.45, H 6.74, S 7.40.

Chiral Diastereomer 7c: M.p. 271°C, less soluble in CH_2Cl_2 or $CHCl_3$. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 226 nm, sh (4.45), 242 sh (4.12), 254 sh (3.93). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2852 (m), 1581 (w), 849 (w), 717 (m). − ^{1}H NMR ($CDCl_3$): δ = 7.11 (dd, 15-H), 6.53 (dd, 12-H), 6.47 (dd, 13-H), 6.43 (dd, 7-H), 6.40 (d, 16-H), 6.39 (dd, 8-H), 6.32 (d, 5-H), 3.27 (ddd, 2-H_s), 3.23 (m_c, 1-H_s), 3.04 (m, 1-H_a), 3.04−2.98 (m, 3 H, 9-H_a, 10-H_a,H_s), 2.85 (m_c, 9-H_s), 2.65 (ddd, 2-H_a); $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.7, $J_{12,13}$ = 7.8, $J_{12,16}$ = 1.9, $J_{13,15}$ = 1.9, $J_{15,16}$ = 7.8, $J_{1a,1s}$ = −13.1, $J_{1a,2a}$ = 10.5, $J_{1a,2s}$ = 2.2, $J_{1s,2a}$ = 6.2, $J_{1s,2s}$ = 10.1, $J_{2a,2s}$ = −13.4. − ^{13}C NMR ($CDCl_3$): δ = 141.20 (s, C-3), 140.39 (s, C-6), 139.58 (s, C-14), 139.23 (s, C-11), 136.80 (s, C-4), 136.33 (d, C-5), 135.33 (d, C-8), 133.26 (d, C-13), 132.87 (d, C-12), 132.03 (d, C-16), 131.66 (d, C-7) 129.16 (d, C-15), 35.39 (t, C-10), 34.92 (t, C-9), 34.51 (t, C-2), 33.87 (t, C-1). − MS (70 eV); *m*/*z* (%): 446 (100) [M^+], 342 (52), 328 (64), 237 (34), 223 (64), 104 (18). − $C_{32}H_{30}S$ (446.7): calcd. C 86.05, H 6.77, S 7.18; found C 85.69, H 6.75, S 7.34. − HR MS: calcd. 446.2068; found 446.206±0.001.

***meso*$_1$-, *meso*$_2$- and Chiral Bis([2.2]paracyclophan-4-yl)phosphinic Acid Methyl Ester (8m$_1$/8m$_2$/8c):** To a solution of **13** in THF, prepared from **12** (700 mg, 2.44 mmol) as described above, $POCl_3$ (134.5 mg, 0.88 mmol, freshly distilled) was added at −78°C and the solution was left overnight to reach room temp. The black-violet reaction mixture was quenched with CH_3OH and turned yellow. The solvent was completely removed in vacuo and the residue dissolved in CH_2Cl_2 and adsorbed on silica gel. [2.2]Paracyclophane was eluted by dry column flash chromatography (eluent: CH_2Cl_2). The desired product was isolated from the column by elution with acetone/CH_2Cl_2 (1:20), yield 284 mg (66%). As expected, the ^{31}P-NMR spectrum contained three signals and the preparation did not show any diastereoselectivity. Flash column chromatography (SiO_2; acetone/CH_2Cl_2, 1:20) gave, as the first fraction, a mixture of a *meso* diasteromer (**8m$_1$**) and the *chiral* pair of enantiomers (**8c**). The second fraction contained only the other *meso* diastereomer (**8m$_2$**). The separation of **8m$_1$** and **8c** was achieved by twofold recrystallization from boiling CH_3OH in which **8m$_1$** was better soluble than **8c**. Single crystals suitable for X-ray structural analysis were not obtained.

***meso* Diastereomer 8m$_1$:** M.p. 218°C. −UV/Vis (CH_3CN): λ_{max} (lg ε) = 226 nm, sh (4.44), 242 sh (4.08), 262 sh (3.78). − IR (KBr): $\tilde{\nu}$ = 2927 cm^{-1} (s), 2852 (m), 1636 (w), 1219 (m), 1032 (s), 723 (m), 587 (s), 508 (m). − ^{1}H NMR: δ = 7.03 (dd, 5-H), 6.57 (dddd, 7-H), 6.54 (m_c, 2 H, 12-H, 13-H), 6.47 (dd, 15-H), 6.44 (dd, 8-H), 6.29 (dd, 16-H), 3.86 (d, 3 H, OMe), 3.70 (m_c, 2-H_s), 3.26−3.16 (m, 2 H, 9-H_a, 10-H_s), 3.03−2.93 (m, 5 H, 1-H_a, 1-H_s, 2-H_a, 9-H_s, 10-H_a); $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.7, $J_{7,9a}$ = 0.9, $J_{P,5}$ = 13.6, $J_{P,7}$ = 0.9, $J_{P,8}$ = 5.1, $J_{P,OMe}$ = 10.9, $J_{12,13}$ = 7.9, $J_{12,15}$ + $J_{13,15}$ = 2.3, $J_{12,16}$ = 1.9, $J_{15,16}$ = 8.0. − ^{13}C NMR: δ = 144.08 (s, $J_{P,C}$ = 10.6 Hz, C-3), 139.96 (s, $J_{P,C}$ = 12.8 Hz, C-6), 139.64 (s, C-14), 139.29 (s, C-11), 137.01 (d, $J_{P,C}$ = −3.2 Hz, C-7), 136.11 (d, $J_{P,C}$ = 14.2 Hz, C-8), 135.58 (d, $J_{P,C}$ = 9.1 Hz, C-5), 133.43 (d, C-15),

132.43 (d, C-16), 132.28 (d, C-13), 132.16 (d, C-12), 129.84 (s, $J_{P,C}$ = 135.8 Hz, C-4), 50.96 (q, $J_{P,C}$ = −6.1 Hz, OMe), 35.29 (t, $|J_{P,C}|$ = 1.2 Hz, C-1), 35.25 (t, $|J_{P,C}|$ = 0.5 Hz, C-10), 35.24 (t, $|J_{P,C}|$ = 0.5 Hz, C-9), 34.94 (t, $J_{P,C}$ = 3.0 Hz, C-2). − ^{31}P NMR: δ = 33.0. − MS (70 eV); *m/z* (%): 492 (100) [M^+], 388 (29), 283 (16), 205 (16), 104 (12). − $C_{33}H_{33}O_2P$ (492.6): calcd. C 80.46, H 6.75; found C 80.65, H 6.85.

***meso* Diastereomer 8m$_2$:** M.p. 196°C. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 226 nm, sh (4.39), 244 sh (4.02), 264 sh (3.74). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2852 (m), 1456 (w), 1220 (s), 1029 (s), 723 (m), 586 (s), 507 (s). − ^{1}H NMR: δ = 7.13 (dd, 5-H), 6.59 (dddd, 7-H), 6.55 (m_c, 13-H), 6.53 (m_c, 12-H), 6.51 (dd, 8-H), 6.14 (m_c, 16-H), 6.07 (m_c, 15-H), 3.81 (d, 3 H, OMe), 3.75 (m_c, 2-H_s), 3.18 (m_c, 9-H_a), 3.12 (m_c, 10-H_s), 3.00 (m_c, 4 H, 2-H_a, 1-H_a, 9-H_s, 1-H_s), 2.95 (m_c, 10-H_a); $J_{5,7}$ = 1.9 Hz, $J_{7,8}$ = 7.7, $J_{7,9a}$ = 0.9, $J_{P,5}$ = 14.8, $J_{P,7}$ = 0.9, $J_{P,8}$ = 5.0, $J_{P,OMe}$ = 10.9. − ^{13}C NMR: δ = 144.10 (s, $J_{P,C}$ = 8.6 Hz, C-3), 139.86 (s, $J_{P,C}$ = 13.7 Hz, C-6), 139.38 (s, C-14), 139.28 (s, C-11), 136.92 (d, $J_{P,C}$ = −3.2 Hz, C-7), 136.21 (d, $J_{P,C}$ = 13.9 Hz, C-8), 135.84 (d, $J_{P,C}$ = 11.5 Hz, C-5), 133.21 (d, C-15), 132.63 (d, C-16), 132.16 (d, C-13), 132.13 (d, C-12), 129.60 (s, $J_{P,C}$ = 135.2 Hz, C-4), 51.37 (q, $J_{P,C}$ = −6.7 Hz, OMe), 35.74 (t, $J_{P,C}$ = 2.3 Hz, C-2), 35.52 (t, $|J_{P,C}|$ = 1.2 Hz, C-1), 35.22 (t, $|J_{P,C}|$ ≤ 1 Hz, C-10), 35.21 (t, $J_{P,C}$ ≤ 1 Hz, C-9). − ^{31}P NMR: δ = 36.2. − MS (70 eV); *m/z* (%): 492 (100) [M^+], 388 (28), 283 (20), 205 (19), 104 (12). − $C_{33}H_{33}O_2P$ (492.6): calcd. C 80.46, H 6.75; found C 80.53, H 6.62.

Chiral Diastereomer 8c: M.p. 254°C. − UV/Vis (CH_3CN): λ_{max} (lg ε) = 228 nm, sh (4.44), 248 sh (3.95), 264 sh (3.75). − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2852 (m), 1436 (w), 1220 (s), 1022 (s), 722 (s), 589 (s), 507 (s). − ^{1}H NMR: δ = 6.97 (dd, 5-H), 6.78 (dd, 15-H), 6.62 (m_c, 7-H), 6.60 (m_c, 5′-H), 6.59 (dd, 13-H), 6.55 (dd, 12-H), 6.52 (m_c, 8-H), 6.51 (dd, 13′-H), 6.49 (dd, 12′-H), 6.46 (m_c, 7′-H), 6.42 (dd, 15′-H), 6.41 (dd, 16-H), 6.36 (dd, 8′-H), 6.13 (dd, 16′-H), 4.04 (d, 3 H, OMe), 3.98 (m_c, 2-H_s), 3.60 (m_c, 2′-H_s), 3.43 (m_c, 1-H_s), 3.22 (m_c, 10-H_s), 3.22 (m_c, 9-H_a), 3.21 (m_c, 1′-H_a), 3.10 (m_c, 1-H_a), 3.07 (m_c, 10′-H_s), 3.07 (m_c, 9′-H_a), 3.02 (m_c, 10-H_a), 3.02 (m_c, 9-H_s), 2.98 (m_c, 1′-H_s), 2.92 (m_c, 2-H_a), 2.90 (m_c, 10′-H_a), 2.88 (m_c, 2′-H_a), 2.82 (m_c, 9′-H_s); $J_{5,7}$ = 1.9 Hz, $J_{5',7'}$ = 2.0 Hz, $J_{7',8'}$ = 7.7, $J_{P,5}$ = 12.9, $J_{P,8'}$ = 4.9, $J_{P,OMe}$ = 10.7, $J_{12,13}$ = 8.0, $J_{12',13'}$ = 7.9, $J_{12,16}$ = 1.9, $J_{12',16'}$ = 1.9, $J_{13,15}$ = 1.9, $J_{13',15'}$ = 1.9, $J_{15,16}$ = 7.9, $J_{15',16'}$ = 7.9. − ^{13}C NMR: δ = 144.70 (s, $J_{P,C}$ = 11.4 Hz, C-3), 143.63 (s, $J_{P,C}$ = 8.4 Hz, C-3′), 140.18 (s, C-14), 139.51 (s, $J_{P,C}$ = 12.2 Hz, C-6), 139.51 (s, C-14′), 139.22 (s, C-11′), 139.18 (s, $J_{P,C}$ = 14.1 Hz, C-6′), 139.17 (s, C-11), 137.03 (d, $J_{P,C}$ = −3.4 Hz, C-7), 136.57 (d, $J_{P,C}$ = −3.2 Hz, C-7′), 136.27 (d, $J_{P,C}$ = 14.9 Hz, C-8), 135.92 (d, $J_{P,C}$ = 13.7 Hz, C-8′), 135.24 (d, $J_{P,C}$ = 12.2 Hz, C-5′), 135.10 (d, $J_{P,C}$ = 8.0 Hz, C-5), 134.07 (d, C-15), 133.00 (d, C-15′), 132.46 (d, C-16′), 132.41 (d, C-16), 132.39 (d, 2 C, C-12,13), 132.32 (d, C-13′), 132.03 (d, C-12′), 131.16 (s, $J_{P,C}$ = 137.1 Hz, C-4′), 129.31 (s, $J_{P,C}$ = 135.1 Hz, C-4), 51.53 (q, $J_{P,C}$ = −6.3 Hz, OMe), 35.79 (t, $|J_{P,C}|$ = 1.3 Hz, C-1), 35.38 (t, $|J_{P,C}|$ = 1.2 Hz, C-1′), 35.34 (t, $|J_{P,C}|$ = 0.5 Hz, C-10), 35.31 (t, $|J_{P,C}|$ = 0.5 Hz, C-9), 35.20 (t, $J_{P,C}$ = 2.8 Hz, C-2), 35.14 (t, $|J_{P,C}|$ = 0.5 Hz, C-10′), 35.01 (t, $|J_{P,C}|$ = 0.6 Hz, C-9′), 34.90 (t, $J_{P,C}$ = 3.1 Hz, C-2′). − ^{31}P NMR: δ = 35.1. − MS (70 eV); *m/z* (%): 492 (100) [M^+], 388 (30), 283 (22), 205 (23), 104 (21). − $C_{33}H_{33}O_2P$ (492.6): calcd. C 80.46, H 6.75; found C 80.54, H 6.75.

***meso*- and Chiral 1,2-Bis([2.2]paracyclophan-4-yl)-1,2-ethanedione (9m/9c). − a) By Acylation of 10:** In a Schlenk flask under N_2 **10** (387 mg, 1.86 mmol) and 2-oxo-2-([2.2]paracyclophan-4-yl)ethanoyl chloride (**14**;[11] 693 mg, 2.32 mmol) were dissolved in abs. CH_2Cl_2 (40 mL) and the solution was cooled to −10°C. Finely ground $AlCl_3$ (309 mg, 2.32 mmol) was added in small portions while the solution turned dark red. The reaction was completed without cooling overnight. Hydrolysis with ice/water (10 mL), extraction with CH_2Cl_2, drying of the organic phase with $MgSO_4$ and removal of the solvent in vacuo gave a mixture of **4m/4c**, **9m/9c**, and **10**. By dry column flash chromatography **10** was first eluted with petroleum ether followed by the fraction containing **4m/4c** and **9m/9c** with petroleum ether/CH_2Cl_2 (1:1). TLC (SiO_2; petroleum ether/CH_2Cl_2, 1:1) furnished **4m/4c** (535 mg, 65%) and **9m/9c** (195 mg, 22%).

b) From 13: To a solution of **13** in THF, prepared from **12** (500 mg, 1.74 mmol) as described above, oxalyl chloride (88.5 mg, 0.70 mmol, freshly distilled) was added at −78°C. The solution turned dark red immediately and was left overnight to reach room temp. Workup as under a) gave 101 mg (31%) of the 1:1 diastereomeric mixture **9m/9c**.

Diastereomers **9m/9c** could not be separated by recrystallization from 2-propanol. Attempts of sublimation (150°C, 0.7 Torr) led to decomposition of the product. Enrichment of one diastereomer was achieved by TLC (SiO_2; petroleum ether/CH_2Cl_2, 1:1): Removal of the upper 15% of the zone resulted in a diastereomeric ratio of ca. 7:3 (assignment unknown), m.p. 203°C (ref.[10] 198−215°C). − ^{1}H NMR ($CDCl_3$): δ = 6.93 (d, 0.7 H), 6.79−6.45 (m, 5.6 H), 6.33 (dd, 0.7 H), 4.28 (m_c, 0.3 H), 4.11 (ddd, 0.7 H), 3.35−2.80 (m, 7 H). − ^{13}C NMR ($CDCl_3$): major diastereomer: δ = 195.96 (s), 145.38 (s), 140.05 (s), 139.90 (s), 139.23 (s), 138.20 (d), 136.88 (d), 136.07 (d), 133.60 (s), 132.85 (d), 132.80 (d), 132.50 (d), 132.03 (d), 35.65 (t), 35.09 (t), 34.98 (t), 34.87 (t); minor diastereomer: δ = 196.15 (s), 143.73 (s), 139.18 (s), 138.15 (d), 137.08 (d), 136.92 (d), 132.77 (d), 132.77 (d), 132.66 (d), 35.75 (t), 35.15 (t), 34.95 (t), 34.74 (t); not all signals of the minor diastereomer were detected in the mixture.

Note added in proof (May 5, 1999):

Popova et al.[33] have recently described the *meso* diastereomers of Q_2GeMe_2 and Q_2SnMe_2 and the chiral diastereomer of Q_2GeMe_2 (Q = [2.2]paracyclophan-4-yl). The NMR data of these compounds were reported mostly without specific assignments.

Acknowledgments

We are grateful to the Fonds der Chemischen Industrie, Frankfurt/Main, for partial support of this work, to Ms. Petra Holba-Schulz for giving very good NMR service, to Ms. Claudia Marquard for installing the MM3 software on the Silicon Graphics computer and to Ms. Ina Dix for her help with the geometrical calculations to estimate the ring current effects. Professor Henning Hopf kindly granted access to the facilities of his group and of the Institute of Organic Chemistry.

[1] L. Pasteur, *Compt. Rend. Hebd. Séanc. Acad. Sci.* **1853**, *37*, 162−166.
[2] [2a] J.-A. Le Bel, *Bull. Soc. Chim. Paris* [2] **1874**, *22*, 337−347. − [2b] J.-H. van't Hoff, *Bull. Soc. Chim. Paris* [2] **1875**, *23*, 295−301.
[3] E. Browning, R. Adams, *J. Am. Chem. Soc.* **1930**, *52*, 4098−4107.
[4] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, John Wiley & Sons, Inc., New York **1994**, [4a] p. 1166, [4b] p. 66.
[5] H. J. Reich, D. J. Cram, *J. Am. Chem. Soc.* **1969**, *91*, 3534−3543.
[6] For possible ambiguities in the stereochemical description of

planar-chiral molecules, see: P. J. Pye, K. Rossen, *Tetrahedron: Asymmetry* **1998**, *9*, 539−541.
[7] M. W. Haenel, *Chem. Ber.* **1978**, *111*, 1789−1797.
[8] P. R. Ashton, S. E. Boyd, S. Menzer, D. Pasini, F. M. Raymo, N. Spencer, J. F. Stoddart, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1998**, *4*, 299−310.
[9] [9a] P. Kuś, *Pol. J. Chem.* **1994**, *68*, 1983−1988. − [9b] P. G. Jones, P. Kuś, *Pol. J. Chem.* **1998**, *72*, 1106−1111.
[10] R. G. H. Kirrstetter, U. Vagt, *Chem. Ber.* **1981**, *114*, 630−637.
[11] M. Psiorz, R. Schmid, *Chem.Ber.* **1987**, *120*, 1825−1828.
[12] P. G. Jones, L. Ernst, I. Dix, L. Wittkowski, unpublished results.
[13] N. L. Allinger, *MM3 − 1994 Force Field for UNIX and VAX*, University of Georgia, **1994**.
[14] M. Saunders, *J. Am. Chem. Soc.* **1987**, *109*, 3150−3152.
[15] The subscripts in $\mathbf{8m}_r$ and $\mathbf{8m}_s$ refer to the (*r*) and (*s*) configuration, respectively, of the pseudoasymmetric phosphorus atom.
[16] P. G. Jones, L. Ernst, I. Dix, L. Wittkowski, *Acta Crystallogr., Sect. C* **1997**, *53*, 612−615.
[17] L. Ernst, *Liebigs Ann.* **1995**, 13−17; Correction: *Liebigs Ann.* **1996**, 153.
[18] H. Günther, *NMR-Spektroskopie*, 3rd ed., Georg Thieme Verlag, Stuttgart, **1992**, p. 446.
[19] H.-O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, Wiley, Chichester, **1988**, p. 110.
[20] V. M. S. Gil, W. von Philipsborn, *Magn. Reson. Chem.* **1989**, *27*, 409−430.
[21] G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, D. J. Fenoglio, *J. Am. Chem. Soc.* **1967**, *89*, 5067−5068.
[22] C. W. Haigh, R. B. Mallion, *Prog. NMR Spectrosc.* **1979**, *13*, 303−344.
[23] *HYPERCHEM*, Version 3, Hypercube, Inc., **1993**.
[24] *XP − Interactive Molecular Graphics*, Version 5.03, Siemens, **1994**.
[25] [25a] C. E. Johnson, F. A. Bovey, *J. Chem. Phys.* **1958**, *29*, 1012−1014. − [25b] F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, 1st ed., Academic Press, London, **1969**, appendix C, pp. 264−274.
[26] C. W. Haigh, R. B. Mallion, *Org. Magn. Reson.* **1972**, *4*, 203−228.
[27] H. Gilman, F. K. Cartledge, *J. Organomet. Chem.* **1964**, *2*, 447−454.
[28] S. Braun, H.-O. Kalinowski, S. Berger, *150 and More Basic NMR Experiments. A Practical Course*, 2nd ed., Wiley-VCH, Weinheim, **1998**, [28a] p. 180, [28b] p. 111, [28c] p. 114, [28d] p. 353, [28e] p. 356, [28f] p. 375,]28g] p. 381.
[29] [29a] A. Bax, *J. Magn. Reson.* **1983**, *53*, 517−520. − [29b] V. Rutar, *J. Magn. Reson.* **1984**, *58*, 306−310.
[30] M. Clark, J. S. Thrasher, *J. Chem. Educ.* **1990**, *67*, 235−236.
[31] T. C. Wong, V. Rutar, J.-S. Wang, *J. Am. Chem. Soc.* **1984**, *106*, 7046−7051.
[32] J. Blackwell, W. J. Hickinbottom, *J. Chem. Soc.* **1961**, 1405−1407.
[33] E. Popova, D. Antonov, E. Sergeeva, E. Vorontsov, A. Stash, V. Rozenberg, H. Hopf, *Eur. J. Inorg. Chem.* **1998**, 1733−1737.

Received January 20, 1998
[O99022]