Cyclophanes, XXXVIII[1]

[2]Metacyclo[2]indenophanes: Synthesis, Anions and Iron Complexes☆

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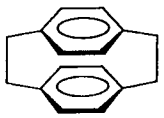
[2.2]Metacyclophane can be directly formylated according to the Rieche method to give 4-formyl[2.2]metacyclophane (**12**) in 44% yield. The synthesis of the [2]metacyclo[2]indenophane **8** from the aldehyde **12** by the pathway previously employed for the corresponding [2.2]paracyclophanes failed due to the harsh conditions of the cyclization step. An alternative synthesis of **8** and its isomer **9** involving the construction of the five-membered ring prior to that of the cyclophane unit succeeded. Compounds **8** and **9** were obtained as an 82:18 mixture, deprotonation of which afforded the anion **10**, which shows long-term stability. The ^{1}H-NMR spectrum of this anion does not exhibit a through-space charge transfer due to its structure. The ^{1}H-NMR parameters and molecular mechanics calculations are discussed. Both faces of **10** react in the presence of $FeCl_2 \cdot 2$ THF and a twentyfold excess of LiCp to give a 70:30 mixture of the ferrocene derivatives **7** and **35**.

A common feature of the "stacked" molecules [2.2]paracyclophane **1** and ferrocene **2** is that there is electronic communication between the two remote aromatic decks[2]. For the last few years, we have been investigating systems in which these two structural units have been united, e.g. **3**, with the ultimate goal of preparing molecules which exhibit very-long-range communication[3]. The first synthesis of **3**[4] was accomplished via the [2]paracyclo[2]indenophane **4** and its anion **5** which are interesting molecules in their own right. We recently showed[5] that, by comparison of their NMR data with that of related compounds, it was possible to separate-charge transfer from anisotropic effects.



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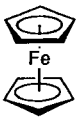

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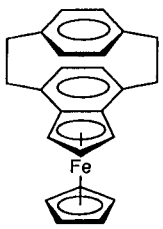

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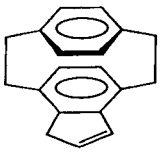

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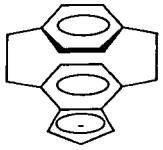

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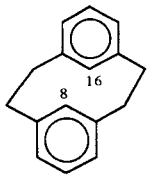
Like **1**, the "stepped" compound *anti*-[2.2]metacyclophane **6** is rigid [$\Delta G^{\neq}$(ring inversion) $\approx$ 31 kcal/mol][6] and has rings with overlapping π systems. Spectroscopic evidence[7] suggests that there are significant interactions between the rings although some authors have refuted this[8]. By fusing the structural elements of **2** and **6** it should be possible to gauge the degree to which the remote aromatic systems communicate. We now describe our initial efforts towards this goal and present the preparation of the first member of this series, the metallocenophane **7** and the precursor molecules **8**–**10**.



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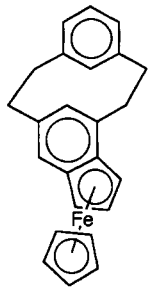

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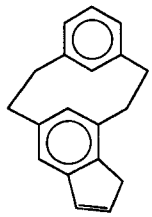

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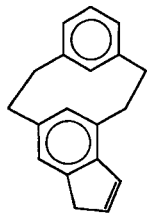

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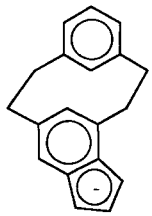

10

It has been reported[9] that treatment of **6** with Lewis acids gives rise to ring closure at C-8 and -16. This would apparently rule out the synthetic methodology used for the preparation of **4**, in which two of the steps are Lewis acid catalyzed electrophilic aromatic substitutions. However, the

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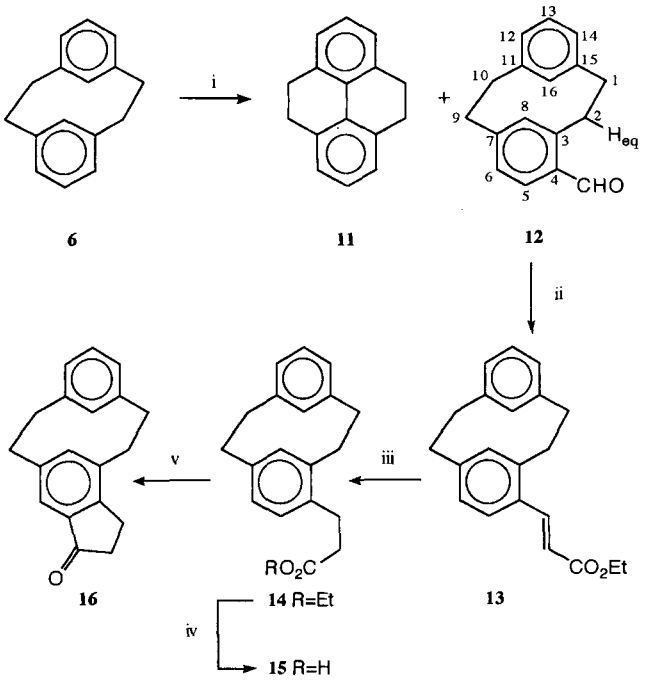
Rieche formylation[10], which takes place under relatively mild conditions, has not yet been described for **6**, and the reaction was therefore attempted (Scheme 1). Although 48% of the ring-closed product 4,5,9,10-tetrahydropyrene (**11**) was formed, a 44% yield of the formylated metacyclophane **12** was indeed isolated. This constitutes the first example of a direct electrophilic aromatic substitution of **6**. In the 400-MHz ^{1}H-NMR spectrum of **12** the signal of the equatorial proton at C-2 (2-H_{eq}), which is copolanar to the formyl group, appears at $\delta = 4.29$, deshielded by $\Delta\delta = 1.24$ from the signal of the corresponding proton in **6**.

Scheme 1



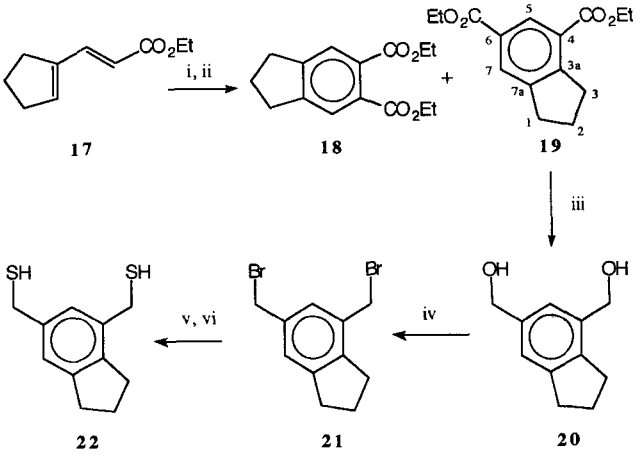
6 **11** **12** **13** **14** R=Et **15** R=H **16**

i) Cl_2CHOCH_3, $TiCl_4$. – ii) $(EtO)_2POCH_2CO_2Et$, NaH. – iii) H_2, 10% Pd/C. – iv) NaOH. – v) PPA (polyphosphoric acid), 80°C.

The Wadsworth-Emmons reaction of **12** to give **13** proceeded in 89% yield, and the subsequent hydrogenation and saponification steps afforded the ester **14** and the acid **15** in 96 and 94% yields, respectively. Unfortunately the conditions of the PPA-promoted cyclization of **15** proved to be too rigorous for the cyclophane unit to withstand, none of the desired product being obtained. Thus, an alternative synthetic pathway had to be devised in which the five-membered ring is constructed before the cyclophane.

We elected to work with an indane system rather than an indanone or an indene because of its comparative chemical inertness. A retrosynthetic analysis of the problem led back to the Diels-Alder reaction between the diene **17**[11] and ethyl propiolate (Scheme 2). In the synthetic direction this gave, after aromatization of the crude reaction mixture with DDQ, two products, **18** and **19**. Depending on the conditions used (Table 1), the total yield ranged between 54 and 67%, whereas the ratio of **18**:**19** was between 2.5:1 and 5.7:1. The reaction did not proceed in refluxing benzene. At 0°C in CH_2Cl_2 with 0.1 equivalents of $TiCl_4$ the ethyl propiolate polymerized.

Scheme 2



17 **18** **19** **20** **21** **22**

i) $HC{\equiv}CCO_2Et$, ΔT. – ii) DDQ. – iii) $LiAlH_4$. – iv) PBr_3. – v) $(H_2N)_2CS$. – vi) NaOH.

Table 1. The Diels-Alder reaction of **17** and ethyl propiolate

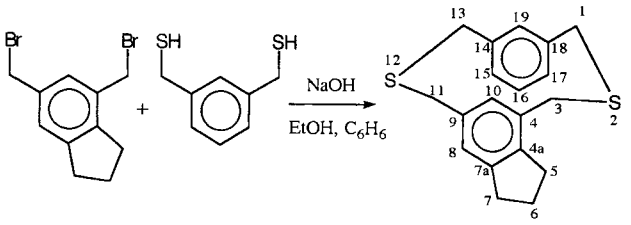
17 [mmol]	$HC{\equiv}C$-CO_2Et [mmol, equiv.]	Solvent Amount [ml]	Time [h]	Yields (%) **18**	**19**	Ratio
15.0	30.2, 2.0	xylenes, 4	65	48	19	2.5:1
43.3	86.6, 2.0	xylenes, 10	52	43	16	2.7:1
98.1	147, 1.5	xylenes, 20	40	41	13	3.2:1
137	186, 1.4	none[a]	30	51	9	5.7:1
33.6	168, 5.0	toluene, 50	48	47	19	2.5:1

[a] Oil bath heated at 135°C.

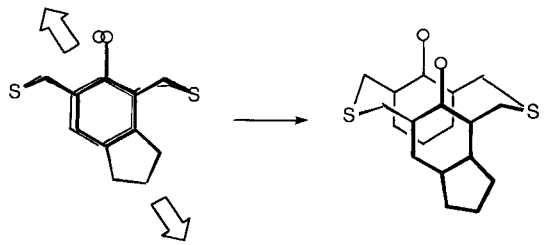
Even though the desired precursor **19** was the minor product, its synthesis is short, it is readily separable from **18** by column chromatography, and the reaction could be carried out on a large enough scale to provide synthetically useful amounts of material. The major product provided access to the [2]orthocyclo[2]indenophane series, on which we shall be reporting in the near future.

Reduction of the diester **19** with $LiAlH_4$ afforded 90% of the diol **20**, which was brominated with PBr_3 in dichloromethane in 86% yield. The dibromide **21** was then converted into the dithiol **22** in 99% yield. The high-dilution coupling of **21** and the dithiol **23** yielded 85% of the 2,12-dithia[3]metacyclo[3]indanophane **24**. The aromatic region of the ^{1}H-NMR spectrum of this compound consists of two broad one-proton singlets at $\delta = 6.50$ (10-H) and 6.78 (8-H) as well as a four-proton multiplet at $\delta = 6.88-6.98$ (15-, 16-, 17-, 19-H). While the positions of the internal protons (10-, 19-H) are consistent with the *syn* conformation[12], the signal of 10-H appears at somewhat higher field than expected (even considering the effect of the annulated five-membered ring) and that of 19-H at lower field. This can be explained in terms of steric repulsions between the external protons on the non-annulated ring (15-, 16-, 17-H) and inward point-

ing protons of the five-membered one. In order to relieve these repulsions the molecule can distort, whereby 10-H moves further into the shielding zone of the opposite ring, and 19-H moves away. In the aliphatic region of the spectrum, the proton signals of the five-membered ring appear as two triplets and a quintuplet. The two faces of this ring are therefore equivalent on the NMR time scale, and this can only be explained by a rapid *syn/syn'* flip. This result supports the findings of Mitchell[13], who has postulated that the same conformational process takes place in the parent compound 2,11-dithia[3.3]metacyclophane.

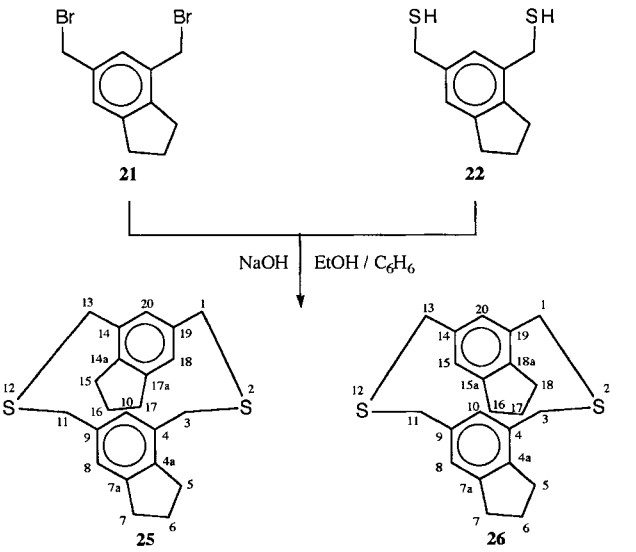


21 **23** **24**



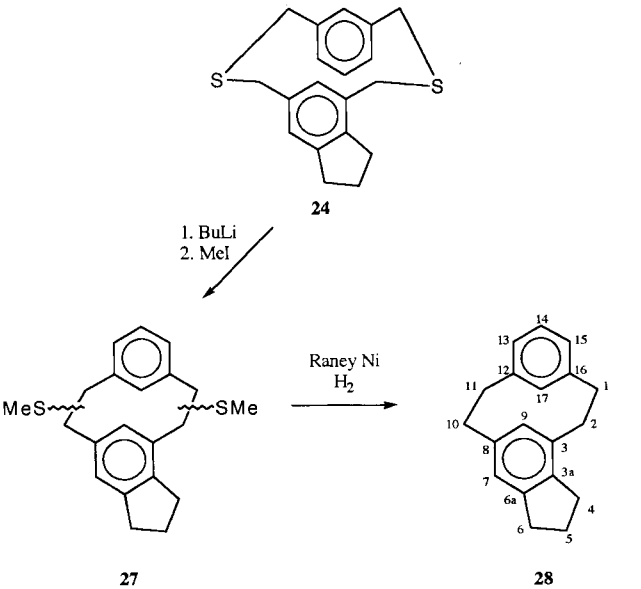
syn-**24** *syn'*-**24**

As expected, the coupling of **21** and **22** gave a mixture of **25** and **26** (total yield 82%). The product ratio, as determined by the integral ratios in the ^{1}H-NMR spectrum, was 53:47, but it was not immediately obvious which compound predominated. No TLC conditions could be found which gave a separation, and attempted fractional crystallization afforded only a very slight enrichment of the major product. The signals of the internal protons of **25**/**26** (10-, 20-H) appear at lower field (δ = 6.71 and 6.67) than the signal of 10-H in **24**. This observation is consistent with invoking distortions in **24** to explain the unusual chemical shifts of the internal protons. With symmetrically substituted rings, **25** and **26** cannot undergo the type of distortion postulated for **24**, and their internal protons do not receive additional shielding from the opposite deck. As in the case of **24**, the signals of the five-membered ring protons show up as triplets and quintuplets, again implying a rapid *syn/syn'* flip at room temperature.



21 **22** **25** **26**

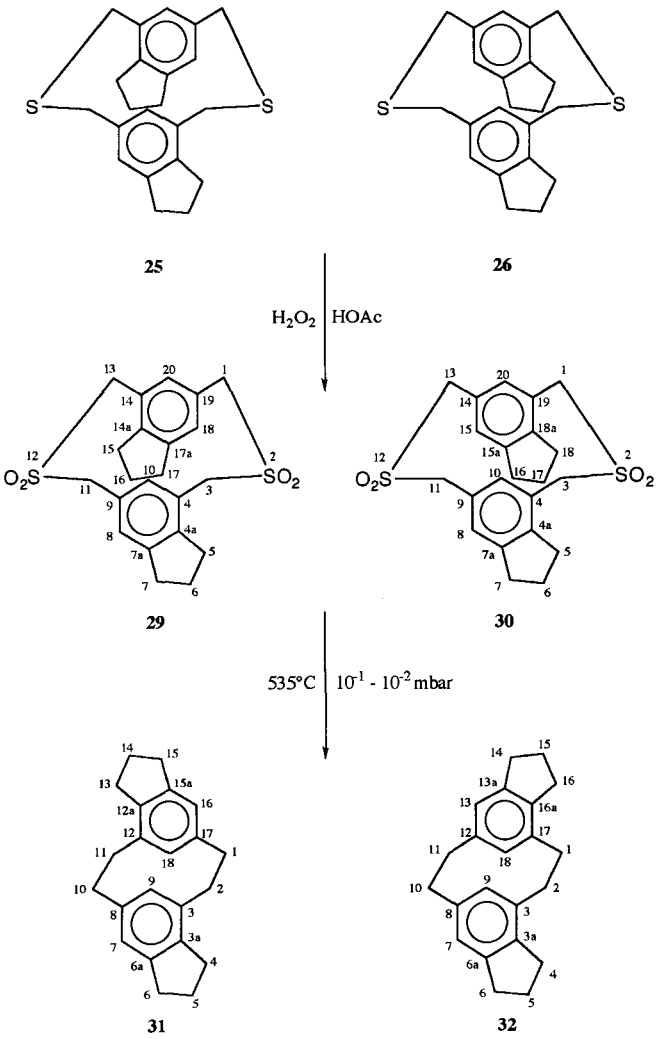
The [2]metacyclo[2]indanphane **28** was prepared by the Wittig rearrangement of **24** and treatment of the resultant mixture of thioethers with Raney nickel. The overall yield was 42%. Since *anti*-[2.2]metacyclophanes are rigid at room temperature, the two faces of the five-membered ring are now inequivalent, and a considerably more complex ^{1}H-NMR spectrum is observed. The spectrum is further complicated by overlap of the signals due to the equatorial bridge protons with those of 5-H and 7-H and of the signals due to the axial bridge protons with those of 6-H.



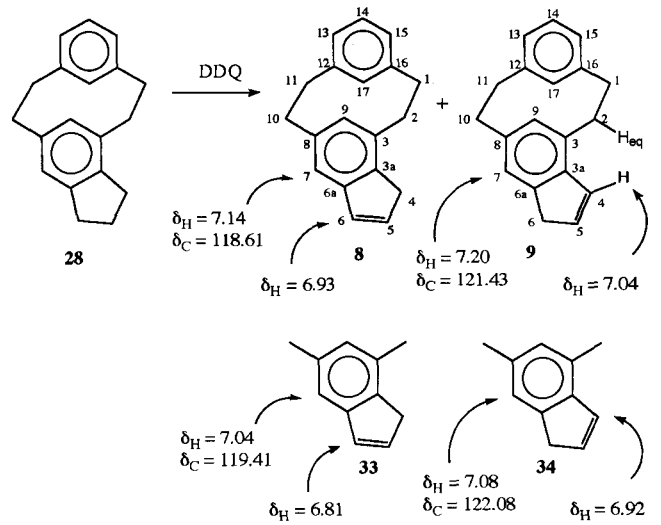
24 **27** **28**

The doubly annulated phanes **25** and **26** were oxidized with H_2O_2/HOAc to give the disulfones **29** and **30** in 76% yield, and pyrolysis at 535°C/10^{-1}–10^{-2} mbar afforded 76% of the ring-contracted cyclophanes **31** and **32** (Scheme 3). As determined by integral ratios in the ^{1}H-NMR spectrum, the product ratios of **29**:**30** and **31**:**32** were 52:48. That the ratio did not change during the sulfone pyrolysis step is consistent with the intramolecular, stepwise mechanism described by Haenel[14] for this reaction.

Scheme 3

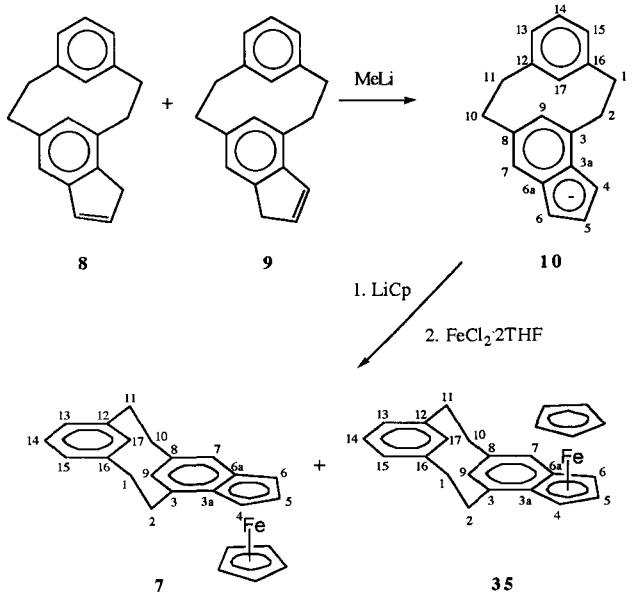


Dehydrogenation of **28** with 1.2 equiv. of DDQ gave an inseparable mixture of the [2]metacyclo[2]indenophanes **8** and **9**. The integral ratio of the products was 82:18, but it was not immediately clear which was the major product. By comparing the NMR data of **8** and **9** with those of the two "half phanes" **33** and **34**[15], it was possible to assign the major product as **8**. The preference for this compound can be explained by destabilizing steric interactions between the coplanar protons 2-H_{eq} and 4-H in **9**.



The reaction of **8** and **9** with 1.0 equiv. of MeLi followed by ca. 20 equiv. of LiCp and then 11 equiv. of $FeCl_2 \cdot 2$ THF proceeded in 70% yield (Scheme 4). Again the ^{1}H- and ^{13}C-NMR spectra revealed the presence of two products, **7** and **35**, in a 70:30 ratio. Clearly, the non-annulated ring does not present a sufficient steric barrier to completely prevent complexation of the *endo* face. On the basis of steric arguments, the major product was tentatively assigned to be **7**. All attempts to separate **7** and **35** failed.

Scheme 4



The dehydrogenation of the mixture of **31** and **32** with DDQ was not carried out in light of the prospect of a complex mixture of isomeric [2.2]indenophanes, which in turn would give a complex mixture of iron complexes. Future work on this area will concentrate on a more directed route to the [2.2]indenophanes.

We have previously shown that a through-space interaction in the anions of [2]paracyclo[2]indenophanes does exist[5]. However, the spatial structure of the corresponding metacyclophanes does not permit such an interaction. The anion **10** was formed by the reaction of a mixture of **8** and **9** with MeLi in [D_8]tetrahydrofuran. Typical signals appear at δ = 3.92 and 4.25, corresponding to protons 17-H and 9-H, respectively. These high-field shifts originate from the shielding effect of the aromatic ring facing these protons, i.e. from a through-space aniosotropy effect. As for the through-space charge transfer it can be seen that, contrary to what we have shown in the case of the [2]paracyclo[2]indenophanes, the proton signals of the benzene ring appear in the aromatic region. In anion **10**, the signals of benzene-layer protons 13-H and 14-H appear at δ = 7.04–6.97 and those of 15-H at δ = 7.13. The corresponding proton signals of the starting material are found at δ = 7.20–7.00 (13-, 14-

H) and 7.30 (15-H). The proton signals of the charged system are observed in the same region as those of the neutral one, and we therefore deduce that the benzene layer does not bear any significant charge. A comparison of the spectrum of **10** with that of the 4,6-dimethylindenyl anion[15] shows similarity to that of the indenyl layer of **10**. For example, proton signals of the five-membered ring of **10** appear at δ = 6.03 (4-H), 6.14 (6-H) and 6.59 (5-H) whereas those of the indenyl anion are observed at δ = 5.96–5.89 (4-, 6-H) and 6.49 (5-H)[15]. The only meaningful effect is the high-field shift of 17-H due to the through-space magnetic effect, which serves to emphasize its sensitivity to the change in the magnetic environment brought about by charging. A molecular mechanics calculation of the neutral and charged cyclophane reveals a structure which resembles in its steric properties the crystal structure of the parent metacyclophane[16]. It is clear from these results that the end-to-end overlap of the remote π systems in *anti*-[2.2]metacyclophanes is insufficient to cause wholesale mixing of the two, i.e. they will tend to behave independently rather than as a single unit. Both the ^{1}H-NMR spectra of **10** and the molecular mechanics calculations lend strength to the observation that the non-annulated ring of **10** does not present a sufficient steric barrier to prevent complexation to the *endo* face in the formation of **35**. The lack of a meaningful through-space electronic or anisotropic effect of the modified molecule due to charging emphasizes that the benzene layer is sterically remote from the five-membered ring in **10**.

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Experimental

General: Melting points (uncorrected): Büchi 510 Melting Point apparatus. – Dry CH_2Cl_2 was distilled from CaH_2, dry THF from benzophenone ketyl. – Chromatography: Kieselgel 60, 70–230 mesh. – IR (KBr): Perkin-Elmer 1410. – UV (C_2H_5OH): Beckman UV-5230. – ^{1}H NMR ($CDCl_3$): Bruker WM-400 (400.1 MHz). – ^{13}C NMR ($CDCl_3$): Bruker WM-400 (100.6) MHz. – ^{1}H-NMR studies of the anion **10**: Bruker WP-200 equipped with an ASPECT 2000 computer and a ^{2}H lock. – MS (EI, 70 eV): Varian MAT CH7 or Varian MAT 8222. – Elemental analyses: Analytical Laboratory of the Institute for Pharmaceutical Chemistry of the Technical University of Braunschweig.

anti-[2.2]Metacyclophane-4-carbaldehyde (**12**): To a solution of *anti*-**6** (3.10 g, 14.9 mmol) in dry CH_2Cl_2 (400 ml) under N_2 was added at 0°C $TiCl_4$ (4.0 ml, 36 mmol). After the orange solution had been stirred for 5 min, Cl_2CHOCH_3 (4.0 ml, 35 mmol) was added, and the resulting black mixture was stirred for 25 min. Ice-cold water (200 ml) was added and, after stirring for 30 min, the layers were separated. The organic layer was stirred with an $NaHCO_3$ solution for 45 min, and the layers were separated. The aqueous layer was washed with a portion of CH_2Cl_2, and the combined organic layers were washed with an NaCl solution, dried, and concentrated. Chromatography (CH_2Cl_2) of the residue afforded first **11** (1.48 g, 48%) and then **12** (1.55 g, 44%) as a colourless solid, m.p. (subl. 80°C/10^{-3} mbar) 102–103°C. – IR: $\tilde{\nu}$ = 3050 cm^{-1}, 3010, 2945, 2920, 2870, 2850, 2765, 1695, 1682, 1592, 1580, 1558, 1435, 1425, 1395, 1198, 1180, 860, 815, 788, 762, 745, 715, 600. – UV: λ_{max} (lg ε) = 208 nm (4.450), 216 (4.326, sh), 272 (4.021), 302 (3.431, sh). – ^{1}H NMR: δ = 1.85 (td, *J* = 12.1, 3.3 Hz, 1H, 2-H_{ax}), 2.00–2.14 (m, 3H, 1-H_{ax}, 9-H_{ax}, 10-H_{ax}), 3.09–3.21 (m, 3H, 1-H_{eq}, 9-H_{eq}, 10-H_{eq}), 4.22 (s, 1H, 16-H), 4.29 (dt, *J* = 11.9, 3.5 Hz, 1H, 2-H_{eq}), 4.31 (s, 1H, 8-H), 7.05 (d, *J* = 7.4 Hz, 1H, 12-H/14-H), 7.08 (d, *J* = 7.6 Hz, 1H, 12-H/14-H), 7.20 (dd, *J* = 7.7, 1.4 Hz, 1H, 6-H), 7.30 (t, *J* = 8.0 Hz, 1H, 13-H), 7.79 (d, *J* = 7.7 Hz, 1H, 5-H), 10.25 (s, 1H, CHO). – ^{13}C NMR: δ = 36.71 (t, C-2); 40.41, 40.62, 41.08 (t, C-1, C-9, C-10); 125.44, 125.78, 126.03 (d, C-6, C-12, C-14); 129.35 (d, C-13); 131.63 (s, C-4); 133.08 (d, C-5); 135.69 (d, C-16); 137.97 (s, C-11, C-15); 138.73 (d, C-8); 141.09 (s, C-3); 145.54 (s, C-7); 191.92 (d, CHO). – MS: *m/z* (%) = 237 (24), 236 (96) [M^+], 208 (38), 207 (100), 205 (38), 203 (17), 179 (23), 178 (15), 165 (17), 131 (59), 103 (15).

$C_{17}H_{16}O$ (236.31) Calcd. C 86.36 H 6.82
Found C 86.20 H 6.80

Ethyl (3E)-3-(anti-[2.2]metacyclophan-4-yl)-2-propenoate (**13**): The reaction was carried out under N_2. 60% NaH (391 mg, 9.78 mmol) was washed with THF (2 × 25 ml) and slurried with THF (50 ml). To this was added over 5 min ethyl 2-(diethylphosphono)-acetate (2.27 g, 10.1 mmol). After H_2 evolution had ceased, a solution of **12** (1.54 g, 6.52 mmol) in THF (50 ml) was added dropwise over 30 min, and the resulting solution was heated at reflux for 2 h. After cooling, an NH_4Cl solution (100 ml) and CH_2Cl_2 (200 ml) were added. The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (50 ml). The combined organic layers were washed with a saturated NaCl solution (2 × 100 ml), dried, and concentrated. Chromatography (CH_2Cl_2) of the residue yielded **13** (1.78 g, 91%) as a colourless solid, m.p. (subl. 60°C/10^{-3} mbar) 93–94°C. – IR: $\tilde{\nu}$ = 3020 cm^{-1}, 2980, 2960, 2945, 2920, 2870, 2850, 1705, 1630, 1595, 1445, 1365, 1320, 1312, 1298, 1282, 1205, 1185, 1175, 1170, 1168, 1158, 1035, 980, 828, 792, 718. – UV: λ_{max} (lg ε) = 207 nm (4.436), 243 (4.121), 300 (4.312). – ^{1}H NMR: δ = 1.33 (t, *J* = 7.1 Hz, 3H, CH_3), 1.92 (td, *J* = 12.4, 3.1 Hz, 1H, 2-H_{ax}), 2.01–2.15 (m, 3H, 1-H_{ax}, 9-H_{ax}, 10-H_{ax}), 3.09–3.16 (m, 3H, 1-H_{eq}, 9-H_{eq}, 10-H_{eq}), 3.62 (dt, *J* = 12.5, 3.3 Hz, 1H, 2-H_{eq}), 4.24–4.30 (m, 4H, 8-H, 16-H, CH_2CH_3), 6.42 (d, *J* = 15.8 Hz, 1H, CH=$CHCO_2$), 7.05–7.09 (m, 2H, 12-H, 14-H), 7.30 (t, *J* = 7.4 Hz, 1H, 13-H), 7.61 (d, *J* = 7.9 Hz, 1H, 5-H), 8.09 (d, *J* = 15.8 Hz, 1H, CH=$CHCO_2$). – ^{13}C NMR: δ = 14.38 (q, CH_3); 37.55 (t, C-2); 39.83, 40.76, 40.86 (t, C-1, C-9, C-10); 60.43 (t, CH_3CH_2); 118.63 (d, CH=$CHCO_2$); 125.43, 125.64 (d, C-12, C-14); 1265.21, 126.75 (d, C-5, C-6); 129.17 (d, C-13); 130.17 (d, C-4); 136.06, 137.77 (d, C-8, C-16); 138.42, 138.44, 138.60 (s, C-3, C-11, C-15); 141.36 (s, C-7); 141.60 (d, CH=$CHCO_2$); 167.29 8s, CH=$CHCO_2$). – MS: *m/z* (%) = 307 (24), 306 (100) [M^+], 278 (29), 277 (33), 260 (52), 241 (21), 232 (23), 217 (21), 203 (38), 202 (31), 201 (62), 129 (58), 128 (38), 105 (41).

$C_{21}H_{22}O_2$ (306.41) Calcd. C 82.32 H 7.24
Found C 82.30 H 7.33

Ethyl 3-(anti-[2.2]Metacyclophan-4-yl)propanoate (**14**): A solution of **13** (496 mg, 1.62 mmol) in ethyl acetate (150 ml) was shaken under a slight positive pressure of H_2 for 3 h (hydrogenation apparatus). The solution was filtered through a pad of Na_2SO_4, and the solvent was removed under reduced pressure. Chromatography of the residue (SiO_2/CH_2Cl_2) gave **14** as a viscous, colourless oil, (480 mg, 96%). A portion of the product was further purified by kugelrohr distillation (150°C/10^{-3} mbar) for analysis. – IR (film): $\tilde{\nu}$ = 3030 cm^{-1}, 3010, 2980, 2940, 2855, 1738, 1630, 1582, 1462, 1440, 1430, 1410, 1372, 1290, 1255, 1180, 1160, 1040, 820, 790, 720.

– UV: λ_{max} (lg ε) = 214 nm (4.450), 282 (3.362). – ^{1}H NMR: δ = 1.25 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.89 (td, J = 12.6, 3.3 Hz, 1H, 2-H_{ax}), 2.00–2.10 (m, 3H, 1-H_{ax}, 9-H_{ax}, 10-H_{ax}), 2.63–2.68 (m, 2H, $CH_2CH_2CO_2$), 2.90–2.98 (m, 2H, $CH_2CH_2CO_2$), 3.03–3.10 (m, 3H, 1-H_{eq}, 9-H_{eq}, 10-H_{eq}), 3.39 (dt, J = 12.7, 3.4 Hz, 1H, 2-H_{eq}), 4.15 (q, J = 7.1 Hz, 2H, CH_2CH_3), 4.22 (d, J = 1.6 Hz, 1H, 8-H), 4.29 (s, 1H, 16-H), 6.99 (dd, J = 7.6, 1.7 Hz, 1H, 6-H), 7.05–7.08 (m, 2H, 12-H, 14-H), 7.14 (d, J = 7.6 Hz, 1H, 5-H), 7.28 (t, J = 7.4 Hz, 1H, 13-H). – ^{13}C NMR: δ = 14.20 (q, CH_2CH_3); 27.82 (t, $CH_2CH_2CO_2$); 36.08 (t, $CH_2CH_2CO_2$); 37.33 (t, C-2); 39.63, 40.55, 40.93 (t, C-1, C-9, C-10); 60.45 (t, CH_2CH_3); 125.36, 125.54, 125.69 (d, C-6, C-12, C-14); 128.92, 129.10 (d, C-5, C-13); 135.38, 136.08, 137.05 (s, C-3, C-4, C-7); 136.49 (d, C-16); 137.30 (d, C-8); 138.81, 138.86 (s, C-11, C-15); 173.12 (s, $CH_2CH_2CO_2$). – MS: m/z (%) = 308 (38) [M^+], 234 (45), 220 (24), 219 (36), 207 (71), 206 (34), 205 (100), 203 (27), 179 (18).

$C_{21}H_{24}O_2$ (308.42) Calcd. C 81.78 H 7.84
Found C 81.71 H 7.62

3-(anti-[2.2]Metacyclophan-4-yl)propionic Acid (**15**): A solution of **14** (1.52 g, 4.93 mmol) in 100 ml of a 10:1 mixture of a 2 M NaOH solution and ethanol was boiled under reflux for 16 h, then filtered hot, cooled to 0°C, and carefully neutralized with concentrated HCl. The precipitate was collected by suction filtration and slurried with toluene (ca. 50 ml). The solvent was then removed at reduced pressure, and the residue was dried for ca. 16 h under high vacuum (1.30 g, 94%). A portion of the product was sublimed (80°C/10^{-3} mbar; colourless, fluffy powder) for analysis, m.p. 140–142°C. – IR: $\tilde{\nu}$ = 3280–2350 cm^{-1} (br.), 1710, 1620, 1498, 1430, 1405, 1315, 1310, 1278, 1262, 1229, 1175, 1075, 955, 875, 835, 825, 790, 780, 728, 712, 670. – UV: λ_{max} (lg ε) = 215 nm (4.526), 275 (3.061). – ^{1}H NMR: δ = 1.90 (td, J = 12.5, 3.1 Hz, 1H, 2-H_{ax}), 2.02–2.12 (m, 3H, 1-H_{ax}, 9-H_{ax}, 10-H_{ax}), 2.71–2.75 (m, 2H, $CH_2CH_2CO_2$), 2.88–3.14 (m, 5H, 1-H_{eq}, 9-H_{eq}, 10-H_{eq}, $CH_2CH_2CO_2$), 3.38 (dt, J = 12.6, 3.2 Hz, 1H, 2-H_{eq}), 4.23 (s, 1H, 8-H), 4.30 (s, 1H, 16-H), 7.01 (d, J = 7.6 Hz, 1H, 6-H), 7.05–7.09 (m, 2H, 12-H, 14-H), 7.16 (d, J = 7.6 Hz, 1H, 5-H), 7.29 (t, J = 7.4 Hz, 1H, 13-H). – ^{13}C NMR: δ = 27.46 (t, $CH_2CH_2CO_2$); 35.74 (t, $CH_2CH_2CO_2$); 37.33 (t, C-2); 39.60, 40.56, 40.91 (t, C-1, C-9, C-10); 125.40, 125.56, 125.80 (d, C-6, C-12, C-14); 134.95, 136.07, 136.23 (s, C-3, C-4, C-7); 136.48, 137.37 (d, C-8, C-16); 138.81 (s, C-11, C-15); 179.22 (s, $CH_2CH_2CO_2$). – MS: m/z (%) = 280 (34) [M^+], 252 (22), 219 (19), 208 (26), 207 (100), 205 (44), 179 (25), 165 (26), 105 (21).

$C_{19}H_{20}O_2$ (280.37) Calcd. C 81.40 H 7.19
Found C 81.41 H 7.37

Diethyl 4,6- and 5,6-Indanyldicarboxylate (**19** and **18**): A stirred solution of **17** and ethyl propynoate was heated (for conditions see Table 1) under N_2. After cooling, 0.8 equiv. of DDQ was added, and stirring was continued for ca. 15 min. The mixture was suction-filtered, the filtrate was concentrated, and the residue chromatographed (SiO_2/CH_2Cl_2).

Eluted first (R_f = 0.45) was **19**, which was further purified by sublimation (35°C/10^{-1} mbar, colourless microcrystalline solid), m.p. 43.5–45°C. – IR: $\tilde{\nu}$ = 2980 cm^{-1}, 2960, 2900, 2845, 1722, 1610, 1582, 1462, 1370, 1340, 1315, 1300, 1275, 1248, 1230, 1195, 1172, 1145, 1092, 1030, 930, 765. – UV: λ_{max} (lg ε) = 220 nm (4.553), 234 (4.097), 293 (3.410), 301 (3.431). – ^{1}H NMR: δ = 1.41 (t, J = 7.1 Hz, 3H, CH_3); 2.12 (quint, J = 7.6 Hz, 2H, 2-H); 2.97 (t, J = 7.6 Hz, 2H, 1-H); 3.32 (t, J = 7.6 Hz, 2H, 3-H); 4.38, 4.39 (q, J = 7.1 Hz, 2H, CH_2CH_3); 8.03 (s, 1H, 7-H); 8.56 (s, 1H, 5-H). – ^{13}C NMR: δ = 14.38, 14.39 (q, CH_3); 24.99 (t, C-2); 32.33 (t, C-1); 34.15 (t, C-3); 34.15 (t, C-3); 60.93, 61.07 (t, CH_2CH_3); 126.90 (s, C-4); 128.94 (d, C-5); 129.84 (s, C-6); 129.71 (d, C-7); 146.42 (s, C-7a); 151.91 (s, C-3a); 166.30, 166.49 (s, $CO_2CH_2CH_3$). – MS: m/z (%) = 263 (18), 262 (93) [M^+], 234 (25), 233 (100), 217 (36), 216 (21), 189 (22), 161 (22), 117 (35).

$C_{15}H_{18}O_4$ (262.31) Calcd. C 68.68 H 6.92
Found C 68.84 H 7.04

Eluted second (R_f = 0.37) was **18**, which was further purified by kugelrohr distillation (55°C/10^{-2} mbar). – IR (film): $\tilde{\nu}$ = 2980 cm^{-1}, 2955, 2940, 2900, 2870, 2840, 1725, 1610, 1568, 1475, 1462, 1442, 1368, 1330, 1285, 1260, 1202, 1172, 1112, 1035, 1022, 895, 855, 790. – UV: λ_{max} (lg ε) = 221 nm (4.487), 224 (3.933), 267 (3.362, sh). – ^{1}H NMR: δ = 1.36 (t, J = 7.2 Hz, 6H, CH_3), 2.12 (quint, J = 7.5 Hz, 2H, 2-H), 2.94 (t, J = 7.5 Hz, 4H, 1-H, 3-H), 4.34 (q, J = 7.2 Hz, 4H, CH_2CH_3), 7.56 (s, 2H, 4-H, 7-H). – ^{13}C NMR: δ = 14.14 (q, CH_3); 25.31 (t, C-2); 32.71 (t, C-1, C-3); 61.39 (t, CH_2CH_3); 124.77 (d, C-4, C-7); 130.61 (s, C-5, C-6); 147.71 (s, C-7a, C-3a); 168.13 (s, $CO_2CH_2CH_3$). – MS: m/z (%) = 262 (22) [M^+], 217 (41), 190 (18), 189 (100), 115 (11).

$C_{15}H_{18}O_4$ (262.31) Calcd. C 68.68 H 6.92
Found C 68.60 H 6.96

4,6-Indandiyldimethanol (**20**): A solution of **19** (1.70 g, 6.48 mmol) in dry THF (50 ml) was added at 0°C over 30 min to a stirred slurry of $LiAlH_4$ (737 mg, 19.4 mmol) in THF (50 ml). The mixture was brought to reflux for 3 h, cooled, and water was carefully added until no more H_2 was evolved. A 6 M HCl solution was then added until the solids had completely dissolved, and the mixture was diluted with CH_2Cl_2 (200 ml). The layers were separated, and the organic layer was washed with a $NaHCO_3$ solution (2 × 100 ml), water (2 × 100 ml), dried and concentrated. The residue was crystallized from hexane as colourless leaves (1.04 g, 90%); m.p. 69–70°C. – IR: $\tilde{\nu}$ = 3335 cm^{-1} (br.), 3225 (br.), 3000, 2960, 2895, 2845, 1592, 1472, 1462, 1440, 1335, 1200, 1122, 1080, 1018, 1000, 990, 958, 940, 888, 872, 720, 632. – UV: λ_{max} (lg ε) = 206 nm (4.149), 216 (3.977, sh), 271 (3.045), 279 (3.045). – ^{1}H NMR: δ = 2.07 (quint, J = 7.5 Hz, 2H, 2-H), 2.60 (br. s, 2H, OH), 2.82 (t, J = 7.5 Hz, 2H, 3-H), 2.88 (t, J = 7.5 Hz, 2H, 1-H), 4.55, 4.57 (s, 2H, CH_2OH), 7.11, 7.13 (s, 1H, 5-H, 7-H). – ^{13}C NMR: δ = 25.17 (t, C-2); 30.39 (t, C-3); 32.66 (t, C-1); 63.17 (t, 4-CH_2); 65.28 (t, 6-CH_2); 122.46 (d, C-7); 123.61 (d, C-5); 136.52 (s, C-4); 139.41 (s, C-6); 141.42 (s, C-3a); 145.03 (s, C-7a). – MS: m/z (%) = 178 (21) [M^+], 161 (14), 160 (100), 131 (30), 129 (54), 128 (27), 117 (33), 115 (38), 91 (66).

$C_{11}H_{14}O_2$ (178.23) Calcd. C 74.13 H 7.92
Found C 73.96 H 7.71

4,6-Bis(bromomethyl)indan (**21**): To a solution of **20** (1.82 g, 10.2 mmol) in dry CH_2Cl_2 (100 ml) was added dropwise over 30 min a solution of PBr_3 (2.76 g, 10.2 mmol), and the mixture was stirred for 2 h. The solution was then washed with water until neutral, dried and concentrated. The residue was chromatographed (SiO_2/CH_2Cl_2) to yield the product (3.96 g, 86%); subl. 50°C/10^{-2} mbar. – IR: $\tilde{\nu}$ = 2965 cm^{-1}, 2935, 2900, 2840, 1582, 1472, 1455, 1442, 1312, 1285, 1265, 1210, 1138, 1108, 1030, 965, 890, 880, 872, 715. – UV: λ_{max} (lg ε) = 213 nm (4.403), 233 (4.114, sh), 281 (3.204). – ^{1}H NMR: δ = 2.13 (quint, J = 7.6 Hz, 2H, 2-H); 2.92, 2.94 (t, J = 7.7 Hz, 2H, 1-H, 3-H); 4.45, 4.47 (s, 2H, CH_2Br); 7.17, 7.22 (s, 1H, 5-H, 7-H). – ^{13}C NMR: δ = 24.84 (t, C-2); 30.60 (t, 4-CH_2); 31.57 (t, C-3); 32.76 (t, 6-CH_2); 33.59 (t, C-1); 125.59 (d, C-7); 127.74 (t, C-5); 133.55 (s, C-4); 136.50 (s, C-6); 144.28 (s, C-3a); 146.10 (s, C-7a). – MS: m/z (%) = 306 (6), 304 (12), 302 (6) [M^+], 225 (100), 223 (95), 179 (41), 144 (39), 143 (56), 129 (33), 128 (47), 115 (26).

$C_{11}H_{12}Br_2$ (304.03) Calcd. C 43.46 H 3.98
Found C 43.23 H 4.43

4,6-Bis(thiomethyl)indan (**22**): A solution of **21** (2.19 g, 7.21 mmol) and thiourea (1.10 g, 14.4 mmol) in ethanol (150 ml) was boiled under reflux for 4 h and, after cooling, the solvent was removed at reduced pressure. Then a solution of NaOH (1.44 g, 36.0 mmol) in water (150 ml) was added, to the residue under N_2 and the mixture was kept at reflux for 4 h. The solution was cooled, carefully acidified (pH = 5–6) with concentrated H_2SO_4 and extracted with CH_2Cl_2 (2 × 150 ml). The combined organic layers were dried and concentrated to give the product as a pale yellow oil (1.50 g, 99%). A portion of the product was subjected to kugelrohr distillation (55 °C/10^{-2} mbar, colourless oil) for analysis. – IR (film): $\tilde{\nu}$ = 3000 cm^{-1}, 2955, 2940, 2890, 2865, 2840, 2560, 1605, 1590, 1475, 1460, 1435, 1312, 1280, 1242, 1160, 1115, 980, 880, 870, 722, 678. – UV: λ_{max} (lg ε) = 212 nm (4.358), 276 (3.000), 284 (3.000). – ^{1}H NMR: δ = 1.68, 1.76 (t, *J* = 7.4 Hz, 1H, SH), 2.10 (quint, *J* = 7.5 Hz, 2H, 2-H), 2.90 (t, *J* = 7.4 Hz, 4H, 1-H, 3-H), 3.68, 3.70 (d, *J* = 7.4 Hz, 2H, CH_2SH), 7.03 (s, 1H, 5-H), 7.09 (s, 1H, 7-H). – ^{13}C NMR: δ = 24.97 (t, C-2); 26.83 (t, 4-CH_2); 28.83 (t, 6-CH_2); 30.57 (t, C-3); 32.86 (t, C-1); 122.96 (d, C-7); 125.50 (d, C-5); 136.76 (s, C-4); 139.88 (s, C-6); 141.24 (s, C-3a); 145.57 (s, C-7a). – MS: *m/z* (%) = 210 (21) [M^+], 177 (45), 176 (100), 144 (20), 143 (94), 129 (18), 128 (32), 117 (17).

$C_{11}H_{14}S_2$ (210.36) Calcd. C 210.05370 Found 210.0537

syn-2,12-Dithia[3]metacyclo[3](4,6)indanophane (**24**): A solution of **21** (1.14 g, 3.75 mmol) and **23** (639 mg, 3.75 mmol) in benzene (500 ml) was added dropwise under N_2 over 16 h to a vigorously stirred solution of NaOH (752 mg, 18.8 mmol) in 80% ethanol (1500 ml). The majority of the solvent was removed at reduced pressure, and equal volumes of water and CH_2Cl_2 were added to the resulting mixture until all solids had dissolved. The layers were separated, and the aqueous layer was washed with a portion of CH_2Cl_2. The combined organic layers were dried and concentrated, and the residue was preadsorbed and chromatographed on SiO_2 [CH_2Cl_2/petroleum ether (1:1)] (996 mg, 85%); m.p. 101–102 °C. – IR: $\tilde{\nu}$ = 3050 cm^{-1}, 3020, 2950, 2940, 2925, 2900, 2880, 2855, 2835, 1602, 1582, 1482, 1475, 1455, 1438, 1430, 1408, 1395, 900, 862, 768, 742, 710, 698. – UV: λ_{max} (lg ε) = 208 nm (4.398), 223 (4.179, sh), 230 (3.872, sh), 272 (3.079, sh), 289 (2.914). – ^{1}H NMR: δ = 1.96 (quint, *J* = 7.4 Hz, 2H, 6-H); 2.68 (t, *J* = 7.4 Hz, 2H, 7-H); 2.76 (t, *J* = 7.4 Hz, 2H, 5-H); 3.71, 3.71, 3.74, 3.75 (s, 2H, 1-H, 3-H, 11-H, 13-H); 6.50 (s, 1H, 10-H); 6.78 (s, 1H, 8-H); 6.88–6.98 (m, 4H, 15-H, 16-H, 17-H, 19-H). – ^{13}C NMR: δ = 25.15 (t, C-6); 30.79 (t, C-5); 32.50 (t, C-7); 36.10 (t, C-3); 37.73, 37.95 (t, C-1, C-11, C-13); 123.43 (d, C-8); 126.22, 127.12, 127.86 (d, C-15, C-16, C-17); 129.79 (d, C-10); 131.72 (s, C-4); 131.89 (d, C-19); 135.35 (s, C-9); 136.86, 137.06 (s, C-14, C-18); 141.05 (s, C-4a); 144.64 (s, C-7a). – MS: *m/z* (%) = 313 (18), 312 (79) [M^+], 176 (10), 175 (24), 145 (25), 144 (58), 143 (100), 129 (26), 128 (28), 116 (43), 91 (13).

$C_{19}H_{20}S_2$ (312.50) Calcd. C 73.07 H 6.45
Found C 73.14 H 6.52

syn,anti- and syn-syn-2,12-Dithia[3.3](4,6)indanophane (**25** and **26**): A solution of **21** (1.14 g, 2.57 mmol) and **22** (639 mg, 2.57 mmol) in benzene (500 ml) was added dropwise under N_2 over 16 h to a vigorously stirred solution of NaOH (515 mg, 12.9 mmol) in 80% ethanol (1500 ml). The majority of the solvent was removed at reduced pressure, and equal volumes of water and CH_2Cl_2 were added to the resulting mixture until all solids had dissolved. The layers were separated, and the aqueous layer was washed with a portion of CH_2Cl_2. The combined organic layers were dried and concentrated, and the residue was preadsorbed and chromatographed on SiO_2 [CH_2Cl/petroleum ether (1:1)] (906 mg, 82%); m.p. 111–130 °C. – IR: $\tilde{\nu}$ = 2950 cm^{-1}, 2930, 2895, 2860, 2840, 1605, 1585, 1472, 1458, 1430, 1410, 865, 742. – UV: λ_{max} (lg ε) = 207 nm (4.511), 241 (3.873, sh), 278 (3.279), 283 (3.079, sh). – ^{1}H NMR: δ = 1.91–2.01 (2 q, *J* = 7.4 Hz, 2H, 6-H and 16-H of **25**, 6-H and 17-H of **26**), 2.64–2.83 (4 t, *J* = 7.4 Hz, 2H, 5-H, 7-H, 15-H and 17-H of **25**, 5-H, 7-H, 16-H and 18-H of **26**), 3.71–3.75 (m, 8H, 1-H, 3-H, 11-H, 13-H), 6.67 (s, 0.47H, Ar-$H_{internal}$), 6.71 (s, 0.53H, Ar-$H_{internal}$), 6.78 (s, 0.47H, Ar-$H_{external}$), 6.81 (s, 0.53H, Ar-$H_{external}$). – ^{13}C NMR: δ = 25.19, 25.31 (t, C-6 and C-16 of **25**, C-6 and C-17 of **26**); 30.73, 30.81 (t, C-5 and C-15 of **25**, C-5 and C-18 of **26**); 32.58, 32.63 (t, C-7 and C-17 of **25**, C-7 and C-16 of **26**); 36.09, 36.71 (t, C-3 and C-13 of **25**, C-3 and C-1 of **26**); 37.82, 37.97 (t, C-11, and C-1 of **25**, C-11 and C-13 of **26**); 122.27, 123.14 (d, C-8 and C-18 of **25** C-8 and C-15 of **26**); 130.00, 130.10 (d, C-10, C-20); 131.68, 131.73 (s, C-4 and C-19 of **25**, C-4 and C-14 of **26**); 135.12, 135.34 (s, C-9 and C-14 of **25**, C-9 and C-19 of **26**); 140.85, 140.91 (s, C-4a and C-14a of **25**, C-4a and C-18a of **26**); 144.25, 144.56 (s, C-7a and 17a of **25**, C-7 and 15a of **26**). – MS: *m/z* (%) = 352 (52) [M^+], 177 (20), 176 (53), 175 (28), 145 (46), 144 (100), 143 (60), 142 (24), 141 (29), 129 (44), 128 (48), 115 (22).

$C_{22}H_{24}S_2$ (352.56) Calcd. C 74.95 H 6.86
Found C 74.99 H 7.09

anti-[2]Metacyclo[2](4,6)indanophane (**28**): To a solution of **24** (1.44 g, 4.61 mmol) in dry tetrahydrofuran (60 ml) was added at 0 °C BuLi (5.8 ml, 9.3 mmol), and, after stirring for 5 min, the reaction was quenched with methyl iodide (0.60 ml, 1.4 g, 9.6 mmol). The mixture was poured into a separating funnel containing water (150 ml) and CH_2Cl_2 (150 ml), and the layers were separated. The aqueous layer was washed with a portion of CH_2Cl_2, and the united organic layers were dried and concentrated, leaving the crude **27** as a foul-smelling yellow oil (mixture of isomers; 1.56 g, 99%). – ^{1}H NMR (60 MHz): δ = 1.2–3.8 (m, 16H, CH_2, SCH_3), 4.0–4.5 (m, 2H, Ar-$H_{internal}$), 4.8–5.6 (m, 2H, C*H*SCH_3), 6.9–7.7 (m, 4H, Ar-$H_{external}$). To a refluxing solution of the mixture of isomers of **27** in ethanol (150 ml), was added a spatula end of freshly prepared Raney nickel[17] every 10–15 min until TLC showed that the reaction had run to completion. After cooling, the mixture was filtered through a pad of Na_2SO_4. (***Warning:*** As soon as the residual Raney nickel is dry it must be covered with water to avoid ignition!) The filtrate was concentrated, and the residue was chromatographed on SiO_2 (petroleum ether) to afford **28** as a colourless oil which was crystallized from pentane (colourless stars) (477 mg, 42%); m.p. 101–102 °C. – IR: $\tilde{\nu}$ = 3040 cm^{-1}, 3010, 2940, 2920, 2880, 2840, 1588, 1578, 1480, 1468, 1452, 1332, 1318, 1308, 1225, 1192, 1172, 1165, 1075, 998, 960, 950, 890, 870, 858, 788, 725, 715. – UV: λ_{max} (lg ε) = 216 nm (4.502), 281 (3.079), 284 (3.041). – ^{1}H NMR: δ = 1.95 (td, *J* = 12.1, 3.4 Hz, 1H, 2-H_{ax}), 2.03–2.18 (m, 5H, 1-H_{ax}, 10-H_{ax}, 11-H_{ax}, 20-H), 2.81–3.08 (m, 7H, 1-H_{eq}, 5-H, 10-H_{eq}, 11-H_{eq}, 19-H), 3.18 (dt, *J* = 11.9, 3.3 Hz, 1H, 2-H_{eq}), 4.09 (s, 1H, 9-H), 4.27 (s, 1H, 17-H), 6.93 (s, 1H, 7-H), 7.03–7.06 (m, 2H, 13-H, 15-H), 7.25 (t, *J* = 7.4 Hz, 1H, 14-H). – ^{13}C NMR: δ = 25.12 (t, C-5); 30.55 (t, C-14); 33.13 (t, C-16); 38.08 (t, C-2); 39.01 (t, C-1); 40.78, 41.14 (t, C-10, C-11); 121.65 (d, C-7); 125.31, 125.45 (d, C-13, C-15); 128.61 (d, C-14); 134.14 (s, C-3); 134.17 (d, C-9); 136.31 (d, C-17); 137.30 (s, C-8); 138.90, 138.99 (s, C-12, C-16); 139.55 (s, C-4a); 144.77 (s, C-6a). – MS: *m/z* (%) = 249 (30), 248 (100) [M^+], 247 (31), 220 (85), 210 (72), 205 (44), 203 (21), 191 (14), 128 (24).

$C_{19}H_{20}$ (248.37) Calcd. C 91.88 H 8.12
Found C 91.73 H 8.12

syn,anti- and syn,syn-2,12-Dithia[3.3](4,6)indanophane 2,2,12,12-Tetraoxide (**29** and **30**): A mixture of **25** and **26** (680 mg, 1.93 mmol), a 30% H_2O_2 solution (80 ml) and a catalytic amount of glacial acetic acid was heated at reflux for 8 h. After cooling to 0 °C, the

mixture was filtered, and the solids were washed with water and then methanol. The product was dried for several hours under high vacuum, leaving a colourless powder (611 mg, 76%); m.p. >250°C. – IR: $\tilde{\nu}$ = 2950 cm^{-1}, 2920, 2900, 2840, 1472, 1460, 1432, 1395, 1310, 1282, 1265, 1180, 1168, 1112, 1030, 1015, 910, 898, 705. – UV (acetonitrile): λ_{max} (lg ε) = 202 nm (4.733), 215 (4.334, sh), 220 (4.274, sh), 225 (4.210, sh), 275 (3.462), 292 (3.146). – ^{1}H NMR (CF_3CO_2D): δ = 209–2.18 (m, 4H, 6-H and 16-H of **29**, 6-H and 16-H of **30**); 2.81–3.04 (m, 8H, 5-H, 7-H, 15-H and 17-H of **29**, 5-H, 7-H, 16-H and 18-H of **30**); 4.59, 4.64, 4.68 (s, 8H, 1-H, 3-H, 11-H, 13-H); 7.02, 7.18, 7.31, 7.34 (s, 4H, 8-H, 10-H, 18-H and 20-H of **29**, 8-H, 10-H, 15-H and 20-H of **30**). – ^{13}C NMR (CF_3CO_2D): δ = 26.56, 26.66 (t, C-6 and C-16 of **29**, C-6 and C-17 of **30**); 33.46, *33.49*, *34.39* (t, C-5, C-7, C-15 and C-17 of **29**, C-5, C-7, C-16 and C-18 of **30**); 62.17, 62.66, 63.35, 63.59 (t, C-1, C-3, C-11, C-13); 124.37, 124.98 (d, C-9 and C-19 of **29**, C-9 and C-14 of **30**); 126.91, 127.38 (s, C-4 and C-14 of **29**, C-4 and C-19 of **30**); 128.56, 128.93 (d, C-8 and C-18 of **29**, C-8 and C-15 of **30**); 134.34, 134.69 (d, C-10, C-20); 148.90, 149.10, 149.23, 149.31 (s, C-4a, C-7a, C-14a and C-17a of **29**, C-4a, C-7a, C-15a and C-18a of **30**). – MS: *m/z* (%) = 416 (2) [M^+], 352 (4), 289 (13); 288 (56), 287 (26), 260 (100), 259 (64), 245 (22), 145 (45), 144 (46), 143 (94), 141 (24), 129 (81), 128 (93), 115 (39), 57 (35).

$C_{22}H_{24}O_4S_2$ (416.56) Calcd. C 63.43 H 5.81
Found C 63.87 H 5.53

anti,anti- and anti,syn-[2.2](4,6)Indanophane (**31** and **32**): A mixture of the sulfones **29** and **30** (521 mg, 1.25 mmol) was pyrolysed in a pyrolysis oven as described by Haenel[14]. The starting temperature of the first oven was 250°C, and this was raised to 400°C during the course of the reaction. The temperature of the second oven was 520–535°C, and the pressure was kept between 10^{-1} and 10^{-2} mbar. The pyrolysate was chromatographed on SiO_2 [CH_2Cl_2/cyclohexane (1:1)] (274 mg, 76%). – IR: $\tilde{\nu}$ = 3005 cm^{-1}, 2995, 2935, 2925, 2840, 1580, 1468, 1455, 1435, 1418, 1320, 1302, 1168, 1030, 995, 942, 890, 870, 850, 730, 605. – UV: λ_{max} (lg ε) = 216 nm (4.561), 281 (3.688), 291 (3.458). – ^{1}H NMR: δ = 1.91–2.16 (m, 8H, 1-H_{ax}, 2-H_{ax}, 5-H, 10-H_{ax}, 11-H_{ax} and 15-H of **31**, 1-H_{ax}, 2-H_{ax}, 5-H, 10-H_{ax}, 11-H_{ax} and 16-H of **32**); 2.79–3.02 (m, 10H, 1-H_{eq}, 4-H, 6-H, 10-H_{eq}, 13-H and 15-H of **31**, 4-H, 6-H, 10-H_{eq}, 11-H_{eq}, 14-H and 16-H of **32**); 3.11–3.18 (m, 2H, 2-H_{eq} and 11-H_{eq} of **31**, 1-H_{eq} and 2-H_{eq} of **32**); 4.09 (s, 9-H, 18-H); 6.91, 6.93 (s, 2H, 7-H and 16-H of **31**, 7-H and 13-H of **32**). – ^{13}C NMR: δ = 25.12 (t, C-5 and C-14 of **31**, C-5 and C-15 of **32**); 30.55 (t, C-4 and C-13 of **31**, C-4 and C-16 of **32**); 33.12 (t, C-6 and C-15 of **31**, C-6 and C-16 of **32**); 36.14, 38.24, 38.88, 40.98 (t, C-1, C-2, C-10, C-11); 121.56, 121.67 (d, C-7 and C-16 of **31**, C-7 and C-13 of **32**); 134.17, 134.25 (s, C-3 and C-12 of **31**, C-3 and C-17 of **32**); 134.77 (d, C-9, C-18); 137.34, 137.43 (s, C-8 and C-17 of **31**, C-8 and C-12 of **32**); 139.46, 139.56 (C-3a and C-12a of **31**, C-3 and C-16a of **32**); 144.56, 144.57 (s, C-6a, C-15a of **31**, C-6a and C-13a of **32**). – MS: *m/z* (%) = 289 (19), 288 (75) [M^+], 261 (22), 260 (100), 259 (56), 145 (29), 131 (28), 129 (36), 128 (39).

$C_{22}H_{24}$ (288.43) Calcd. C 91.61 H 8.39
Found C 91.62 H 8.40

anti-[2]Metacyclo[2](5,7)(1H)indenophane (**8**) *and anti-[2]Metacyclo[2](4,6)(1H)indenophane* (**9**): A solution of **28** (100 mg, 0.48 mmol) and 2,3-dichloro-5,6-dicyanoquinone (109 mg, 0.48 mmol) in benzene (50 ml) was heated at reflux for 1 h. After cooling, the precipitate was removed by filtration, the filtrate was concentrated, and the residue was chromatographed on SiO_2 (CCl_4) (98 mg, 83%; 82:18 mixture of **8**:**9**); m.p. 80–86°C. – IR: $\tilde{\nu}$ = 3050 cm^{-1}, 3020, 2940, 2920, 2850, 1600, 1580, 1480, 1438, 1428, 1392, 1328, 1175, 1160, 1078, 1000, 958, 950, 940, 918, 855, 790, 720. – UV: λ_{max} (lg ε) = 223 nm (4.455), 265 (4.041), 302 (2.908, sh), 320 (2.568). – ^{1}H NMR: **8**: δ = 2.03–2.18 (m, 4H, 1-H_{ax}, 2-H_{ax}, 10-H_{ax}, 11-H_{ax}), 3.03–3.14 (m, 3H, 1-H_{eq}, 10-H_{eq}, 11-H_{eq}), 3.28–3.32 (m, 1H, 2-H_{eq}), 3.35, 3.44 (dt, *J* = 23.0, 2.0 Hz, 1H, 4-H, 4-H'), 4.13 (d, *J* = 1.1 Hz, 1H, 9-H), 4.26 (s, 1H, 17-H), 6.54 (dt, *J* = 5.5, 2.0 Hz, 1H, 5-H), 6.93 (dt, *J* = 5.5, 1.9 Hz, 1H, 6-H), 7.05–7.09 (m, 2H, 13-H, 15-H), 7.14 (d, *J* = 1.1 Hz, 1H, 7-H), 7.27 (t, *J* = 7.5 Hz, 1H, 14-H); **9**: δ = 2.03–2.18 (m, 4H, 1-H_{ax}, 2-H_{ax}, 10-H_{ax}, 11-H_{ax}), 3.03–3.14 (m, 3H, 1-H_{eq}, 10-H_{eq}, 11-H_{eq}), 3.28–3.32 (m, 1H, 2-H_{eq}), 4.22 (s, 2H, 9-H, 17-H), 6.52–6.56 (m, 1H, 5-H), 7.03–7.09 (m, 3H, 4-H, 13-H, 15-H), 7.20 (s, 1H, 7-H), 7.27 (t, *J* = 7.5 Hz, 1H, 14-H). – ^{13}C NMR: **8**: δ = 37.11, 37.78 (t, C-2, C-4); 38.85 (t, C-1); 41.02, 41.11 (t, C-10, C-11); 118.61 (d, C-7); 125.42, 125.48 (d, C-13, C-15); 128.63 (d, C-14); 132.71, 133.10, 133.41 (d, C-5, C-6, C-9); 133.54 (s, C-3); 136.72 (d, C-17); 137.48 (s, C-8); 139.07, 139.25, 139.33 (s, C-3a, C-12, C-16); 145.57 (s, C-6a); **9**: δ = 37.64 (t, C-6); 39.45, 39.66 (t, C-1, C-2); 40.97 (t, C-10, C-11); 121.43 (d, C-7); 125.35 (d, C-13, C-15); 128.63 (d, C-14); 129.86 (d, C-4); 132.88 (d, C-5); 135.01 (d, C-9); 136.58 (d, C-17); signals of quaternary carbon atoms not observed. – MS: *m/z* (%) = 247 (21), 246 (100) [M^+], 245 (39), 231 (16), 218 (72), 217 (61), 215 (43), 203 (64), 202 (66), 189 (20), 141 (23), 115 (36), 101 (16).

$C_{19}H_{18}$ (246.35) Calcd. C 92.63 H 7.37
Found C 92.40 H 7.53

exo- and endo-(η^5-anti-[2]Metacyclo[2](4,6)(1H)indenophanyl)-(η^5-cyclopentadienyl)iron (**7** and **35**): The reaction, workup and purification were carried out under N_2 by using dry, degassed solvents. To a solution of **8** and **9** (100 mg, 0.406 mmol) in tetrahydrofuran (30 ml) was added at –50°C 1 equiv. of methyllithium, and the mixture was stirred for 1 h. Freshly prepared lithium cyclopentadiene (590 mg, 8.2 mmol) was then added, and stirring was continued for 1 h before the addition of $FeCl_2 \cdot 2$ THF (1.18 g, 4.34 mmol). The solvent was removed in vacuo, and the residue was slurried with petroleum ether (50 ml) with gentle warming. Following filtration the solvent was removed in vacuo, and the ferrocene byproduct was removed by sublimation (75°C/10^{-3} mbar), leaving a red-purple powder (104 mg, 70%); m.p. >170°C (dec.). – IR: $\tilde{\nu}$ = 3080 cm^{-1}, 3010, 2940, 2920, 2850, 1520, 1480, 1438, 1430, 1408, 1328, 1180, 1168, 1105, 1032, 1002, 820, 792, 740, 720, 710. – UV (acetonitrile): λ_{max} (lg ε) = 202 nm (4.522), 232 (4.330), 263 (4.322), 500 (2.477). – ^{1}H NMR (CS_2, 10% C_6D_6): **7**: δ = 1.84–1.92 (m, 2H, H_{ax}), 2.00 (td, *J* = 12.1, 3.6 Hz, 1H, H_{ax}), 2.17 (td, *J* = 12.0, 3.8 Hz, 1H, H_{ax}), 2.86 (td, *J* = 12.0, 3.6 Hz, 1H, H_{eq}), 2.89 (dd, *J* = 8.1, 3.6 Hz, 1H, H_{eq}), 2.93 (dt, *J* = 11.8, 3.4 Hz, 1H, H_{eq}), 3.19 (dd, *J* = 8.2, 3.6 Hz, 1H, H_{eq}), 3.52 (s, 5H, C_5H_5), 3.80 (d, *J* = 1.4 Hz, 1H, 9-H), 3.86 (t, *J* = 2.5 Hz, 1H, 5-H), 4.36 (s, 1H, 17-H), 4.63 (dd, *J* = 2.5, 0.9 Hz, 1H, 6-H), 4.69 (dd, *J* = 2.5, 1.1 Hz, 1H, 4-H), 6.85, 6.88 (dt, *J* = 7.5, 1.4 Hz, 1H, 13-H, 15-H), 7.08 (s, 1H, 7-H), 7.08 (t, *J* = 7.4 Hz, 1H, 14-H); **35**: δ = 2.01–2.08 (m, 2H, H_{ax}), 2.17 (td, *J* = 12.2, 3.4 Hz, 1H, H_{ax}), 2.29 (td, *J* = 12.0, 3.6 Hz, 1H, H_{ax}), 2.97–3.07 (m, 1H, H_{eq}), 2.92 (dtd, *J* = 12.0, 3.4, 1.4 Hz, 1H, H_{eq}), 3.17 (dt, *J* = 12.0, 3.7 Hz, H_{eq}), 3.29 (dt, *J* = 12.2, 3.5 Hz, 1H, H_{eq}), 3.94 (s, 5H, C_5H_5), 4.02 (s, 1H, 9-H), 4.07 (t, *J* = 2.5 Hz, 1H, 5-H), 4.81 (dd, *J* = 2.6, 1.0 Hz, 1H, 6-H), 4.89 (dd, *J* = 2.5, 1.1 Hz, 1H, 4-H), 5.22 (t, *J* = 1.5 Hz, 1H, 17-H), 7.07 (s, 1H, 7-H), 7.06, 7.09 (dt, *J* = 7.6, 1.4 Hz, 1H, 12-H, 15-H), 7.28 (t, *J* = 7.4 Hz, 1H, 14-H). – ^{13}C NMR (CS_2, 10% C_6D_6): **7**: δ = 38.89, 39.01 (t, C-1, C-2); 41.37, 42.21 (t, C-10, C-11); 59.35, 62.28 (d, C-4, C-6); 69.19 (d, C_5H_5); 70.17 (d, C-5); 87.64, 91.71 (s, C-3a, C-6a); 122.95 (d, C-7); 125.44, 125.66 (d, C-13, C-15); 128.98 (d, C-14); 131.36 (d, C-9); 136.63, 136.69 (s, C-3, C-8); 137.04 (d, C-1); 138.42, 139.72 (s, C-12, C-16); **35**: δ = 38.13, 38.46 (t, C-1, C-2); 41.32, 41.51 (t, C-10, C-

11); 59.57, 62.44 (d, C-4, C-6); 68.45 (d, C_5H_5); 69.41 (d, C-5); 87.93, 88.85 (s, C-3a, C-6a); 122.92 (d, C-7); 125.48, 126.07 (d, C-13, C-15); 129.28 (d, C-14); 133.79 (d, C-9); 131.84, 135.36 (s, C-3, C-8); 135.72 (d, C-17); 139.58, 140.56 (s, C-12, C-16). – MS: *m/z* (%) = 368 (13), 367 (59), 366 (49) [M^+], 365 (100), 364 (15), 363 (16), 296 (6), 241 (6), 239 (6).

$C_{24}H_{22}Fe$ (366.29) Calcd. 366.10711 Found 366.1071 (MS)

The anti-[2]Metacyclo[2](4,6)(1H)indenophanyl Anion (**10**): Methyllithium (0.5 ml, 1.55 M in diethyl ether, 0.78 mmol) was introduced into an evacuated (10^{-4} Torr) NMR tube capped with a septum, and the solvent was removed (white crystals). To the evacuated tube was added a mixture of **8** and **9** (10 mg, 0.041 mmol) in [D_8]tetrahydrofuran (0.6 ml) at −78 °C. After several minutes, the reaction mixture was allowed to reach room temperature. The control of the evolution of gas was performed by cooling the sample as soon as it became too violent. A deep orange colour developed as the anion **10** formed. – ^{1}H NMR (C_4D_8O): δ = 2.47–2.91, 2.93–3.10 (m, 4H, 1-H_{ax}, 1-H_{eq}, 2-H_{ax}, 2-H_{eq}, 10-H_{ax}, 10-H_{eq}, 11-H_{ax}, 11-H_{eq}); 3.92 (s, 1H, 17-H); 4.23 (s, 1H, 9-H); 6.03 (m, 1H, 4-H); 6.14 (m, 1H, 6-H); 6.59 (t, *J* = 3.6 Hz, 1H, 5-H); 6.97–7.04 (m, 2H, 13-H, 14-H); 7.13 (d, *J* = 7.4 Hz, 1H, 15-H); 7.25 (s, 1H, 7-H).

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* Dedicated to Professor *Klaus Hafner* on the occasion of his 65th birthday.

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