

DNMR, Molecular Mechanics, and Crystal Structures of 2,11-Dithia[3.3]orthometacyclophane and 2,11-Dithia[3.3]orthoparacyclophane

Graham J. Bodwell^a, Ludger Ernst^b, Henning Hopf^{*a}, Peter G. Jones^c, John P. McNally^d, and Dietmar Schomburg^e

Institut für Organische Chemie der Technischen Universität Braunschweig^a,
Hagenring 30, D-3300 Braunschweig, FRG

NMR-Laboratorium der Chemischen Institute, Technische Universität Braunschweig^b,
Hagenring 30, D-3300 Braunschweig, FRG

Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig^c,
Hagenring 30, D-3300 Braunschweig, FRG

The Dyson Perrins Laboratory^d,
South Parks Rd, Oxford OX1 3QY, UK

Gesellschaft für Biotechnologische Forschung^e,
Mascheroder Weg, D-3300 Braunschweig, FRG

Received April 25, 1990

Key Words: Dithiacyclophanes / DNMR / Molecular mechanics / Cyclophanes

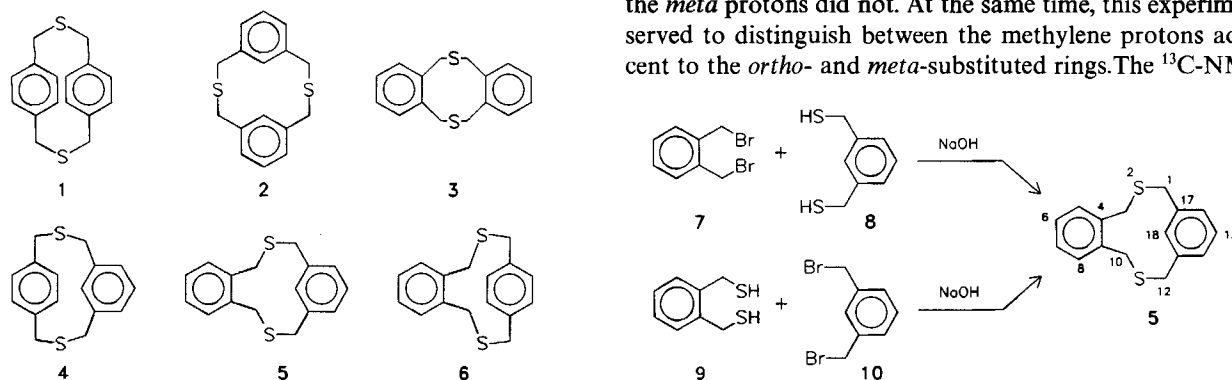
The syntheses of 2,11-dithia[3.3]orthometacyclophane (**5**) and 2,11-dithia[3.3]orthoparacyclophane (**6**) by dithiol-dibromide coupling are described. Whereas the yield of **5** is not significantly affected by the substrate pairing, that of **6** is. Both compounds exhibit a temperature-dependent ¹H-NMR spectrum. An energy barrier of 11.0 ± 0.2 kcal/mol (45.7 ± 0.8 kJ/mol) has been calculated for **5**, but that of **6** was too low to be

determined. Slightly contrasting results were obtained from two different molecular mechanics programs for the relative energies of the six limiting conformations of **5**. Crystal structure determinations of **5** and **6** have been carried out, and the conformational behavior of **5** and **6** in solution and in the solid state is discussed.

As in the case of the [2.2]cyclophanes, there are six isomers in the series of 2,11-dithia[3.3]cyclophanes (**1–6**), and with our recent syntheses of the orthometa (**5**)^{2,3)} and orthopara (**6**)^{2,4)} isomers the series is now complete. A common feature of **1**⁵⁾, **2**⁶⁾, **3**⁷⁾, and **4**⁸⁾ is that they are conformationally mobile, undergoing either a ring flip or a bridge wobble in solution. The crystal structures of **1**⁹⁾, **2**⁶⁾, and **3**^{7b)} have also been documented. In this paper we describe the DNMR, molecular mechanics, conformational behavior, and crystal structures of **5** and **6**.

Results and Discussion

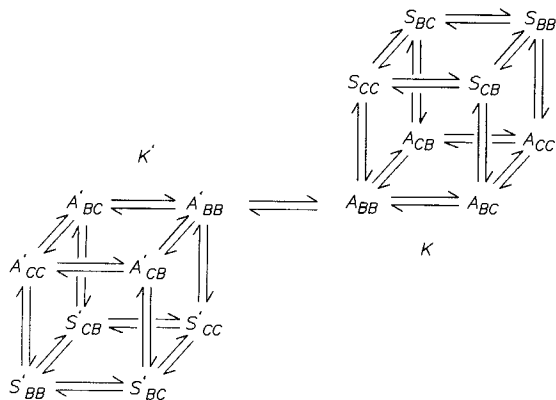
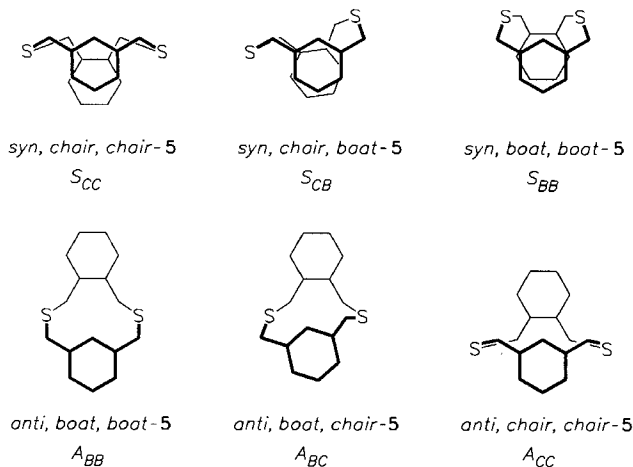
The dithiol-dibromide coupling to give **5** appears not to be significantly influenced by the choice of the starting materials. The coupling of **7** and **8** proceeded in 79% yield^{2,3)} whereas that of **9** and **10** afforded 77% of the target compound. In the ¹H-NMR spectrum of **5** the signals of the *meta*-substituted aromatic ring were assigned from their coupling patterns and those of the *ortho*-substituted ring from a 2D H,H-COSY spectrum with parameters optimized for long-range couplings (COSY-LR)¹⁰⁾: the *ortho* protons exhibited cross peaks with the methylene protons whereas the *meta* protons did not. At the same time, this experiment served to distinguish between the methylene protons adjacent to the *ortho*- and *meta*-substituted rings. The ¹³C-NMR



spectrum was then assigned by C,H -COSY¹¹⁾ and C,H -COLOC¹²⁾ for the proton-bearing and quaternary carbon atoms, respectively. The spectra of **6** were assigned in a similar manner.

Since the aliphatic region of the 1H -NMR spectrum of **5** consists of two singlets, the molecule is clearly mobile³⁾. A highly unlikely chemical shift degeneracy at both of the benzylic positions can be ruled out by the observation of a temperature-dependent 1H -NMR spectrum. Upon cooling, the singlets broadened and eventually split into two well resolved AB systems. The energy barrier of 11.0(2) kcal/mol [45.7(8) kJ/mol] was calculated according to the method of Friebolin et al.¹³⁾ (see Table 1). Examination of molecular models revealed that a cubic set of equilibria exists (hereafter referred to as K), linking the six limiting conformations shown in Scheme 1. However, none of these interconversions involves an exchange within the two pairs of geminal protons. Therefore, the process observed in the DNMR must be the equilibrium between K and its mirror image K' . According to models, such an interconversion, which does exchange the benzylic protons, can only take place through the *anti,boat,boat* conformation.

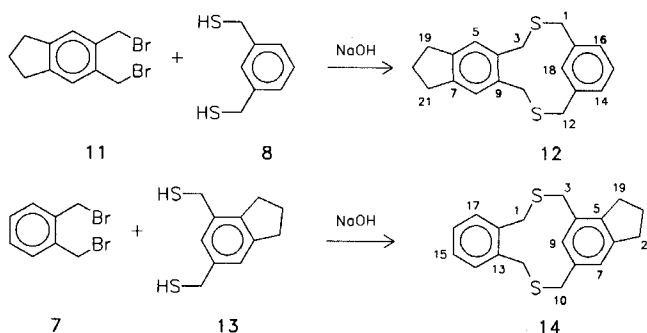
Scheme 1



The internal proton (18-H) of **5** resonates at $\delta = 5.92$, strongly indicating that the *anti,chair,chair* conformation is heavily populated, this being the only one in which the in-

ternal proton extends into the shielding zone of the opposite deck.

Having recently studied the conformational behavior of **3** in solution by anellating one and two five-membered rings to it¹⁴⁾, we synthesized the two *mono*-anellated compounds **12** and **14**. The coupling of **11**¹⁴⁾ and **8** proceeded in 79% yield and that of **7** and **13**^{2,11)} in 69% yield. As in the case of **5**, the 1H -NMR spectra of **12** and **14**, which were assigned in an analogous fashion to those of **5**, are temperature-dependent. However, the low symmetry of **14** renders the four bridging benzylic centers non-equivalent. This resulted in a very broad coalescence range and an unresolved spectrum at the lower temperature limit of the spectrometer ($-103^\circ C$). Consequently, no energy barrier could be determined. The DNMR of **12** was very similar to that of **5**, and an energy barrier of 11.1(2) kcal/mol [46.5(8) kJ/mol] was calculated (see Table 1). That this value is almost identical to that of **5** contrasts with our results for the 2,11-dithia-[3.3]orthocyclophanes, which showed an increase in the energy barrier of 0.5–0.7 kcal/mol (2.1–2.9 kJ/mol) per five-membered ring. This would suggest that there is little motion of the *ortho*-substituted ring at the transition state of the K/K' interconversion. This is consistent with an A_{BB}/A'_{BB} interconversion, which takes place by rotations about the four carbon–sulfur bonds.

Table 1. Parameters in the variable-temperature 400-MHz 1H -NMR spectra of the CH_2 groups in **5** and **12**

	5		12	
Δv_{AB} [Hz]	51.3	21.3	28.7	22.7
J_{AB} [Hz]	12.4	16.1	12.4	16.3
$v_{1/2}$ [Hz]	3.2	4.4	5.5	6.9
T_c [K]	227	219	225	223
ΔG_c^* [kJ/mol]	45.9 ± 0.8	45.5 ± 0.8	46.5 ± 0.8	46.5 ± 0.8
	11.0 ± 0.2	10.9 ± 0.2	11.1 ± 0.2	11.1 ± 0.2

The structure of **5** in the crystalline state is shown in Figure 1. The molecule has adopted the S_{CC} conformer. The interplanar angle between the two aromatic rings is 16.1° , which is much larger than the corresponding angle in the *ortho,para* derivative **6** (vide infra) but somewhat smaller than in the *meta,meta* derivative **2**, where it is 20.6° ⁶⁾. Both rings are essentially planar, the largest deviations from planarity being 0.016 Å at C(4) and C(7) in the *ortho*-substituted ring and 0.024 Å at C(18) in the *meta* ring. The carbon atoms

benzylic to the *meta* ring, C(1) and C(12), lie 0.19 and 0.17 Å out of the plane, respectively. The C–S bond lengths (1.82 Å) and all other bonding parameters are within the usually observed range.

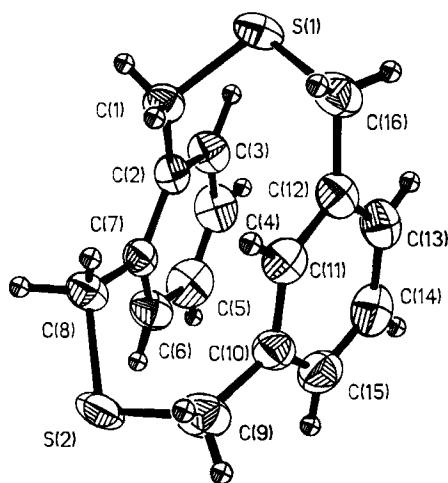


Figure 1. Structure of **5** in the crystal

The six limiting conformations of **5** were optimized using molecular mechanics force field calculations. The QUANTA¹⁵ and Chem-X¹⁶ molecular modeling packages were used individually for these calculations. Perturbation of any of the optimized low-energy conformers followed by reoptimization gave either the initial unperturbed conformer or one of the other five local minima resulting from a single bridge flip. The results of the calculations are listed in Table 2. The lowest energy conformers have been assigned an energy of 0.0 kcal/mol. Plots of the optimized structures generated by Chem-X are shown in Figure 2.

These results clearly indicate that both the S_{CB} and S_{BB} conformers are high in energy relative to the other four conformers and will not be present in significant concentrations at room temperature. Both sets of calculations indicate that the three *anti* conformers lie close in energy (within 1.0 kcal/mol according to QUANTA and within 0.4 kcal/mol according to Chem-X) but do not agree on the exact order of stability. The principal difference between the two sets of calculations is the energy of the S_{CC} conformer relative to the three *anti* conformers. The Chem-X calculations place it roughly 2 kcal/mol lower whereas the QUANTA calculations find it to be 1–2 kcal/mol higher in energy than the *anti* group. In either case, the presence of four low-energy conformations within approximately 2 kcal/mol of each other points towards a conformationally active system. The differences in the results offered by the two packages are not dramatic and are probably indicative of the limits of accuracy of molecular mechanics calculations in medium-sized rings.

Interestingly, the selenium analog of **5** is known¹⁷. The internal proton was reported to absorb at $\delta = 6.00$ and the bridge protons at $\delta = 3.66$ and 3.31. **15** would thus appear to behave similarly to **5** in solution.

Table 2. Energies [kcal/mol] of the optimized conformers of **5**

	QUANTA	Chem-X
S_{CC}	2.2	0.0
S_{CB}	6.2	5.8
S_{BB}	9.9	9.8
A_{CC}	1.0	1.9
A_{CB}	0.0	2.3
A_{BB}	0.1	2.3

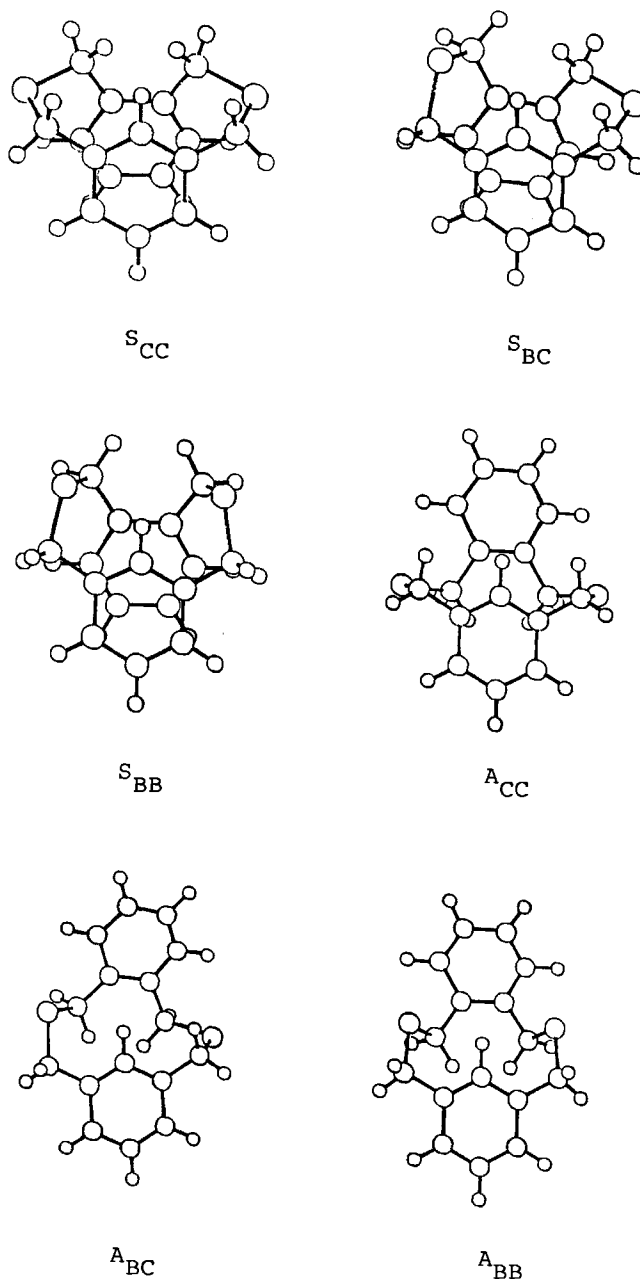
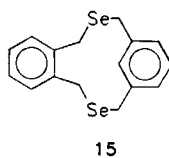
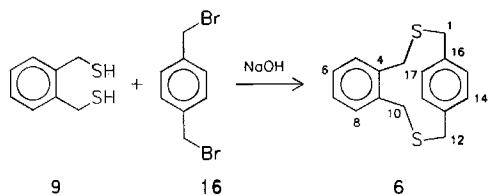


Figure 2. Chem-X plots of the conformers of **5**

In sharp contrast to the *ortho/meta* coupling, the choice of starting materials in the coupling to give **6** ultimately determines the outcome of the reaction³. Only the *ortho*-dithiol/*para*-dibromide pairing affords the desired product. This has been explained in terms of stereoelectronic effects³.



The aliphatic region of the $^1\text{H-NMR}$ spectrum of **6** consists of singlets at $\delta = 3.92$ and 3.12 , which again implies mobility. Upon cooling to the lower temperature limit of the spectrometer (-103°C), only a broadening of these signals was observed. We estimate the upper limit of the energy barrier to be ca. 8.9 kcal/mol (37 kJ/mol). According to models, the sole conformational process available to **6** is the flipping of the *ortho* ring from one side to the other of the *para* ring.



The structure of **6** in the crystalline state is shown in Figure 3. The interplanar angle between the phenyl rings is 7.5° . These rings are also slightly skewed with respect to each other; the vectors $\text{C}(13)\text{--C}(16)$ and $\text{C}(5)\text{--C}(8)$ form an angle of 4.2° . The *para*-substituted ring displays a slight distortion to a boat conformation, as is usual for paracyclophane systems. The atoms $\text{C}(13)$ and $\text{C}(16)$ lie 0.08 Å out of the plane of the four central atoms, and this is amplified to 0.44 Å for the substituent atoms $\text{C}(1)$ and $\text{C}(12)$.

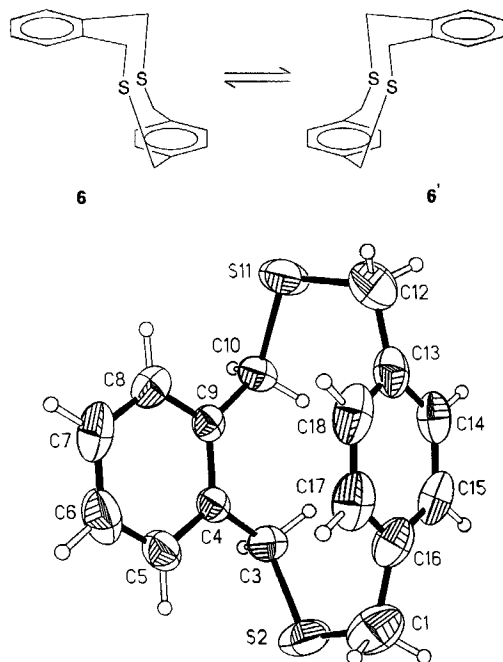


Figure 3. Thermal ellipsoid plot (40% level) of the structure of **6** in the crystal; bond lengths [Å] and angles [$^\circ$] at sulfur: $\text{S}(2)\text{--C}(1)$ $1.827(5)$, $\text{S}(2)\text{--C}(3)$ $1.811(3)$, $\text{C}(1)\text{--S}(2)\text{--C}(3)$ $106.4(2)$, $\text{S}(11)\text{--C}(10)$ $1.810(3)$, $\text{S}(11)\text{--C}(12)$ $1.809(5)$, $\text{C}(10)\text{--S}(11)\text{--C}(12)$ $107.0(2)$

The authors wish to thank the *Natural Sciences and Engineering Research Council of Canada*, the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Deutscher Akademischer Austauschdienst* for their generous support of this work.

Experimental

General: Mp: Büchi SMP-200. — NMR: Bruker AM-400, 400 MHz (^1H), 100.6 MHz (^{13}C), ca. 0.05% Me_4Si as internal standard. — IR: Perkin-Elmer 1420. — UV: Beckman UV-5230. — MS: Varian MAT CH7, EI (70 eV). — Analyses: Analytical Laboratory of the Institute for Pharmaceutical Chemistry of the Technical University of Braunschweig, FRG.

General Procedure for Couplings: The reactions were carried out under N_2 using N_2 -degassed solutions. An equimolar solution of the dithiol and dibromide was added slowly to a vigorously stirred solution of sodium hydroxide (5.0 equiv.) in 80% ethanol. The solvent was removed under reduced pressure, and equal volumes of water and dichloromethane were added until all of the solids had dissolved. The phases were separated, and the aqueous layer was washed with a portion of dichloromethane. The combined organic layers were washed with two portions of water, dried (MgSO_4), and the solvent was removed. The residue was preadsorbed on silica gel and chromatographed [SiO_2 , dichloromethane/petroleum ether ($40\text{--}60^\circ\text{C}$) 1:1]. The product was then recrystallized from cyclohexane. Yields stated are those obtained after recrystallization. Analytically pure samples were obtained by a second recrystallization from methanol solutions.

2,11-Dithia[3.3]orthometacyclophane (5): 6.47 g (24.5 mmol) of **7** and 4.17 g (24.5 mmol) of **8** in 500 ml of benzene were added over 7 h to 4.90 g (123 mmol) of sodium hydroxide in 750 ml of 80% ethanol. Workup afforded 5.14 g (77%) of **5**. Alternatively, 2.40 g (14.1 mmol) of **9** and 3.72 g (14.1 mmol) of **10** in 500 ml of benzene were added over 7 h to 2.82 g (70.5 mmol) of sodium hydroxide in 750 ml of 80% ethanol. Workup afforded 3.11 g (79%) of **5** as colorless prisms; m.p. $168\text{--}169^\circ\text{C}$. — $^1\text{H NMR}$: $\delta = 7.82$ (AA'BB' half-spectrum, 2H, 5-, 8-H), 7.37 (t, $J = 7.4$ Hz, 1H, 15-H), 7.30 (AA'BB' half-spectrum, 2H, 6-, 7-H), 7.25 (dd, $J = 7.4$ and 1.4 Hz, 2H, 14-, 16-H), 5.90 (s, 1H, 18-H), 3.57 (s, 4H, 1-, 12-H), 3.12 (s, 4H, 3-, 10-H). — $^{13}\text{C NMR}$: $\delta = 136.32$ (s, C-13, -17), 135.84 (s, C-4, -9), 133.26 (d, C-18), 130.09 (d, C-15), 129.02 (d, C-5, -8), 127.14 (d, C-14, -16), 127.01 (d, C-6, -7), 33.65 (t, C-1, -12), 28.06 (t, C-3, -10). — IR: $\tilde{\nu} = 3050$ cm^{-1} , 3020, 2950, 2920, 2895, 1605, 1590, 1480, 1445, 1438, 1412, 1220, 1190, 890, 805, 770, 752, 712, 700, 675. — UV: λ_{max} ($\lg \epsilon$) = 209 nm (4.427), 246 (3.415) sh. — MS: m/z (%) = 272 (18) [M^+], 136 (14), 135 (100), 104 (11), 91 (11).

$\text{C}_{16}\text{H}_{16}\text{S}_2$ (272.43) Calcd. C 70.54 H 5.92

Found C 70.52 H 6.00

2,11-Dithia[3.3](1,3)(5,6-indano)cyclophane (12): 0.678 g (3.23 mmol) of **11** and 0.380 g (3.23 mmol) of **8** in 200 ml of benzene were added over 5 h to 0.446 g (11.2 mmol) of sodium hydroxide in 750 ml of 80% ethanol. Workup afforded 0.551 g (79%) of **12** as colorless prisms; m.p. $193\text{--}194^\circ\text{C}$. — $^1\text{H NMR}$: $\delta = 7.69$ (s, 2H, 5-, 8-H), 7.39 (t, 1H, $J = 7.5$ Hz, 15-H), 7.26 (d, partly obscured by solvent signal, 2H, 14-, 16-H), 6.04 (s, 1H, 18-H), 3.59 (s, 4H, 1-, 12-H), 3.10 (s, 4H, 3-, 10-H), 2.95 ("t", " J " = 7.4 Hz, 4H, 19-, 21-H), 2.12 ("q", " J " = 7.4 Hz, 2H, 20-H). — $^{13}\text{C NMR}$: $\delta = 143.37$ (s, C-6, -7), 136.39 (s, C-13, -17), 133.48 (d, C-18), 133.43 (s, C-4, -9), 130.03 (d, C-15), 127.08 (d, C-14, -16), 124.65 (d, C-5, -8), 33.66 (t, C-1, -12), 32.69 (t, C-19, -21), 28.26 (t, C-3, -10), 25.51 (t, C-20). — IR: $\tilde{\nu} = 3030$ cm^{-1} , 2985, 2960, 2950, 2935, 2900, 2840, 1605, 1585, 1558, 1478, 1440, 1412, 1232, 1225, 895, 720, 702. — UV: λ_{max}

(lg ϵ) = 210 (4.575), 278 (3.415), 282 (3.362), 288 (3.431). — MS: m/z (%) = 312 (14) [M^+], 176 (14), 175 (100), 159 (10), 147 (10), 135 (14), 131 (16), 129 (12), 91 (18).

$C_{19}H_{20}S_2$ (312.50) Calcd. C 73.07 H 6.45
Found C 73.05 H 6.48

2,11-Dithia[3.3](1,2)(4,6-indano)cyclophane (14): 0.515 g (1.95 mmol) of **7** and 0.410 g (1.95 mmol) of **13** in 250 ml of benzene were added over 4 h to 0.390 g (7.80 mmol) of sodium hydroxide in 750 ml of 80% ethanol. Workup afforded 0.420 g (69%) of **14** as colorless microcrystals; m.p. 179–180.5°C. — 1H NMR: δ = 7.80–7.75 (m, 2H, 14-, 17-H), 7.28–7.23 (m, 2H, 15-, 16-H), 7.06 (s, 1H, 7-H), 5.81 (s, 1H, 9-H), 3.58 (s, 4H, 3-, 10-H), 3.20, 3.18 (s, 2H, 1-, 12-H), 2.93 (“t”, “J” = 7.4 Hz, 19-H), 2.86 (“t”, “J” = 7.4 Hz, 21-H), 2.08 (“q”, “J” = 7.4 Hz, 20-H). — ^{13}C NMR: δ = 146.30 (s, C-6), 141.77 (s, C-5), 136.13, 136.02 (s, C-13, -18), 134.16 (s, C-8), 131.18 (d, C-9), 131.15 (s, C-4), 129.06, 128.91 (d, C-14, -17), 126.66, 126.64 (d, C-15, -16), 123.41 (d, C-7), 33.96 (t, C-10), 32.81 (t, C-21), 32.47 (t, C-3), 30.18 (t, C-19), 28.52, 28.28 (t, C-1, -12), 24.99 (t, C-20). — IR: $\tilde{\nu}$ = 2980 cm^{-1} , 2965, 2950, 2920, 2840, 1585, 1475, 1450, 1432, 1422, 1410, 1048, 910, 870, 832, 760, 730, 715. — UV: λ_{max} (lg ϵ) = 211 nm (4.521), 248 (3.562) sh, 267 (3.176) sh, 279 (3.114), 288 (3.079). — MS: m/z (%) = 312 (8) [M^+], 144 (19), 143 (12), 142 (9), 141 (19), 136 (11), 135 (100), 134 (15), 129 (28), 128 (25), 115 (11), 91 (10).

$C_{19}H_{20}S_2$ (312.50) Calcd. C 73.07 H 6.45
Found C 73.14 H 6.42

Crystal Structure Determination of Compound 5¹⁸: Crystal Data: $C_{16}H_{16}S_2$; M_r = 272.43; monoclinic; space group $P2_1/n$; a = 11.920(2), b = 7.855(1), c = 14.092(2) Å; β = 92.20(1)°; V = 1319 Å³; Z = 4; D = 1.372 Mg/m³; $\lambda(Cu-K\alpha)$ = 1.5418 Å; μ = 3.31 mm⁻¹; $F(000)$ = 576; T = 293 K. Data collection and reduction: Data were collected from a crystal $0.5 \times 0.3 \times 0.2$ mm. Of 2345 unique reflections, recorded with a Nicolet P3 diffractometer ($2\theta_{max}$ = 135°), 1822 reflections with $I \geq 3.0\sigma(I)$ were used for refinement. Structure solution and refinement: The structure was solved by Direct Methods and subjected to full-matrix anisotropic refinement. Hydrogen atoms were located from difference Fourier syntheses and included in the refinement with isotropic temperature factors. The final R value was 0.072, and R_w = 0.083 for 227 parameters; the weighting scheme used was $w^{-1} = \sigma^2(F) + 0.008 F^2$. A final difference map displayed no electron density higher than 0.75 $e \text{ \AA}^{-3}$. The program SHELX-76¹⁹ and our own programs (D.S.) were used. Positional and equivalent isotropic displacement parameters are listed in Table 3.

Table 3. Positional and equivalent isotropic displacement parameters [\AA^2] of **5**

	X/A	Y/B	Z/C	UEQ
S(1)	0.3854(1)	0.1910(2)	0.0226(1)	0.046(0)
S(2)	0.4419(1)	0.2048(2)	0.4551(1)	0.051(0)
C(1)	0.4393(3)	0.0851(6)	0.1296(3)	0.040(1)
C(2)	0.5390(3)	0.1687(5)	0.1812(3)	0.034(1)
C(3)	0.6251(4)	0.2350(6)	0.1266(3)	0.046(1)
C(4)	0.7182(4)	0.3131(6)	0.1700(4)	0.054(1)
C(5)	0.7275(4)	0.3251(7)	0.2661(4)	0.059(1)
C(6)	0.6467(3)	0.2553(7)	0.3209(3)	0.046(1)
C(7)	0.5505(3)	0.1761(5)	0.2800(3)	0.034(1)
C(8)	0.4661(3)	0.0944(6)	0.3453(3)	0.041(1)
C(9)	0.3372(5)	0.3631(8)	0.4192(4)	0.056(1)
C(10)	0.3618(3)	0.4446(5)	0.3263(3)	0.041(1)
C(11)	0.3088(3)	0.3856(6)	0.2441(3)	0.039(1)
C(12)	0.3400(3)	0.4391(5)	0.1553(3)	0.040(1)
C(13)	0.4227(3)	0.5632(6)	0.1494(3)	0.046(1)
C(14)	0.4472(4)	0.6286(6)	0.2322(4)	0.051(1)
C(15)	0.4432(4)	0.5692(6)	0.3202(4)	0.050(1)
C(16)	0.2928(4)	0.3540(7)	0.0683(3)	0.049(1)

Crystal Structure Determination of Compound 6¹⁸: Crystal Data: $C_{16}H_{16}S_2$; M_r = 272.43; orthorhombic; space group $Pbca$; a = 9.416(3), b = 17.854(6), c = 16.426(6) Å; V = 2761 Å³; Z = 8; D_x = 1.310 Mg/m³; $\lambda(Mo-K\alpha)$ = 0.71069 Å; μ = 0.35 mm⁻¹; $F(000)$ = 1152; T = 293 K. Data collection and reduction: An approximately rectangular block of $0.5 \times 0.4 \times 0.3$ mm was cut from a larger crystal and mounted on a glass fiber. 4705 intensities were recorded with a Nicolet P3 diffractometer ($2\theta_{max}$ = 50°); octant $-h + k + l$ and some $+h$ equivalents. Merging equivalents gave 2436 unique reflections (R_{int} = 0.015) of which 2436 with $F > 4\sigma(F)$ were used for calculations (program system SHELX¹⁹, modified by its author). Structure solution and refinement: The structure was solved by Direct Methods and subjected to full-matrix anisotropic refinement on F . H atoms were included using a riding model. The final R value was 0.055, with R_w = 0.050; the weighting scheme employed was $w^{-1} = \sigma^2(F) + 0.0002 F^2$. 163 parameters, S = 2.1, max. $\Delta\rho$ = 0.3 $e \text{ \AA}^{-3}$. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4.

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) [\AA^2] of **6**; U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
C(1)	4130(5)	8181(3)	3569(3)	103(2)
S(2)	2431(1)	8084(1)	3042(1)	95(1)
C(3)	1611(3)	7241(2)	3436(2)	61(1)
C(4)	2273(3)	6496(2)	3224(2)	48(1)
C(5)	2940(3)	6413(2)	2479(2)	65(1)
C(6)	3534(5)	5748(3)	2242(3)	86(2)
C(7)	3448(5)	5135(3)	2740(3)	88(2)
C(8)	2792(4)	5199(2)	3485(2)	66(1)
C(9)	2192(3)	5870(2)	3744(2)	47(1)
C(10)	1451(3)	5894(2)	4562(2)	57(1)
S(11)	2123(1)	5302(1)	5369(1)	86(1)
C(12)	3586(5)	5797(3)	5838(3)	98(2)
C(13)	4034(4)	6469(2)	5369(2)	69(1)
C(14)	3415(4)	7156(2)	5516(2)	71(1)
C(15)	3552(4)	7737(2)	4977(3)	72(1)
C(16)	4286(4)	7646(2)	4257(3)	70(1)
C(17)	5031(3)	6993(3)	4145(3)	75(2)
C(18)	4922(4)	6415(2)	4695(3)	75(2)

CAS Registry Numbers

5: 23144-82-3 / **6:** 118724-09-7 / **7:** 91-13-4 / **8:** 41563-69-3 / **9:** 41383-84-0 / **10:** 626-15-3 / **11:** 91089-33-7 / **12:** 127791-72-4 / **13:** 127762-70-3 / **14:** 127762-71-4

¹⁾ Part XXXIV: P. G. Jones, G. Bodwell, H. Hopf, *Z. Naturforsch., Teil B*, in press.

²⁾ G. Bodwell, *Dissertation*, Technical University of Braunschweig, 1989.

³⁾ G. Bodwell, L. Ernst, M. W. Haenel, H. Hopf, *Angew. Chem.* **101** (1989) 509; *Angew. Chem. Int. Ed. Engl.* **28** (1989) 455; cf.: The dithiacyclophane **5** has first been prepared by F. Vögtle, *Tetrahedron* **25** (1969) 3231, who also noted its temperature-dependent NMR spectrum already. However, since no full experimental and analytical data were given at the time, and since the yields in our procedures are considerably higher than the reported ones (20% range) we feel justified in describing the preparation of **5** again.

⁴⁾ G. Bodwell, L. Ernst, H. Hopf, *Chem. Ber.* **122** (1989) 1013.

⁵⁾ F. Vögtle, *Chem.-Ztg.* **94** (1970) 313; see also: S. E. Potter, I. O. Sutherland, *J. Chem. Soc., Chem. Commun.* **1972**, 754.

⁶⁾ R. H. Mitchell, W. Anker, G. W. Bushnell, *Can. J. Chem.* **57** (1979) 3080.

^{7a)} Y.-H. Lai, M. Nakamura, *J. Org. Chem.* **53** (1988) 2360. —

^{7b)} T. Okajima, Z.-H. Wang, Y. Fukazawa, *Tetrahedron Lett.* **30** (1989) 1551.

^{8a)} V. Boekelheide, P. H. Anderson, T. A. Hylton, *J. Am. Chem. Soc.* **96** (1966) 1558. — ^{8b)} F. Vögtle, *Chem. Ber.* **102** (1969) 3077.

- ⁹⁾ T. L. Chan, C. D. Poon, T. C. W. Mak, *Acta Crystallogr., Sect. C*, **42** (1986) 897.
- ¹⁰⁾ A. Bax, R. Freeman, *J. Magn. Reson.* **44** (1981) 542.
- ¹¹⁾ ^{11a)} A. A. Maudsley, L. Müller, R. R. Ernst, *J. Magn. Reson.* **28** (1977) 463. — ^{11b)} G. Bodenhausen, R. Freeman, *J. Magn. Reson.* **28** (1977) 471.
- ¹²⁾ ^{12a)} H. Kessler, C. Griesinger, J. Lutz, *Angew. Chem.* **96** (1984) 434; *Angew. Chem. Int. Ed. Engl.* **23** (1984) 444. — ^{12b)} H. Kessler, C. Griesinger, J. Zarbock, H. R. Loosli, *J. Magn. Reson.* **57** (1984) 331.
- ¹³⁾ H. Friebolin, H. G. Schmid, S. Kabuß, *Org. Magn. Reson.* **1** (1969) 147.
- ¹⁴⁾ Part XXXIII: G. Bodwell, L. Ernst, H. Hopf, P. G. Jones, *Tetrahedron Lett.* **30** (1988) 6005.
- ¹⁵⁾ QUANTA, developed and distributed by POLYGEN Corp., Waltham, MA, USA.
- ¹⁶⁾ Chem-X, developed and distributed by Chemical Design Ltd., Oxford, U. K.
- ¹⁷⁾ H. Higuchi, K. Tani, Y. Otsubo, Y. Sakata, S. Misumi, *Bull. Chem. Soc. Jpn.* **60** (1987) 4027.
- ¹⁸⁾ Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54663, the names of the authors, and the journal citation.
- ¹⁹⁾ G. M. Sheldrick, unpublished program.

[149/90]