

Short Communication

## Disordered Crystal Structure of 2,11-Dithia[3.3]metaparacyclophane

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Research interest on thiocrown macrocycles is connected with their ability to stabilize unusual oxidation states of transition metals and especially coinage metals.<sup>1,2</sup> Among these macrocycles 2,11-dithia[3.3]cyclophanes are spectroscopically well characterized, and the crystal structures of five of the six possible isomers have also been reported in the literature.<sup>3–6</sup> We herein report the crystal structure and NMR spectrum of the *meta-para* compound. The synthesis of the title compound has been reported by Vögtle.<sup>7</sup>

### Experimental

**Synthesis.** In the synthesis of the title compound two solutions A and B were added under a nitrogen atmosphere to 500 ml of refluxing methanol at a rate of 3 ml h<sup>-1</sup>. Solution A was formed by *m*-dichloroxylylene (2 g, 11.4 mmol) dissolved in 50 ml methanol. Solution B was *p*-dimercaptoxylylene (1.94 g, 11.4 mmol) and 22.8 mmol sodium methanolate in 50 ml methanol. The methanol was dehydrated (using Mg) and deoxygenated (under vacuum) before use. After complete addition for 17 h, the mixture was refluxed for 1 h. A white precipitate (NaCl) was rejected. The clear solution was evaporated until the appearance of a white solid, which was extracted twice with diethyl ether (50 ml). The combined organic layers were washed twice with aqueous 1 M NaOH (50 ml) and twice with water (100 ml), dried over MgSO<sub>4</sub> and evaporated under vacuum. Yield 1.05 g (33.8%). Anal. C<sub>16</sub>H<sub>16</sub>S<sub>2</sub>: C, H. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.45, 3.84 (s, *m*-xylene-CH<sub>2</sub>-S); 6.86–7.12 (*m*, Ar-H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 140, 137, 129, 128, 127, 126 (Ar); 37, 35 (Ar-CH<sub>2</sub>-S). Microanalyses were performed on a Perkin-Elmer 240B instrument and

NMR spectra were recorded on a Bruker 400 MHz AM instrument.

**Crystal data.** C<sub>16</sub>H<sub>16</sub>S<sub>2</sub>, *M<sub>r</sub>* = 272.43, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.293(2), *b* = 12.539(4), *c* = 7.621(1) Å, β = 97.84(1)°, *V* = 690.4(3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.310 Mg m<sup>-3</sup>, λ(MoKα) = 0.710 69 Å, μ = 0.35 mm<sup>-1</sup>, *F*(000) = 288, *T* = 295 K, final *R* = 0.087 and *R<sub>w</sub>* = 0.080 for 1179 unique reflections and 52 variables.

The unit cell parameters were determined by least-squares refinement from 20 carefully centered reflections (15 < 2Θ < 36°) measured at ambient temperature on a Nicolet P3F diffractometer. The data were corrected for Lorentz and polarization effects but neither for extinction nor absorption.

**Data collection, structure determination and refinement.** A total of 1792 reflections were collected (2Θ<sub>max</sub> = 55°), giving 1591 unique reflections (*R<sub>int</sub>* = 0.032), of which 1179 were considered observed according to the criteria |*F*| > 4σ(*F*). The three check reflections measured after every 197 reflections showed only statistical fluctuations during the data collection. The structure was solved by

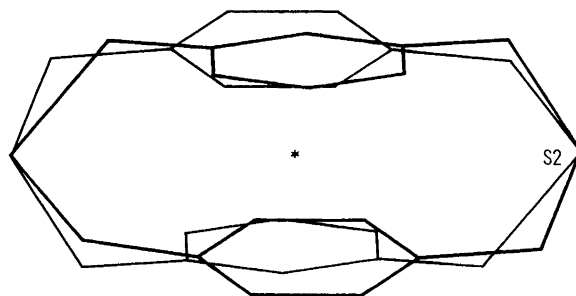


Fig. 1. Disordered structure of 2,11-dithia[3.3]metaparacyclophane resulting an apparent center of inversion (\*) inside the molecule at  $\frac{1}{2}, 0, \frac{1}{2}$ .

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**Table 1.** Non-hydrogen positional and isotropic displacement (in Å<sup>2</sup>) parameters.<sup>a</sup>

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>iso</sub>
C1	0.157(2)	0.1900(7)	0.390(1)	0.080(2)
S2	0.1029(2)	0.1048(1)	0.2234(2)	0.1069(6)
C3	0.275(1)	0.0430(7)	0.1417(9)	0.063(2)
C4	0.367(1)	-0.0480(4)	0.2544(6)	0.0588(7)
C5	0.2605(4)	-0.1345(7)	0.2961(6)	0.0588(7)
C6	0.340(1)	-0.2138(4)	0.4108(7)	0.0588(7)
C7	0.526(1)	-0.2065(4)	0.4837(6)	0.0588(7)
C8	0.6328(4)	-0.1200(7)	0.4419(6)	0.0588(7)
C9	0.554(1)	-0.0407(4)	0.3273(7)	0.0588(7)
C10	0.828(1)	-0.1110(9)	0.528(1)	0.074(2)
C12	0.810(1)	0.0213(7)	0.828(1)	0.084(2)
C13	0.6396(7)	0.0721(6)	0.7296(6)	0.0614(7)
C14	0.467(1)	0.0245(3)	0.7333(6)	0.0614(7)
C15	0.3105(6)	0.0649(6)	0.6277(6)	0.0614(7)
C16	0.3273(7)	0.1527(6)	0.5184(6)	0.0614(7)
C17	0.500(1)	0.2003(3)	0.5146(6)	0.0614(7)
C18	0.6565(6)	0.1599(6)	0.6202(6)	0.0614(7)

<sup>a</sup>The site occupation factor for S2 is 1.0 and for all other atoms 0.5.

direct methods by using the SHELXS86<sup>8</sup> program and subsequent Fourier synthesis. Because the molecule lacks an inversion centre and *Z* = 2, it is disordered, with two molecules sharing four equivalent positions. One molecule occupies either site randomly in the crystal lattice, and this results in an apparent centre of symmetry inside the molecule (Fig. 1). During the refinement procedure all atoms except sulfur were positioned at two sites with population parameters 0.5, and only one of each pair was included in the calculations. However, the quite large anisotropic temperature factors of the sulfur atom, *U*<sub>11</sub> = 0.142(1), *U*<sub>22</sub> = 0.0897(9) and *U*<sub>33</sub> = 0.0864(8), as well as the considerable differences in the S–C bond lengths, indicate a possible disorder of the S atom, too. The phenyl groups and the methylene groups have been included in the calculations as rigid groups (C–C = 1.40, C–H = 1.00 Å) and refined isotropically. The disorder is also reflected in a somewhat high *R*-value of 0.087 (*R*<sub>w</sub> = 0.080, *w* = [σ<sup>2</sup>(*F*)]<sup>-1</sup> for 52 parameters). The maximum and minimum residuals in the final difference Fourier map were 0.4 and -0.3 e Å<sup>-3</sup>, respectively.

As in the structures of azulene<sup>9</sup> and thieno[3,4-*d*]thiepin,<sup>10</sup> there is another possibility that the true space

**Table 2.** Selected bond lengths (in Å) and angles (in °).

C1–S2	1.665(9)	C10–S2*	1.892(9)
C1–C16	1.54(1)	C10–C8	1.489(9)
C3–S2	1.665(9)	C12–S2*	1.768(9)
C3–C4	1.53(1)	C12–C13	1.50(1)
S2–C1–C16	112.1(7)	C10–S2*–C12	101.7(4)
C1–S2–C3	118.1(6)	S2*–C10–C8	123.6(6)
S2–C3–C4	115.8(5)	S2*–C12–C13	124.4(6)

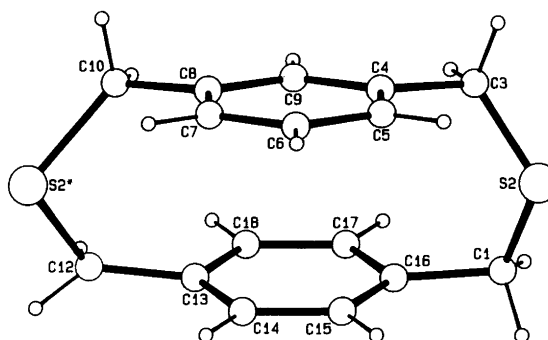
\*denotes symmetry operation 1 - *x*, -*y*, 1 - *z*.

group is *Pc*, supposing that the 0*k*0 absences are accidental. This would mean that the two molecules in the unit cell are not necessarily disordered. However, our calculations in the lower-symmetry space group *Pc* also yielded the disordered structure. Therefore we refined the structure in the higher-symmetry space group *P2*<sub>1</sub>/*c*.

The scattering factors used were those included in the program systems, and anomalous dispersion corrections were applied.<sup>11</sup> All calculations were carried out on VAX 8650 and CONVEX C3820 computers, and refinements and all subsequent calculations used the XTAL program system.<sup>12</sup> Figures were drawn with PLUTO.<sup>13</sup> Final atomic coordinates for non-hydrogen atoms are listed in Table 1 and relevant bond lengths and angles in Table 2. Lists of final coordinates for the hydrogen atoms, temperature factors, least-squares planes, structure factors, and complete list of bond lengths and angles are available from the authors on request.

## Results and discussion

Figure 2 shows a perspective drawing of the molecule. The type of disorder observed for the title compound is very rarely reported in the common centrosymmetric space group *P2*<sub>1</sub>/*c*. As far as we know, there are only a few compounds, azulene<sup>9</sup> and thieno[3,4-*d*]thiepin,<sup>10</sup> exhibiting a similar type of disorder in this space group. Although the crystal disorder limits the accuracy of the analysis, the C–C bond lengths C1–C16, C3–C4, C8–C10 and C12–C13 of 1.489(9)–1.54(1) Å are as expected. The bridging chains ought to be *anti* to each other according to the space group symmetry, but they are *syn* in the real molecule. The carbon atoms of the methylene groups are slightly inclined towards the centre of molecule. This is indicated by the carbon atoms C1, C12, C3 and C10, which deviate from the neighbouring benzene ring by -0.13(2), -0.15(1), 0.12(1) and 0.07(1) Å, respectively.

**Fig. 2.** A perspective drawing of the molecule with the numbering.

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