Fig. 1. A 50% thermal-ellipsoid plot with the atom numbering.

were anisotropic; all H atoms, found by $\Delta\rho$ map, were refined using a riding model and idealized geometry [C—H = 0.96 Å, $U(H) = 1.2\ U_{eq}(C)$]. 154 parameters were refined, with the weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$, which led to a featureless analysis of variance in terms of $\sin\theta$ and F_o; maximum $\Delta/\sigma = 0.01$ in the last cycle. Maximum and minimum heights in the final $\Delta\rho$ map were 0.31 and -0.31 e Å^{-3}, respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic parameters are

given in Table 1,* bond distances and angles in Table 2. Fig. 1 shows a thermal-ellipsoid plot with the atom numbering.

Related literature. For partially hydrogenated pyrenes see Jussofie (1984). We have found no structures of hydrogenated pyrenes with boat conformation in the Cambridge Structural Database.

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2,11-Dithia[3.3]metacyclophane-9-carboxylic Acid

By Wilfried Assenmacher and Martin Jansen*

Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Strasse 1, W-5300 Bonn 1, Germany

and Ralf Güther and Fritz Vögtle

Institut für Organische Chemie, Universität Bonn, Gerhardt-Domagk-Strasse 1, W-5300 Bonn 1, Germany

Abstract. 3,11-Dithiatricyclo[11.3.1.1^{5,9}]octadeca-1(17),5,7,9(18),13,15-hexaene-17-carboxylic acid, $C_{17}H_{16}O_2S_2$, $M_r = 316.43$, monoclinic, $P2_1/n$, $a = 9.285(4)$, $b = 11.297(3)$, $c = 14.858(5)$ Å, $\beta = 103.80(2)°$, $V = 1513.5(9)$ Å^3, $Z = 4$, $D_x = 1.39$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 3.376$ cm^{-1}, $F(000) = 664$, $T = 293$ K, final $R = 0.051$, $wR = 0.034$ for 3315 independent reflections with $F > 4\sigma(F)$. In the solid state the molecules form dimers with two O—H···O hydrogen bonds between a pair of carboxylic acid groups. The plane formed by the two COOH groups is twisted with respect to the attached arene rings at an angle of 45.9 (1)°. The arene rings are oriented in *syn* conformation forming a dihedral angle of 15.65 (5)°. The S-containing bridges are in a boat–chair arrangement; of three possible *syn* conformers, this has the longest intramolecular S—S distance. The aromatic rings are nearly planar; the substituents, however, display deviations from the aromatic plane.

Experimental. The title compound was synthesized from 2,6-bis(bromomethyl)benzoic acid *tert*-butyl ester and 1,3-bis(mercaptomethyl)benzene in benzene/ethanol 1:1 with NaOH as base, using high-dilution conditions (*cf.* Vögtle, Grütze, Nätscher,

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$. U_{iso} is given for atom H(1), refined isotropically.

	x	y	z	U_{eq}
C(1)	−0.2786 (2)	0.8010 (2)	1.3000 (1)	0.0542 (10)
S(2)	−0.44076 (7)	0.73611 (6)	1.22553 (5)	0.0534 (3)
C(3)	−0.4966 (2)	0.8453 (2)	1.1352 (2)	0.0493 (9)
C(4)	−0.3893 (2)	0.8652 (2)	1.0754 (2)	0.0397 (7)
C(5)	−0.3310 (2)	0.9778 (2)	1.0740 (2)	0.0513 (9)
C(6)	−0.2255 (2)	1.0014 (2)	1.0237 (2)	0.0545 (10)
C(7)	−0.1738 (2)	0.9113 (2)	0.9783 (2)	0.0509 (9)
C(8)	−0.2237 (2)	0.7956 (2)	0.9809 (2)	0.0404 (8)
C(9)	−0.3380 (2)	0.7743 (2)	1.0261 (1)	0.0357 (8)
C(10)	−0.1484 (2)	0.7006 (2)	0.9362 (2)	0.0523 (10)
S(11)	0.04660 (7)	0.68079 (6)	0.99077 (5)	0.0545 (2)
C(12)	0.0518 (3)	0.6300 (2)	1.1074 (2)	0.0523 (10)
C(13)	0.0199 (2)	0.7250 (2)	1.1719 (1)	0.0400 (8)
C(14)	0.1089 (2)	0.8253 (2)	1.1906 (2)	0.0511 (9)
C(15)	0.0726 (3)	0.9160 (2)	1.2438 (2)	0.0539 (10)
C(16)	−0.0520 (3)	0.9076 (2)	1.2785 (2)	0.0489 (9)
C(17)	−0.1401 (2)	0.8072 (2)	1.2623 (1)	0.0409 (8)
C(18)	−0.1013 (2)	0.7157 (2)	1.2102 (1)	0.0387 (7)
C(19)	−0.4060 (2)	0.6530 (2)	1.0215 (1)	0.0378 (7)
O(20)	−0.3333 (1)	0.5615 (1)	1.0316 (1)	0.0478 (6)
O(21)	−0.5514 (2)	0.6545 (1)	1.0027 (1)	0.0476 (6)
H(1)	−0.582 (3)	0.580 (3)	0.996 (2)	0.11 (1)

Table 2. *Selected interatomic distances* (Å), *interatomic angles* (°) *and torsion angles* (°)

C(1)—S(2)	1.798 (2)	S(2)—C(1)—C(17)	116.7 (2)
C(1)—C(17)	1.522 (3)	C(1)—S(2)—C(3)	103.2 (1)
S(2)—C(3)	1.805 (2)	S(2)—C(3)—C(4)	115.4 (2)
C(3)—C(4)	1.502 (3)	C(3)—C(4)—C(9)	123.6 (2)
C(4)—C(5)	1.385 (3)	C(3)—C(4)—C(5)	117.5 (2)
C(4)—C(9)	1.408 (3)	C(5)—C(4)—C(9)	118.7 (2)
C(5)—C(6)	1.393 (4)	C(4)—C(5)—C(6)	120.7 (2)
C(6)—C(7)	1.369 (4)	C(5)—C(6)—C(7)	119.8 (2)
C(7)—C(8)	1.390 (3)	C(6)—C(7)—C(8)	121.8 (2)
C(8)—C(9)	1.404 (3)	C(7)—C(8)—C(10)	117.5 (2)
C(8)—C(10)	1.518 (3)	C(7)—C(8)—C(9)	118.0 (2)
C(9)—C(19)	1.504 (3)	C(9)—C(8)—C(10)	124.5 (2)
C(10)—S(11)	1.813 (2)	C(4)—C(9)—C(8)	120.7 (2)
S(11)—C(12)	1.815 (3)	C(8)—C(9)—C(19)	119.4 (2)
C(12)—C(13)	1.514 (3)	C(4)—C(9)—C(19)	119.8 (2)
C(13)—C(14)	1.392 (3)	C(8)—C(10)—S(11)	114.0 (2)
C(13)—C(18)	1.381 (3)	C(10)—S(11)—C(12)	105.2 (2)
C(14)—C(15)	1.383 (4)	S(11)—C(12)—C(13)	114.5 (2)
C(15)—C(16)	1.379 (4)	C(12)—C(13)—C(18)	120.6 (2)
C(16)—C(17)	1.386 (3)	C(12)—C(13)—C(14)	120.5 (2)
C(17)—C(18)	1.389 (3)	C(14)—C(13)—C(18)	118.9 (2)
C(19)—O(20)	1.224 (3)	C(13)—C(14)—C(15)	120.2 (2)
C(19)—O(21)	1.312 (3)	C(14)—C(15)—C(16)	120.3 (2)
O(21)—H(1)	0.89 (3)	C(15)—C(16)—C(17)	120.3 (2)
O(21)···O(20')	2.665 (2)	C(1)—C(17)—C(16)	119.2 (2)
C(9)···C(18)	3.114 (2)	C(16)—C(17)—C(18)	119.0 (2)
C(6)···C(15)	3.869 (4)	C(1)—C(17)—C(18)	121.7 (2)
S(2)···S(11)	6.369 (2)	C(13)—C(18)—C(17)	121.2 (2)
		C(9)—C(19)—O(21)	113.4 (2)
		C(9)—C(19)—O(20)	123.4 (2)
		O(20)—C(19)—O(21)	123.2 (2)
		C(19)—O(21)—H(1)	107 (2)

S(2)—C(1)—C(17)—C(16)	139.6 (2)	C(9)—C(8)—C(10)—S(11)	−115.5 (2)
C(17)—C(1)—S(2)—C(3)	−70.6 (2)	C(8)—C(9)—C(19)—O(21)	−134.2 (2)
C(1)—S(2)—C(3)—C(4)	65.1 (2)	C(4)—C(9)—C(19)—O(21)	45.8 (3)
S(2)—C(3)—C(4)—C(5)	−119.7 (2)	C(8)—C(10)—S(11)—C(12)	63.7 (2)
S(2)—C(3)—C(4)—C(9)	55.3 (2)	C(10)—S(11)—C(12)—C(13)	−74.2 (2)
C(7)—C(8)—C(10)—S(11)	63.4 (3)	S(11)—C(12)—C(13)—C(14)	−59.4 (3)

Wieder, Weber & Grün, 1975), followed by ester cleavage with trifluoracetic acid at 298 K, and recrystallization from acetone. A colourless plate-shaped air-resistant crystal was glued on a glass fibre for data collection on an Enraf–Nonius CAD-4 diffractometer using a graphite monochromator and Mo $K\alpha$ radiation. Unit-cell parameters were

determined by least-squares refinement of 25 reflections, $18 < 2\theta < 24°$, each measured at four different equivalent positions. 7872 reflections were collected in the range $-13 < h < 13$, $0 < k < 15$, $-20 < l < 17$, using ω–2θ scans [scan width = $(0.8 + 0.35\tan\theta)°$, maximum scan time = 60 s, $2\theta_{max} = 60°$]. 5856 reflections were observed with $I > 2\sigma(I)$. Two intensity reference reflections ($\overline{11}5$, $\overline{4}24$) monitored every hour during data collection gave no indication of crystal decay. After Lorentz and polarization corrections (no absorption correction) and merging symmetry equivalent data, 4065 unique reflections remained; $R_{int} = 0.005$. The structure was solved by direct methods (Sheldrick, 1986) and refined by full-matrix least-squares techniques (Sheldrick, 1976). Scattering factors were those incorporated in *SHELX76* (Sheldrick, 1976). H atoms were included at calculated positions (C—H = 1.08 Å) in the final cycles of refinement, except H(1), which was located by difference Fourier synthesis and refined with an isotropic displacement parameter. 3315 reflections were used to refine 196 parameters; refinement converged to a final $R = 0.051$ and $wR = 0.034$ [$w = 3.483/\sigma^2(F)$]; S was not calculated. Maximum/minimum electron density in the difference Fourier map was $0.8/-0.53$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0.015$. Results of the refinement, and selected distances and angles
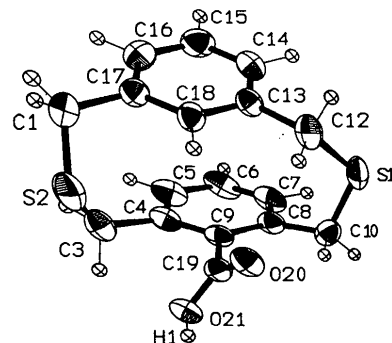

Fig. 1. *ORTEP* (Johnson, 1965) plot of the title compound showing the numbering scheme employed; 50% probability level of the displacement ellipsoids for non-H atoms.
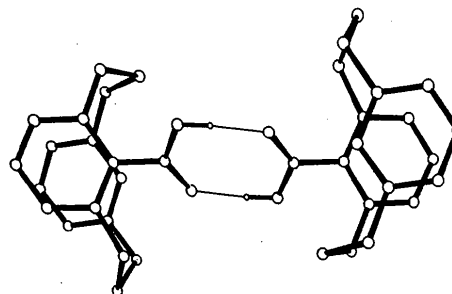

Fig. 2. Perspective drawing of the dimer displaying the boat–chair arrangement of the S-containing bridges.

calculated by *PARST* (Nardelli, 1983) are given in Tables 1 and 2.* The molecular structure and labelling scheme is shown in Fig. 1, and the conformation of the dimer in Fig. 2. Distortions in the benzenoid ring systems have been analysed by calculating best planes, *cf.* Table 3.

Related literature. 2,11-Dithia[3.3]metacyclophanes are a convenient source for preparation of [2.2]metacyclophanes by elimination of sulfur. They have been synthesized with a variety of substituents (Vögtle, 1990). The hydrocarbon [3.3]metacyclophane (Semmelhack, Harrisson, Young, Guiterrez, Shakin & Clardy, 1985) and the unsubstituated 2,11-dithia[3.3]metacyclophane (Anker, Bushnell & Mitchell, 1979) display the *syn* conformation of the two benzene rings in the solid state and in solution, while intra-annular substituents might lead to the *anti* conformation as in 9-methyl- or 9-amino-2,11-dithia[3.3]metacyclophane (Vögtle & Neumann, 1970).

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* Lists of structure factors, anisotropic thermal parameters, complete bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55281 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Deviations (Å) from least-squares planes of the benzoic systems*

Plane 1		Plane 2	
C(1)	0.029 (2)	C(3)	−0.095 (2)
C(12)	0.087 (3)	C(4)	0.021 (3)
C(13)	−0.010 (2)	C(5)	−0.036 (3)
C(14)	−0.008 (3)	C(6)	0.075 (3)
C(15)	0.008 (3)	C(7)	0.041 (3)
C(16)	0.021 (3)	C(8)	−0.034 (3)
C(17)	−0.011 (2)	C(9)	0.026 (2)
C(18)	−0.050 (2)	C(10)	−0.204 (3)
		C(19)	0.096 (2)

Equation of plane 1: $-0.364x + 0.442y - 0.820z = -8.786$ Å; $\chi^2 = 2167$.
Equation of plane 2: $-0.530x + 0.226y - 0.817z = -6.562$ Å; $\chi^2 = 13302$.

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Structure of Phenylazocarboxamide

BY NOBUO OKABE AND HIKARU KISAICHI

Department of Pharmaceutical Sciences, Kinki University, Kowakae 3-4-1, Higashi Osaka, Osaka 577, Japan

Abstract. Phenylazocarboxamide, $C_7H_7N_3O$, $M_r = 149.15$, monoclinic, $P2_1/c$, $a = 5.187$ (3), $b = 14.362$ (5), $c = 19.845$ (4) Å, $\beta = 93.42$ (4)°, $V = 1476$ (1) Å^3, $Z = 8$, $D_m = 1.341$ (2), $D_x = 1.342$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 7.51$ cm^{-1}, $F(000) = 624$, $T = 296$ K, final $R = 0.045$ for 1448 reflections [$I > 3\sigma(I)$]. Two conformers are present. Their structures resemble each other. Each conformer has a fully extended *trans* configuration about the azo double bond. The intermolecular hydrogen bonds are formed between the N and O atoms of the carboxamide groups.

Experimental. Crystals of phenylazocarboxamide were obtained from 50% ethanol as needles, 0.10 ×

0.1 × 0.5 mm. Data were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Lattice parameters were determined by least-squares fit to 2θ values of 25 reflections ($57.2 < 2\theta < 74.3°$). Intensity data were collected up to $2\theta = 120.0°$ using ω–2θ scans with scan speed 32.0° (ω) min^{-1} and scan width $(1.78 + 0.30\tan\theta)°$. The ratio of peak counting time to background counting time was 2:1 at 50 kV and 180 mA. Over h 0–5, k 0–13, l −15–15, 2581 reflections were measured of which 1448 with $I > 3\sigma(I)$ were used for the analysis. Three reference reflections monitored at 100 reflection intervals showed no crystal deterioration. Lorentz, polarization and absorption corrections (maximum and