basis of a careful examination of several relevant crystal structures, that the guanidyl group can and does take part in four different types of specific (implying recognition) interactions, each involving a pair of nearly parallel or convergent hydrogen bonds (Salunke & Vijayan, 1981). The specific interaction observed here between the guanidyl group and the α-carboxylate group of the aspartate ion is type *A* according to the classification of Salunke & Vijayan (1981), and is topologically similar to guanidyl carboxylate interactions in L-arginine dihydrate (Karle & Karle, 1966; Lehmann, Verbist, Hamilton & Koetzle, 1973) and L-arginine L-glutamate monohydrate (Bhat & Vijayan, 1977).

References

BHAT, T. N. & VIJAYAN, M. (1976). *Acta Cryst.* B**32**, 891–895.

BHAT, T. N. & VIJAYAN, M. (1977). *Acta Cryst.* B**33**, 1754–1759.

BHAT, T. N. & VIJAYAN, M. (1978). *Acta Cryst.* B**34**, 2556–2565.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

DERISSEN, J. L., ENDEMAN, H. J. & PEERDEMAN, A. F. (1968). *Acta Cryst.* B**24**, 1349–1354.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

LEHMANN, M. S., VERBIST, J. J., HAMILTON, W. C. & KOETZLE, T. F. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 133–137.

RAO, S. T. (1973). *Acta Cryst.* B**29**, 1718–1720.

SALUNKE, D. M. & VIJAYAN, M. (1981). *Int. J. Pept. Protein Res.* **18**, 348–351.

SALUNKE, D. M. & VIJAYAN, M. (1982). *Acta Cryst.* B**38**, 287–289.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUDHAKAR, V., BHAT, T. N. & VIJAYAN, M. (1980). *Acta Cryst.* B**36**, 125–128.

SUDHAKAR, V. & VIJAYAN, M. (1980). *Acta Cryst.* B**36**, 120–125.

VIJAYAN, M. (1976). In *Handbook of Biochemistry and Molecular Biology*, 3rd ed., edited by G. D. FASMAN. Cleveland, Ohio: CRC Press.

VIJAYAN, M. (1980). *FEBS Lett.* **112**, 135–137.

Structure of Bis{2-[(cyclooctatetraenyl)thio]-4,5-dimethylphenyl} Disulphide. The Product of an Attempted Preparation of a 1,4-Dithia[12]annulene

BY JOHN C. BARNES AND JOHN D. PATON

Chemistry Department, University of Dundee, Dundee DD1 4HN, Scotland

AND WERNER SCHROTH AND LIENA MOEGEL

Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, DDR-402 Halle (Saale), German Democratic Republic

Abstract. $C_{32}H_{30}S_4$, orthorhombic, *Pbcn*, $a = 22.972$, $b = 5.788$, $c = 20.909$ Å, $V = 2780.1$ Å^3, $F(000) = 1152$, $D_c = 1.297$ g cm^{-3}, $Z = 4$, $\mu(\mathrm{Cu}\ K\alpha) = 31.6$ cm^{-1}; $R = 0.0608$, $R_w = 0.0631$ for 513 observations. The title compound was previously thought to be a 1,4-dithia[12]annulene but has now been shown to be a dimeric cyclooctatetraene derivative.

Introduction. 1,4-Dithiaannulenes are heteroanalogues of multi-π-electron hydrocarbons and should show the corresponding properties, particularly aromatic character in special cases. The preparation and investigation of these and other related thia heterocycles have been examined in a series of papers which include the preparation and crystal structures of 8,9-dimethyl-1,6-benzodithiocin (I) (Schroth & Moegel, 1977; Barnes, Schroth & Moegel, 1979) and of 2,3-dimethyl-5a,11a-dihydro-*trans*-cycloocta[1,4]benzodithiin (II) (Kaiser, Richter, Moegel & Schroth, 1979). The latter was reported (Moegel, Schroth & Werner, 1978) to isomerize on reaction with KOBu^t–Me$_2$SO at 313 K to give a product (20%, m.p. 416 K) which

was assigned as a 2,3-benzo-1,4-dithia[12]annulene, assumed from the ^{1}H NMR spectrum and 70 eV mass-spectral fragmentation pattern to be the *cis-cis-cis-trans* isomer (III). The molecular structure of the crystalline product has now been investigated. The correct formulation is that of the title compound, a cyclooctatetraenyl S—S dimer (IV). The discovery of compound (IV) in the solid state has been reconciled with the experimental evidence for (III) in the gas phase and in solution and with the theoretical predictions of (III) as the reaction product, in terms of a simple reaction mechanism. The detailed chemical results and their interpretations will be reported elsewhere (Schroth, Moegel, Barnes & Paton, 1982).

(I)

(II)

(III)

(IV)
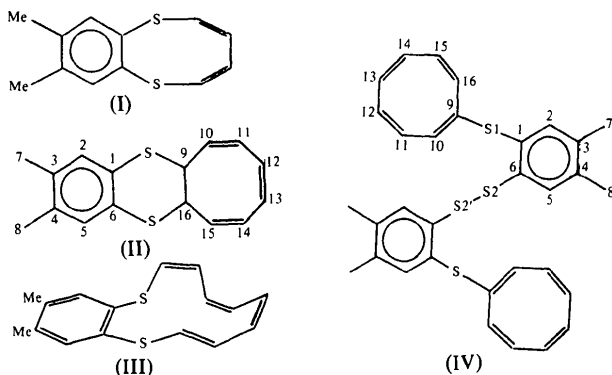
Crystals of (IV) were available from previous work as soft white rectangular prisms. Although the material had to be stored at 268 K the crystals proved sufficiently stable when mounted in capillaries for a structure determination at room temperature (291 ± 2 K). After preliminary examination by oscillation and Weissenberg photographs intensity data were collected by equi-inclination Weissenberg photographs for crystals mounted on the *a* axis (layers 0–3) and the *b* axis (layers 0–5). Intensities were measured with a computer-controlled microdensitometer (SRC Service, Daresbury Laboratory). Absorption corrections were not applied.

All calculations were performed using *SHELX* 76 and *XANADU* (Sheldrick, 1976). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The structure was solved by direct methods using the routine *TANG*. The dimer is oriented so that the two halves of the molecule are related by a twofold axis. The best E map showed the two S atoms and the benzene ring. Successive structure factor calculations and Fourier syntheses revealed the remaining non-hydrogen atoms. Least-squares refinement with an-isotropic S and isotropic C atoms converged at $R =$ 0·13. Refinement continued with anisotropic C atoms and with isotropic H atoms on calculated positions, using the empirical correction for secondary extinction available in *SHELX* 76. Convergence occurred at $R =$ 0·0608, $R_w =$ 0·0631, using 177 refined parameters

with 531 planes observed above background of which 18 reflexions for which $F_o \gg F_c$ and for which examination of the original films suggested that F_o had been incorrectly estimated were omitted in the final calculations.* The weighting scheme used was $w = 1 \cdot 00 / [\sigma^2(F) + 0 \cdot 009432 F^2]$.

Discussion. Atomic coordinates for (IV) are given in Table 1; bond lengths and angles are in Table 2. The dimeric molecule is shown in Fig. 1. The cyclo-octatetraenyl group has typical dimensions for a

---

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters, with estimated standard deviations in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

|	x	y	z	U_{eq} (Å^2)
S(1)	3199 (2)	−1155 (6)	2388 (2)	61 (2)
S(2)	4578 (1)	−1282 (5)	2346 (2)	47 (2)
C(1)	3602 (6)	973 (25)	2784 (6)	44 (9)
C(2)	3324 (6)	2477 (29)	3170 (6)	50 (10)
C(3)	3606 (7)	4087 (24)	3578 (6)	48 (10)
C(4)	4224 (6)	4062 (21)	3571 (6)	41 (10)
C(5)	4523 (6)	2462 (23)	3198 (8)	42 (8)
C(6)	4212 (6)	849 (20)	2839 (6)	36 (9)
C(7)	3250 (6)	5785 (24)	3964 (6)	72 (11)
C(8)	4579 (7)	5750 (18)	3974 (7)	74 (11)
C(9)	3279 (4)	−324 (21)	1567 (5)	34 (7)
C(10)	3061 (5)	−1756 (18)	1123 (7)	50 (9)
C(11)	2994 (7)	−1437 (20)	424 (7)	54 (9)
C(12)	3415 (9)	−909 (29)	30 (8)	88 (14)
C(13)	4034 (6)	−522 (24)	205 (8)	66 (11)
C(14)	4237 (6)	998 (28)	632 (8)	67 (10)
C(15)	3897 (7)	2624 (23)	1025 (6)	55 (9)
C(16)	3485 (5)	2068 (21)	1443 (7)	50 (9)
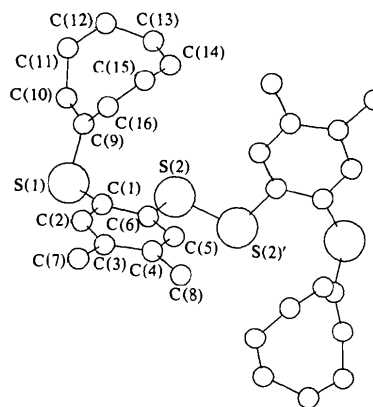
Fig. 1. Dimeric molecule (IV) viewed normal to the plane S(1)C(9)C(14).

Table 2. *Bond lengths* (Å) *and bond angles* (°), *with estimated standard deviations in parentheses*

S(1)–C(1)	1·749 (14)	C(4)–C(8)	1·527 (19)
S(1)–C(9)	1·791 (12)	C(5)–C(6)	1·395 (19)
S(2)–S(2)	2·044 (7)	C(9)–C(10)	1·342 (17)
S(2)–C(6)	1·813 (13)	C(9)–C(16)	1·486 (17)
C(1)–C(2)	1·347 (20)	C(10)–C(11)	1·482 (20)
C(1)–C(6)	1·407 (20)	C(11)–C(12)	1·306 (23)
C(2)–C(3)	1·419 (20)	C(12)–C(13)	1·486 (24)
C(3)–C(4)	1·421 (20)	C(13)–C(14)	1·337 (22)
C(3)–C(7)	1·510 (20)	C(14)–C(15)	1·473 (21)
C(4)–C(5)	1·391 (19)	C(15)–C(16)	1·328 (19)
C(1)–S(1)–C(9)	102·2 (6)	S(2)–C(6)–C(1)	116·8 (10)
S(2)'–S(2)–C(6)	105·4 (6)	S(2)–C(6)–C(5)	121·6 (11)
S(1)–C(1)–C(2)	119·3 (10)	C(1)–C(6)–C(5)	121·3 (12)
S(1)–C(1)–C(6)	121·9 (10)	S(1)–C(9)–C(10)	117·3 (9)
C(2)–C(1)–C(6)	117·1 (12)	S(1)–C(9)–C(16)	116·7 (9)
C(1)–C(2)–C(3)	124·7 (13)	C(10)–C(9)–C(16)	125·0 (11)
C(2)–C(3)–C(4)	116·2 (12)	C(9)–C(10)–C(11)	130·2 (11)
C(2)–C(3)–C(7)	120·1 (13)	C(10)–C(11)–C(12)	125·0 (14)
C(4)–C(3)–C(7)	123·6 (12)	C(11)–C(12)–C(13)	126·1 (15)
C(3)–C(4)–C(5)	120·4 (12)	C(12)–C(13)–C(14)	126·7 (13)
C(3)–C(4)–C(8)	121·4 (12)	C(13)–C(14)–C(15)	127·5 (13)
C(5)–C(4)–C(8)	118·2 (12)	C(14)–C(15)–C(16)	126·2 (13)
C(4)–C(5)–C(6)	119·6 (12)	C(9)–C(16)–C(15)	124·6 (12)

monosubstituted derivative (Bordner, Parker & Stanford, 1972). The average values may be compared with those for cyclooctatetraenecarboxylic acid (Shoemaker, Kindler, Sly & Srivastava, 1965) given in parentheses: C–C 1·482 (1·470), C=C 1·319 Å (1·322 Å), C–C=C 126·4° (126·4°). The torsion angles C=C–C=C lie between 55·6 (15) and 59·3 (13)°, averaging 57·1° (57·1°). The angle between the normals to the planes defined by the double bonds [C(9), (10), (13), (14)] and [C(11), (12), (15), (16)] is 0·8 (7)°. The only significant deviation from an idealized tub structure occurs at C(10) where the angle C(9)–C(10)–C(11) is opened out to 130·2° by the close contact C(10)···S(1) 2·686 Å, compared with C(16)···S(1) 2·795 Å. The conformation requires the protons on C(10) and C(16) to be remote from S(1).

The three C–S bonds are barely significantly different [average 1·784 (13) Å, with a range of 5σ]. S(1) and S(2) both lie on the same side of the benzene ring, 0·165 (6) and 0·060 (6) Å respectively above the plane, whereas in (I) the S atoms are on opposite sides of the benzene plane and 0·175 Å from it.

The dimer is completed by S(2)–S(2)', 2·044 Å, lying across the twofold crystallographic axis. The torsion angle C(6)–S(2)–S(2)'–C(6)' is 90·8 (8)°. The normals to the two benzene-ring planes intersect at 82 (2)°.

This structure could be compared to that of the precursor (II), a cyclooctatriene derivative. However, the structure given by Kaiser, Richter, Moegel & Schroth (1979) shows some surprising features. C(9)–C(16), which is formally a single bond, is only 1·38 Å. These two atoms have by far the largest thermal parameters (apart from the methyl groups): B_{iso} values are 8·18, 8·27 Å^2 compared with an average for the other ring atoms of 5·00 Å^2. Also, the anisotropic thermal parameters of these bridgehead atoms suggest that the major axes of the ellipsoids are perpendicular to the molecular plane. These observations seem very improbable for an ordered structure. It seems likely that there is disorder at C(9), C(16) so that the crystals of (II) contain either two conformers of the cyclooctatriene or possibly include some molecules of the bridged cyclooctatetraene.

References

Barnes, J. C., Schroth, W. & Moegel, L. (1979). *Acta Cryst.* B35, 3833–3834.

Bordner, J., Parker, R. G. & Stanford, R. H. (1972). *Acta Cryst.* B28, 1069–1075.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kaiser, J., Richter, R., Moegel, L. & Schroth, W. (1979). *Tetrahedron*, 35, 505–509.

Moegel, L., Schroth, W. & Werner, B. (1978). *Chem. Commun.* pp. 57–58.

Schroth, W. & Moegel, L. (1977). *Z. Chem.* 17, 441–443.

Schroth, W., Moegel, L., Barnes, J. C. & Paton, J. D. (1982). In preparation.

Sheldrick, G. (1976). *SHELX* 76 and *XANADU*. Programs for crystal structure determination. Cambridge Univ., England.

Shoemaker, D. P., Kindler, H., Sly, W. G. & Srivastava, R. C. (1965). *J. Am. Chem. Soc.* 87, 482–487.

α-Methyl-*trans*-cinnamic Acid (m.p. 355 K)

By Robert F. Bryan and Deborah H. White

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, USA

Abstract. $C_{10}H_{10}O_2$, monoclinic, $P2_1/c$, $a = 7·633$ (2), $b = 11·454$ (3), $c = 11·514$ (3) Å, $\beta = 120·91$ (2)°, $U = 863·7$ Å^3, $M_r = 162·2$, $D_x = 1·247$ Mg m^{-3}, $Z = 4$, D_m (flotation in aqueous KI) = 1·24 Mg m^{-3}, $F(000) = 344$, $\mu(Cu\ K\alpha) = 0·71$ mm^{-1}. The structure was solved by the multisolution tangent-formula method. Least-