

**trans-10-Benzyl-9-phenyl-9,10-dihydro-9-arsanthracene**

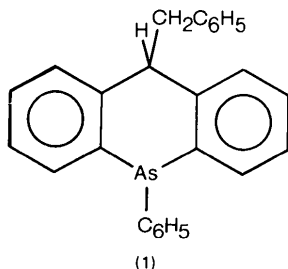
BY C. H. STAM

*Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018WV Amsterdam, The Netherlands*

(Received 18 October 1979; accepted 5 November 1979)

**Abstract.**  $C_{26}H_{21}As$ , monoclinic,  $P2_1$ ,  $a = 12.322$  (1),  $b = 6.308$  (1),  $c = 13.059$  (1) Å,  $\beta = 95.92$  (1)°,  $Z = 2$ . The arsaanthracene ring system is folded with an angle of 133° between the benzene rings. The molecules show conformational chirality, the crystals consisting of molecules of only one type.

**Introduction.** In the preparation of the title compound (1) two isomers were obtained, one liquid at room temperature, the other solid with melting point 304–305 K (Weusting, 1977). The two compounds were assumed to be *cis* and *trans* isomers with the phenyl and benzyl groups on the same side and on opposite sides of the arsaanthracene ring system respectively. Since it was not possible to distinguish between the two compounds spectroscopically, a crystal structure determination of the solid isomer was undertaken. It turned out to consist of molecules with the *trans* configuration.



A crystal  $0.08 \times 0.3 \times 0.13$  mm was mounted on a Nonius CAD-4 diffractometer and 1684 independent reflexions were collected with graphite-monochromatized  $Cu K\alpha$  radiation. 53 of these had  $I < 2\sigma(I)$  and were treated as unobserved. The complete structure, so far as the non-hydrogen atoms are concerned, was derived directly from an  $(E^2 - 1)$  Patterson synthesis. Anisotropic block-diagonal least-squares refinement, followed by a difference synthesis, led to the location of the H atoms. Further refinement with fixed isotropic H atoms at calculated positions resulted in an  $R$  of 3.9%. A difference synthesis at this stage showed absorption effects around the As atom. After application of an absorption correction and inclusion of an extinction parameter further refinement converged to  $R =$

Table 1. Fractional coordinates with their *e.s.d.*'s in parentheses ( $\times 10^5$  for As,  $\times 10^4$  for C,  $\times 10^3$  for H)

	<i>x</i>	<i>y</i>	<i>z</i>
As	29783 (4)	50000	22033 (4)
C(1)	1900 (4)	2935 (9)	1670 (4)
C(2)	2234 (4)	1106 (9)	1196 (4)
C(3)	1457 (4)	-341 (12)	809 (4)
C(4)	352 (4)	57 (18)	885 (4)
C(5)	24 (4)	1810 (11)	1353 (4)
C(6)	785 (5)	3285 (10)	1730 (4)
C(7)	4050 (4)	2897 (10)	2688 (4)
C(8)	4156 (4)	1075 (9)	2103 (4)
C(9)	4947 (5)	-419 (12)	2449 (5)
C(10)	5624 (4)	-75 (20)	3352 (5)
C(11)	5528 (5)	1716 (13)	3924 (5)
C(12)	4755 (5)	3217 (12)	3590 (4)
C(13)	2330 (5)	5679 (9)	3475 (4)
C(14)	2156 (5)	4140 (10)	4201 (5)
C(15)	1602 (5)	4604 (12)	5030 (4)
C(16)	1215 (6)	6659 (12)	5159 (5)
C(17)	1391 (7)	8176 (12)	4445 (6)
C(18)	1952 (6)	7692 (10)	3609 (5)
C(19)	3433 (4)	653 (8)	1105 (4)
C(20)	3855 (5)	1934 (10)	199 (4)
C(21)	3189 (4)	1523 (10)	-818 (4)
C(22)	2432 (6)	2983 (11)	-1232 (4)
C(23)	1782 (6)	2536 (12)	-2148 (5)
C(24)	1898 (5)	653 (10)	-2649 (4)
C(25)	2656 (6)	-781 (11)	-2259 (5)
C(26)	3300 (5)	-346 (13)	-1350 (5)
H(3)	172	-190	44
H(4)	-25	-125	58
H(5)	-84	192	143
H(6)	51	461	208
H(9)	503	-199	200
H(10)	622	-142	361
H(11)	606	184	463
H(12)	468	450	404
H(14)	246	243	411
H(15)	147	329	561
H(16)	76	694	580
H(17)	109	967	455
H(18)	208	884	305
H(19)	351	-113	94
H(201)	468	137	14
H(202)	380	348	38
H(22)	236	437	-85
H(23)	118	357	-243
H(24)	138	25	-336
H(25)	275	-237	-268
H(26)	389	-163	-102

Table 2. Bond lengths (Å) and angles (°)

As—C(1)	1.938 (5)	C(11)—C(12)	1.381 (10)
As—C(7)	1.932 (6)	C(13)—C(14)	1.389 (9)
As—C(13)	1.963 (6)	C(13)—C(18)	1.370 (9)
C(1)—C(2)	1.392 (8)	C(14)—C(15)	1.370 (9)
C(7)—C(8)	1.394 (8)	C(15)—C(16)	1.397 (11)
C(1)—C(6)	1.402 (8)	C(16)—C(17)	1.369 (11)
C(7)—C(12)	1.404 (7)	C(17)—C(18)	1.385 (11)
C(2)—C(3)	1.380 (8)	C(19)—C(20)	1.565 (8)
C(8)—C(9)	1.397 (9)	C(20)—C(21)	1.510 (7)
C(2)—C(19)	1.521 (7)	C(21)—C(22)	1.381 (9)
C(8)—C(19)	1.524 (7)	C(21)—C(26)	1.382 (10)
C(3)—C(4)	1.398 (7)	C(22)—C(23)	1.398 (9)
C(9)—C(10)	1.389 (9)	C(23)—C(24)	1.371 (10)
C(4)—C(5)	1.346 (12)	C(24)—C(25)	1.361 (9)
C(10)—C(11)	1.366 (14)	C(25)—C(26)	1.386 (9)
C(5)—C(6)	1.376 (9)		
C(1)AsC(7)	94.4 (2)	C(7)C(12)C(11)	120.9 (7)
C(1)AsC(13)	97.3 (2)	AsC(13)C(14)	122.0 (5)
C(7)AsC(13)	101.3 (3)	AsC(13)C(18)	118.9 (5)
AsC(1)C(2)	119.6 (4)	C(14)C(13)C(18)	118.8 (6)
AsC(7)C(8)	119.1 (4)	C(13)C(14)C(15)	121.0 (6)
AsC(1)C(6)	120.9 (4)	C(14)C(15)C(16)	119.8 (7)
AsC(7)C(12)	121.3 (5)	C(15)C(16)C(17)	119.1 (7)
C(2)C(1)C(6)	119.5 (5)	C(16)C(17)C(18)	120.7 (7)
C(8)C(7)C(12)	119.6 (6)	C(13)C(18)C(17)	120.6 (6)
C(1)C(2)C(3)	119.0 (5)	C(2)C(19)C(8)	112.8 (5)
C(7)C(8)C(9)	118.7 (5)	C(2)C(19)C(20)	111.3 (4)
C(1)C(2)C(19)	121.6 (5)	C(8)C(19)C(20)	110.2 (4)
C(7)C(8)C(19)	122.2 (5)	C(19)C(20)C(21)	112.5 (5)
C(3)C(2)C(19)	119.3 (5)	C(20)C(21)C(22)	120.9 (5)
C(9)C(8)C(19)	119.0 (5)	C(20)C(21)C(26)	121.0 (6)
C(2)C(3)C(4)	119.9 (7)	C(22)C(21)C(26)	118.0 (5)
C(8)C(9)C(10)	120.5 (8)	C(21)C(22)C(23)	120.3 (6)
C(3)C(4)C(5)	121.3 (7)	C(22)C(23)C(24)	120.3 (6)
C(9)C(10)C(11)	121.0 (9)	C(23)C(24)C(25)	119.9 (6)
C(4)C(5)C(6)	119.5 (5)	C(24)C(25)C(26)	120.0 (7)
C(10)C(11)C(12)	119.3 (6)	C(21)C(26)C(25)	121.5 (7)
C(1)C(6)C(5)	120.6 (6)		

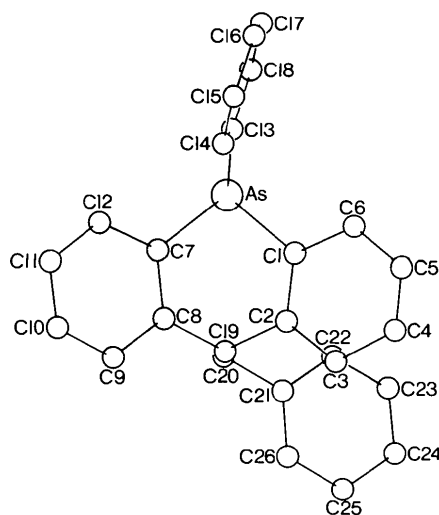


Fig. 1. Projection of the molecule on to the plane of C(1), C(2), C(8) and C(7).

3.2%. In the calculations the anomalous contribution to the scattering of As was taken into account. A similar refinement of the inverted structure resulted in  $R = 2.9\%$ , the inverted structure apparently being correct for the crystal under investigation. In the refinement the weighting function  $w = 0.42 + F_o + 0.011F_o^2$  was used. Atomic coordinates are given in Table 1,\* bond lengths and angles in Table 2. The atomic numbering is indicated in Fig. 1.

**Discussion.** The two chemically equivalent bonds As—C(1) and As—C(7) are equal within the limits of accuracy (average 1.935 Å), but differ by about 0.03 Å from As—C(13) (1.963 Å). These values are within the range (1.94–1.99 Å) found for the As—C lengths in a number of related arsaanthracene derivatives (Kennard *et al.*, 1971; Allen, Coppola, Kennard, Mann, Motherwell & Watson, 1970). The same applies to the angle C(1)AsC(7) of 94.4° (range 92–96°). Corresponding bond lengths and angles in the chemically equivalent halves of the dihydroarsaanthracene moiety do not differ significantly. The shape of the molecule is indicated in Fig. 1. The dihydroarsaanthracene ring system is folded along the line As—C(19) with an angle of 133° between the planes of the two benzene rings. The phenyl and benzyl groups are on opposite sides. The phenyl group is deflected towards one side of the molecule, As being 0.17 Å out of the plane of the phenyl ring which itself is planar within 0.011 Å. The benzyl group is in an asymmetric staggered position about the single bond C(19)—C(20). The shortest contact between the benzyl group and the 9-arsaanthracene ring system is 3.36 Å, between C(21) and C(3). The conformation about C(19)—C(20) requires some further discussion.

In the free molecule there will be rotation around the single bond C(19)—C(20) with the three staggered conformations (Fig. 2) representing minima in the torsional energy. Of these, the symmetrical conformation (I), in which the benzyl group is facing the 9-arsaanthracene ring system, will have a higher energy than conformations (II) and (III). These two conformations are chiral and in solution they will rapidly interconvert. In the crystal the ability to rotate about the single bond is lost and the molecules have to assume a definite conformation. The conformation adopted is one of the asymmetric staggered chiral conformations. Since the space group is  $P2_1$ , all molecules in any one crystal have to possess the same chirality. As the two chiral staggered conformations are equivalent, the probability that crystals of either chirality are formed is the same.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34891 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

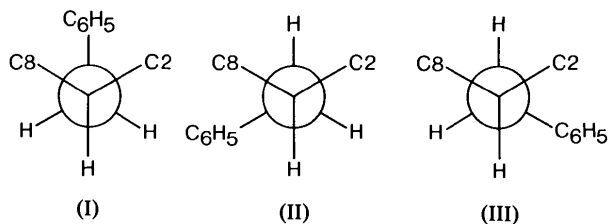


Fig. 2. Newman projection along C(19)–C(20) of the three staggered conformations around this bond.

Therefore, right- and left-handed crystals should occur in approximately equal numbers. This is another example of spontaneous resolution of so-called switchable molecules (Rogers, 1975) into chiral crystals of either chirality.

We have not been able to verify the occurrence of the enantiomorphous crystal forms. The crystals are fine needles along [010] with the forms {001} and  $\bar{1}01$

dominating. No clear top faces enabling the distinction between the enantiomorphous forms were present. Because of the small amount of substance at our disposal, no recrystallization has been attempted.

I thank Professor F. Bickelhaupt and Dr R. J. M. Weusting for suggesting the investigation and providing the crystals.

#### References

- ALLEN, D. W., COPPOLA, J. C., KENNARD, O., MANN, F. G., MOTHERWELL, W. D. S. & WATSON, D. G. (1970). *J. Chem. Soc. C*, pp. 810–815.
- KENNARD, O., WAMPLER, D. K., COPPOLA, J. C., MOTHERWELL, W. D. S., MANN, F. G., WATSON, D. G., MACGILLAVRY, C. H., STAM, C. H. & BENCI, P. (1971). *J. Chem. Soc. C*, pp. 1511–1515.
- ROGERS, D. (1979). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, p. 233. Copenhagen: Munksgaard.
- WEUSTING, R. J. M. (1977). Thesis, Amsterdam.

*Acta Cryst.* (1980). B36, 457–459

## The Structure of Tetrachlorotetrakis(diethyl sulfide)dimolybdenum(II)

BY F. ALBERT COTTON AND PHILLIP E. FANWICK

*Department of Chemistry, Texas A & M University, College Station, Texas 77843, USA*

(Received 7 August 1979; accepted 25 October 1979)

**Abstract.**  $[\text{Mo}_2(\text{C}_4\text{H}_{10}\text{S})_4\text{Cl}_4]$ ,  $\text{C}_{16}\text{H}_{40}\text{Cl}_4\text{Mo}_2\text{S}_4$ , monoclinic,  $Cc$ ,  $a = 18.769$  (5),  $b = 10.096$  (2),  $c = 15.793$  (6) Å,  $\beta = 109.94$  (2)°,  $V = 2813$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $d_x = 1.640$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.537$  mm<sup>-1</sup>. The structure was solved using Patterson and Fourier techniques with diffractometer data and refined by least-squares methods to a final  $R$  of 0.041 based on 1567 independent observed reflections. The molecule possesses non-crystallographic symmetry and consists of two *trans* square-planar arrangements of chloride and sulfide ligands bound to each Mo atom and rotated by 90° with respect to each other. The Mo–Mo distance is 2.144 (1) Å.

**Introduction.** In 1974 the synthesis of a series of tetrahalodimolybdenum(II) dimers of the type  $\text{Mo}_2X_4L_n$ , where  $L$  is either a unidentate ( $n = 4$ ) or bidentate ( $n = 2$ ) sulfide or phosphine ligand, was reported (San Filippo, Sniadoch & Grayson, 1974). There has not yet been a structural characterization of any of these compounds. Since molecules of this type are quite

numerous it was considered worthwhile to determine the structure of at least one to serve as a benchmark.

Crystals of  $[\text{Mo}_2\{(\text{C}_2\text{H}_5)_2\text{S}\}_4\text{Cl}_4]$  were prepared by the literature method and were obtained as dark-blue tablets by evaporation of a methylene chloride solution. The crystals grew with prominent (001) faces. They were extremely dichroic, being dark blue when the plane of polarization was parallel to the  $c$  axis and nearly clear for  $a$  polarization. 2221 reflections were measured for  $0^\circ < 2\theta \leq 45^\circ$  on a Syntex  $P\bar{1}$  four-circle diffractometer using graphite-monochromated  $\text{Mo } K\alpha$  radiation and a  $\theta$ – $2\theta$  scan procedure. The crystal had dimensions  $0.5 \times 0.3 \times 0.1$  mm. No absorption correction was applied. The 1567 reflections with  $I > 3\sigma(I)$  were used for all refinements after  $L_p$  corrections were applied. The cell dimensions were based on the centering of 15 strong reflections with  $16^\circ < 2\theta < 30^\circ$ .

Systematic absences indicated space groups  $Cc$  (No. 9) or  $C2/c$  (No. 15). Since a Howells–Phillips–Rogers test strongly indicated that the unit cell was noncentrosymmetric, refinement was commenced with