

## Refinements of the Structures of 9,10-Dibromo- and 9,10-Dichloroanthracene

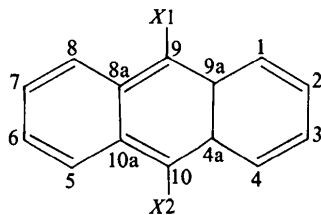
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**Abstract.** 9,10-Dibromoanthracene,  $C_{14}H_8Br_2$ ,  $M_r = 336.05$ , triclinic,  $P\bar{1}$ ,  $a = 4.068$  (1),  $b = 8.902$  (1),  $c = 16.134$  (2) Å,  $\alpha = 99.11$  (1),  $\beta = 96.91$  (2),  $\gamma = 100.39$  (1)°,  $V = 560.7$  (3) Å<sup>3</sup>,  $Z = 2$  (2 half-molecules/asymmetric unit),  $D_m$  (weight loss in  $CCl_4$ ) = 1.983,  $D_x = 1.990$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda\alpha_1 = 0.70930$  Å,  $\mu = 70$  cm<sup>-1</sup>,  $F(000) = 324$ ,  $T = 293$  K,  $R = 0.079$ ,  $0.066$  for 1057, 1222 observed reflections (two data sets; weighted mean cell parameters given above). 9,10-Dichloroanthracene,  $C_{14}H_8Cl_2$ ,  $M_r = 247.12$ , monoclinic,  $P2_1/a$ ,  $a = 7.041$  (1),  $b = 17.950$  (2),  $c = 8.613$  (1) Å,  $\beta = 102.97$  (1)°,  $V = 1060.8$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.547$  g cm<sup>-3</sup>,  $\mu = 5.1$  cm<sup>-1</sup>,  $F(000) = 504$ ,  $R = 0.030$  for 1545 observed reflections. The dibromo structure contains two approximately planar independent molecules lying on symmetry centres at 0,0,0 and  $0, \frac{1}{2}, \frac{1}{2}$ ; the dichloro molecule is slightly folded [by  $0.5$  (1)°] about the C(9)–C(10) axis. Bond lengths in both molecules are similar to those in anthracene, but with some bond-angle differences due to the presence of the halogen substituents, the endocyclic angles at the 9 and 10 positions averaging  $123.9$  (4) and  $123.3$  (2)°, respectively, in the dibromo and dichloro molecules.

**Introduction.** Two-dimensional studies (Trotter, 1958, 1959) of the structures 9,10-dibromo- and 9,10-dichloroanthracene [(I),  $X = Br, Cl$ ] have now been completed with three-dimensional data.



(I)

**Experimental.** Yellow crystals from petroleum ether, plates elongated along  $a$  with (001) developed for

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dibromo compound [(010) for dichloro]; for dibromo compound, two crystals used, first rather thin with weaker intensities (giving high  $R$  value), second thicker but with more severe absorption. Experimental details in Table 1; data common to both dibromo crystals [and dichloro crystal]: CAD-4 diffractometer; intensities for  $\theta \leq 22.5^\circ$  [ $25^\circ$ ];  $hkl$  0 to 4,  $-9$  to 9,  $-17$  to 17 [0 to 8, 0 to 21,  $-10$  to 10];  $\omega-2\theta$  scan,  $\omega$ -scan width ( $1.0 + 0.35 \tan\theta$ )°, extended 25% on each side for background measurement; horizontal aperture ( $2 + 0.5 \tan\theta$ ) mm, vertical aperture 4 mm; three standard reflections;  $L_p$  and absorption corrections;  $\sigma^2(I) = S + 4(B_1 + B_2)$ ,  $S = \text{scan}$ ,  $B_1$  and  $B_2 = \text{background counts}$ . Structures [starting from results of Trotter (1958), with molecular centres shifted to 0,0,0 and  $0, \frac{1}{2}, \frac{1}{2}$ ; and Trotter (1959)] refined (separately with two data sets for dibromo compound) by full-matrix least squares on  $F$  with *SHELX76* (Sheldrick, 1976); anisotropic thermal parameters for non-hydrogen atoms; H atoms in calculated positions ( $C-H = 1$  Å,  $U = 0.05$  Å<sup>2</sup>) not refined; atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** A comparison of the positional parameters from the two dibromo crystals shows no significant differences, a half-normal probability plot (Abrahams & Keve, 1971) being a straight line through the origin of slope 0.9. The standard deviations from the first, smaller, crystal are about double those from the larger crystal, and the weighted (1:4) means for the two sets of results were taken as the final positional parameters (Table 2).† The thermal parameters from the second crystal (particularly  $U_{11}$ ) are somewhat larger than from the smaller crystal, indicating probable inaccuracy in the absorption correction; it was necessary to cut the elongated crystals, and accurate definition of the cut edges was difficult. Final positional parameters for the dichloro compound are included in Table 2.

† Positional parameters (from the two data sets for the dibromo compound), anisotropic thermal parameters, calculated hydrogen positions, bond lengths and angles, mean planes and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42815 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

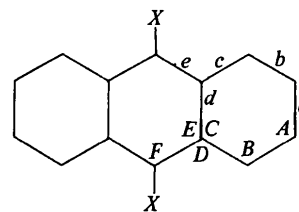
Table 1. *Experimental details*

	9,10-Dibromoanthracene Crystal 1	9,10-Dibromoanthracene Crystal 2	9,10-Dichloro- anthracene
Crystal dimensions (mm)	0.4 × 0.18 × 0.05	0.4 × 0.3 × 0.15	0.4 × 0.08 × 0.4
Reflections for cell: number ( $\pm\theta$ )	18	16	17
$\theta$ range ( $^\circ$ )	4.9–21.8	3.2–21.8	4.5–24.6
$a$ ( $\text{Å}$ )	4.074 (3)*	4.067 (1)*	7.041 (1)
$b$ ( $\text{Å}$ )	8.901 (3)	8.902 (1)	17.950 (2)
$c$ ( $\text{Å}$ )	16.148 (4)	16.131 (2)	8.613 (1)
$\alpha$ ( $^\circ$ )	99.12 (3)	99.11 (1)	90
$\beta$ ( $^\circ$ )	96.81 (4)	96.93 (2)	102.97 (1)
$\gamma$ ( $^\circ$ )	100.37 (4)	100.39 (1)	90
$V$ ( $\text{Å}^3$ )	562.2 (8)	560.5 (3)	1060.8 (4)
$\omega$ -scan speed ( $^\circ \text{ min}^{-1}$ )	1.5–10	0.8–10	0.8–10
Check intensity variation ( $\pm\%$ )	1	0.5	5% decay
Transmission factors	0.27–0.71	0.12–0.39	0.84–0.96
Reflections measured	1726	1726	2099
$R_{\text{int}}(0kl)$	0.050	0.019	0.014
Unique non-zero reflections	1290	1354	1719
Reflections with $I \geq 2\sigma(I)$	1057	1222	1545
Parameters refined	145	145	145
$w^{-1}$	$\sigma^2(F) + 0.005F^2$	$\sigma^2(F) + 0.01F^2$	$\sigma^2(F) + 0.002F^2$
$R [I \geq 2\sigma(I)]$	0.079	0.066	0.030
$wR$	0.101	0.087	0.058
$S$	1.11	0.66	0.88
$R$ (all reflexions)	0.094	0.071	0.038
Max. $\Delta/\sigma$	0.02	0.3	0.03
Final difference density ( $e \text{ Å}^{-3}$ )	–1.2 to +1.7	–1.2 to +1.4	–0.25 to +0.17

\* Weighted mean cell parameters are given in the *Abstract*. The CAD-4 software persistently chose a cell related to that used in the analysis by the transformation  $(100/010/101)$ ,  $a' = 4.07$ ,  $b' = 8.90$ ,  $c' = 16.18 \text{ Å}$ ,  $\alpha' = 78.3$ ,  $\beta' = 82.3$ ,  $\gamma' = 79.6^\circ$ ; this latter cell is not a proper reduced cell, since the Niggli matrix does not satisfy the required relationships (*International Tables for X-ray Crystallography*, 1969),  $c'$  being larger, although only slightly, than  $c$ . A discussion of alternative unit cells for the isostructural  $\beta$ -form of 9,10-dichloroanthracene is given by Krauss, Schulz, Nesper & Thiemann (1979).

Table 2. *Final positional parameters for 9,10-dibromoanthracene (weighted mean parameters, fractional,  $\times 10^5$  for Br,  $\times 10^4$  for C) and 9,10-dichloroanthracene (fractional,  $\times 10^5$ ), and equivalent isotropic thermal parameters  $[(U_{11} + U_{22} + U_{33})/3, \text{Å}^2 \times 10^3]$* 

	$x$	$y$	$z$	$U_{\text{eq}}$
<b>9,10-Dibromoanthracene</b>				
Br	–7058 (24)	–14878 (10)	17220 (5)	71
Br'	2549 (19)	16809 (7)	38090 (5)	50
C(1)	3917 (19)	1640 (9)	1576 (4)	53
C(2)	6106 (22)	3015 (10)	1599 (5)	57
C(3)	6477 (21)	3583 (9)	860 (7)	68
C(4)	4689 (18)	2873 (8)	115 (6)	53
C(4a)	2255 (17)	1423 (8)	29 (4)	44
C(9)	–330 (18)	–615 (8)	723 (4)	49
C(9a)	1913 (15)	788 (7)	790 (4)	39
C(1')	2701 (17)	4998 (8)	3454 (4)	43
C(2')	3843 (20)	6378 (9)	3199 (5)	58
C(3')	3620 (18)	7804 (8)	3698 (5)	50
C(4')	2416 (17)	7830 (7)	4435 (4)	43
C(4a')	1191 (15)	6423 (6)	4741 (4)	32
C(9')	138 (15)	3618 (6)	4508 (4)	33
C(9a')	1316 (15)	4961 (6)	4222 (4)	34
<b>9,10-Dichloroanthracene</b>				
Cl(1)	27014 (8)	29804 (3)	54759 (5)	50
Cl(2)	10854 (7)	11973 (3)	–9184 (5)	52
C(1)	25706 (31)	13072 (11)	52188 (24)	48
C(2)	25453 (35)	5491 (12)	52246 (25)	59
C(3)	21758 (36)	1450 (12)	37846 (28)	60
C(4)	18542 (28)	5056 (11)	23666 (23)	49
C(4a)	18636 (23)	12996 (10)	22907 (21)	36
C(5)	11675 (27)	28850 (13)	–6676 (22)	46
C(6)	11838 (30)	36426 (13)	–6588 (25)	53
C(7)	15403 (30)	40429 (12)	7652 (26)	53
C(8)	18799 (26)	36782 (11)	21889 (23)	43
C(8a)	18847 (21)	28870 (10)	22548 (19)	35
C(9)	22363 (24)	24856 (10)	36894 (19)	33
C(9a)	22337 (24)	17096 (10)	37531 (20)	35
C(10)	15272 (23)	16987 (10)	8628 (20)	37
C(10a)	15206 (22)	24746 (10)	7897 (18)	34

Table 3. *Mean bond lengths ( $\text{Å}$ ) and angles ( $^\circ$ ) in anthracene, 9,10-dibromoanthracene and 9,10-dichloroanthracene (numbers in parentheses are standard deviations of the means, those for the dibromo and dichloro derivatives being the larger of those calculated from the LS e.s.d.'s and from the r.m.s. deviations from the mean)*

	Anthracene		Dibromoanthracene	Dichloroanthracene
	Cruickshank (1956)	Lehmann & Pawley (1972)		
$a$	1.419 (6)	1.432 (3)	1.398 (17)	1.403 (7)
$b$	1.366 (4)	1.368 (2)	1.352 (12)	1.360 (1)
$c$	1.433 (3)	1.433 (2)	1.441 (6)	1.426 (2)
$d$	1.436 (4)	1.439 (3)	1.443 (6)	1.433 (2)
$e$	1.399 (3)	1.402 (2)	1.382 (4)	1.397 (2)
$X-C$	—	—	1.912 (5)	1.744 (1)
$A$	120.7 (2)	120.4 (2)	120.8 (6)	120.7 (2)
$B$	120.6 (2)	120.9 (1)	121.5 (4)	120.9 (1)
$C$	118.7 (1)	—	117.7 (3)	118.4 (2)
$D$	121.8 (2)	121.8 (1)	124.2 (3)	123.2 (2)
$E$	119.5 (2)	—	118.1 (3)	118.4 (1)
$F$	121.0 (3)	121.1 (2)	123.9 (4)	123.3 (2)
$X-C-C$	—	—	118.1 (3)	118.4 (1)

The two independent molecules of 9,10-dibromoanthracene lie on symmetry centres at 0,0,0 and  $0, \frac{1}{2}, \frac{1}{2}$ ; the carbon skeletons are close to planar with Br atoms slightly displaced [by 0.081 (1) and 0.051 (1) Å]. The 9,10-dichloroanthracene molecule is slightly non-planar, with a  $0.5 (1)^\circ$  fold about the C(9)–C(10) axis. The measured values of the C(2)–C(3) and C(6)–C(7) bond lengths in the dichloro compound appear to differ slightly (by only  $3.5\sigma$ ), but otherwise the bond distances and angles in the two molecules correspond closely to  $D_{2h}$  symmetry ( $C_{2v}$  for the dichloro if the slight fold is taken into account), the r.m.s. differences among equivalent lengths and angles being of the same order of magnitude as the least-squares e.s.d.'s.

The mean bond lengths in both molecules are similar to those in anthracene (Table 3), with bonds of the type C(1)–C(2) being shortest. The  $\sigma$ -electron-withdrawing power of the halogen atoms (Domenicano, Vaciago & Coulson, 1975) causes an increase in the endocyclic angles at C(9) and C(10) to  $123.9 (4)$  and  $123.3 (2)^\circ$  for the dibromo and dichloro compounds, respectively, relative to  $121.0 (3)^\circ$  in anthracene (Table 3), with consequent smaller differences in other angles. Molecules of the dibromo compound are stacked along

the short *a* axis, with interplanar spacings 3.52 (1) Å; in the dichloro crystal, molecular planes are nearly parallel to *a* (Trotter, 1959), and separated by 3.52 (1) Å. The shortest *X*...*X*, *X*...*C*, *X*...*H*, *C*...*C*, *C*...*H*, *H*...*H* contacts are 3.966 (1), 3.653 (7), 3.08, > 3.5, 2.97, 2.59 Å, respectively, for the dibromo compound, and 3.765 (1), 3.520 (2), 2.95, 3.491 (3), > 3.1, 2.38 Å for the dichloro compound, corresponding to van der Waals interactions.

The structure of a second polymorphic modification of 9,10-dichloroanthracene, isostructural with 9,10-dibromoanthracene, has been described (Burshtein, Hanson, Ingold & Williams, 1978; Krauss, Schulz, Nesper & Thiemann, 1979).

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## Structure du Chlorhydrate d'Isobutoxy-1 [(Propyne-1 yl)-1 cyclohexyloxy]-3 (Pyrrolidiny-1)-2 Propane

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**Abstract.**  $C_{20}H_{36}NO_2^+ \cdot Cl^-$ ,  $M_r = 357.96$ , m.p. 409.8 K, monoclinic,  $P2_1/a$ ,  $a = 12.416$  (3),  $b = 11.688$  (3),  $c = 14.671$  (3) Å,  $\beta = 92.63$  (1)°,  $V = 2127.1$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.117$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 15.74$  cm<sup>-1</sup>,  $T = 290$  K,  $F(000) = 784$ , final  $R = 0.073$  for 2060 observed reflections. Structure solved by direct methods. The conformations of the pyrrolidine and cyclohexyl rings are respectively chair and twist (half-chair). The cohesion of the crystal is the result of van der Waals interactions and an N–H...Cl hydrogen bond [N...Cl 3.049 (3) Å]. There are no unusual bond distances or angles.

**Introduction.** Le composé étudié est le chlorhydrate d'une nouvelle molécule développée par RIOM Laboratoires-CERM (France) dans la lignée du Bepridil®; celle-ci possède des propriétés antagonistes du calcium, anti-isohémiques et anti-arythmiques. Le schéma de synthèse est décrit par la Fig. 1.

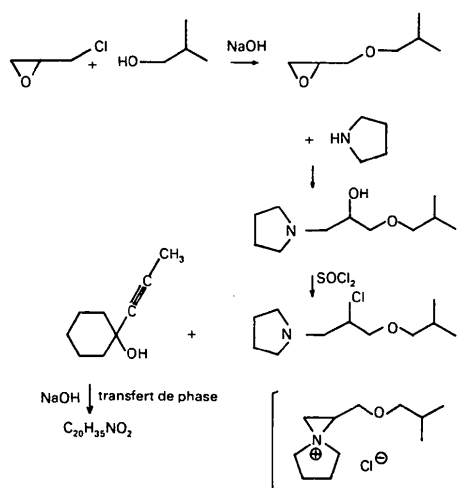


Fig. 1. Schéma de synthèse du CERM 4205.

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