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Structural Studies of Polychlorinated Hydrocarbons.
V. 1,1,1,2-Tetrachloro-2,2-bis(*p*-chlorophenyl)ethane and 1,1,1-Tribromo-2,2-bis(*p*-chlorophenyl)ethane

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The crystal structures of two DDT analogues $\{(p\text{-}C_6H_4Cl)_2CClCCl_3$ [1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane] (I) and $(p\text{-}C_6H_4Cl)_2CHCBr_3$ [1,1,1-tribromo-2,2-bis(*p*-chlorophenyl)ethane] (II)$\}$ have been determined by direct methods. Both are monoclinic, space group $P2_1/c$, with a = 11·099 (8), b = 11·710 (8), c = 12·548 (8) Å, β = 107·50 (1)° for (I), and a = 10·727 (3), b = 21·017 (1), c = 14·030 (2) Å, β = 94·69 (2)° for (II). (I) was refined by least-squares methods to R = 0·067 for 1930 independent observed reflections, and (II) was refined to R = 0·074 for 3346 independent observed reflections. Molecular dimensions for (I) and (II) are similar to those found for dicofol [2,2,2-trichloro-1,1-bis(*p*-chlorophenyl)-ethanol], *p,p'*-DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] and methoxychlor [1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane]. The major differences between both (I) and (II) and these DDT analogues are (*a*) the magnitudes of the dihedral angles between the phenyl rings and the plane containing C(1), C(13) and C(7), and (*b*) the torsion angles C(14)–C(13)–C(1)–C(2) and C(14)–C(13)–C(7)–C(8). The packing of the molecules of (II) in the unit cell results in the formation of two double columns of Br atoms down the a axis (one about $y = \frac{1}{2}$, $z = 0$ and the other about $y = 0$, $z = \frac{1}{2}$), with intermolecular Br–Br contacts ranging from 3·59 to 4·33 Å.

Introduction

In order to investigate the relationship between stereochemistry and insect toxicity in DDT analogues, the crystal structures of a number of these compounds have been determined (DeLacy & Kennard, 1972*a*,*b*; Holan, Kowala & Wunderlich, 1973; Lauher & Ibers, 1975; Kamakura & Kodama, 1975; Arora & Bates, 1976; Smith, Kennard & White, 1976; Hovmöller, Norrestam & Palm, 1977; Shields & Kennard, 1977; Shields, Kennard & Robinson, 1977; Smith & Bennett, 1977; Smith, Kennard & Whitnall, 1977; Smith, Kennard & White, 1978; Hovmöller & Göthe, 1978).

This paper reports the structures of 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (I) and 1,1,1-tribromo-2,2-bis(*p*-chlorophenyl)ethane (II). As regards toxicity no data are available for (I), while (II) is of moderate toxicity to mosquito larvae and is inactive to houseflies (Metcalf & Fukuto, 1968; Fahmy, Fukuto, Metcalf & Holmstead, 1973). Furthermore, (II) is an excellent substrate for DDT-ase, being dehydrohalogenated *in vivo* at four times the rate observed for DDT itself (Berger & Young, 1962).

Crystal data

1,1,1,2-Tetrachloro-2,2-bis(*p*-chlorophenyl)ethane, $C_{14}H_8Cl_6$, a = 11·099 (8), b = 11·710 (8), c = 12·548 (8) Å, β = 107·50 (1)°, t = 25 ± 1°C, V = 1555·4 Å^3, M_r = 388·94, Z = 4, $F(000)$ = 776, D_c = 1·66 g cm^{-3}, μ(Cu $K\alpha$) = 99·14 cm^{-1}; absent reflections: $h0l$ for l odd and $0k0$ for k odd; space group $P2_1/c$ (C^5_{2h}, No. 14), $\theta_{\max}$ = 70°; 2905 independent reflections collected.

1,1,1-Tribromo-2,2-bis(*p*-chlorophenyl)ethane, $C_{14}H_9Br_3Cl_2$, a = 10·727 (3), b = 21·017 (1), c = 14·030 (2) Å, β = 94·69 (2)°, t = 25 ± 1°C, V = 3152·5 Å^3, M_r = 487·86, Z = 8, $F(000)$ = 1856, D_c = 2·05 g cm^{-3}, μ(Cu $K\alpha$) = 135·3 cm^{-1}, m.p. 88°C; absent reflections: $h0l$ for l odd and $0k0$ for k odd; space group $P2_1/c$ (C^5_{2h}, No. 14), $\theta_{\max}$ = 67°; 5612 independent reflections collected.

Experimental

(I) was prepared by chlorination of *p,p'*-DDT under irradiation with ultraviolet light (Grummitt, Buck & Jenkins, 1945). Colourless crystals were grown from aqueous isopropyl alcohol. A sample of (II) was kindly provided by Dr N. Sharpless of the US Public Health Service, NIH, Bethesda, MD, USA. The material was recrystallized from isopropyl alcohol to give colourless crystals. The crystals for data collection had dimensions 0·20 × 0·20 × 0·20 mm and 0·15 × 0·15 × 0·15 mm for (I) and (II) respectively. The data were collected on a four-circle diffractometer (PW 1100) using graphite-crystal-monochromated Cu $K\alpha$ radiation (λ = 1·5418 Å). Cell dimensions were determined by a least-squares fit of 15 θ values measured on the diffractometer.

Intensity data were recorded using the $\theta/2\theta$ scanning mode with a scan speed (θ) of 0·05° s^{-1}, and a fixed scan width of 1·5°. The data were corrected for Lorentz and polarization effects and for absorption.

Scattering factors used were those of the neutral atoms (*International Tables for X-ray Crystallography*, 1974). Both structures were solved by conventional direct-methods procedures. The *SHELX* (Sheldrick, 1976) system of computer programs was used for the crystallographic calculations. Anisotropic thermal parameters were used for all non-hydrogen atoms for (I). For (II), only Br and Cl atoms were refined anisotropically.

Table 1. *Atomic parameters* (×10^4) *with estimated standard deviations in parentheses*

	x	*y*	*z*
Compound (I)			
Cl(1)	6117 (3)	6927 (3)	5224 (3)
Cl(2)	6263 (3)	5414 (2)	−2346 (3)
Cl(3)	10326 (3)	2759 (2)	2172 (3)
Cl(4)	9931 (3)	2898 (3)	4322 (3)
Cl(5)	10347 (3)	4922 (2)	3253 (3)
Cl(6)	7541 (3)	2249 (2)	2405 (3)
C(1)	7559 (8)	4484 (7)	3114 (8)
C(2)	7218 (9)	4073 (8)	4034 (8)
C(3)	6744 (9)	4820 (9)	4685 (8)
C(4)	6650 (9)	5971 (9)	4392 (9)
C(5)	6952 (9)	6400 (8)	3470 (8)
C(6)	7412 (8)	5637 (7)	2826 (8)
C(7)	7758 (8)	4095 (7)	1188 (8)
C(8)	6517 (9)	3880 (8)	555 (9)
C(9)	6028 (10)	4277 (9)	−555 (9)
C(10)	6867 (9)	4905 (7)	−969 (8)
C(11)	8089 (9)	5138 (8)	−364 (9)
C(12)	8538 (9)	4737 (8)	735 (8)
C(13)	8142 (9)	3694 (7)	2419 (8)
C(14)	9561 (10)	3578 (7)	2984 (9)
H(2)	7339	3181	4259
H(3)	6511	4517	5389
H(5)	6829	7279	3256
H(6)	7657	5943	2117
H(8)	5906	3384	916
H(9)	5091	4095	−1026
H(11)	8686	5624	−730
H(12)	9501	4913	1212
Compound (II)			
Molecule *A*			
Br(1)*A*	2380 (2)	742 (1)	4104 (2)
Br(2)*A*	1301 (2)	1986 (1)	4944 (2)
Br(3)*A*	3868 (2)	2002 (1)	3974 (2)
Cl(1)*A*	−718 (5)	4379 (2)	2021 (4)
Cl(2)*A*	3851 (6)	757 (4)	−489 (4)
C(1)*A*	955 (13)	2445 (7)	2741 (10)
C(2)*A*	1535 (16)	2991 (9)	3048 (12)
C(3)*A*	1019 (17)	3591 (9)	2843 (12)
C(4)*A*	−82 (15)	3634 (8)	2277 (11)
C(5)*A*	−692 (17)	3113 (9)	1951 (13)
C(6)*A*	−194 (16)	2515 (9)	2181 (12)
C(7)*A*	2057 (14)	1506 (7)	2064 (10)
C(8)*A*	2897 (16)	1868 (8)	1625 (12)
C(9)*A*	3444 (17)	1645 (9)	842 (13)
C(10)*A*	3116 (18)	1039 (9)	501 (13)
C(11)*A*	2304 (18)	696 (10)	908 (14)
C(12)*A*	1722 (17)	910 (9)	1709 (13)
C(13)*A*	1411 (14)	1773 (7)	2941 (10)
C(14)*A*	2171 (14)	1641 (7)	3886 (11)
H(2)*A*	2371	2965	3449
H(3)*A*	1464	3992	3104
H(5)*A*	−1514	3154	1538
H(6)*A*	−676	2117	1959
H(8)*A*	3148	2311	1887
H(9)*A*	4087	1907	491
H(11)*A*	2045	257	637
H(12)*A*	1106	639	2033
H(13)*A*	617	1504	2969
Molecule *B*			
Br(1)*B*	7435 (2)	3103 (1)	8998 (2)
Br(2)*B*	6312 (2)	4245 (1)	10092 (1)
Br(3)*B*	8889 (2)	4385 (1)	9168 (2)
Cl(1)*B*	4261 (6)	6863 (3)	7610 (5)
Cl(2)*B*	8703 (8)	3544 (4)	4413 (4)
C(1)*B*	5963 (13)	4911 (7)	8006 (10)
C(2)*B*	6594 (16)	5438 (8)	8355 (12)
C(3)*B*	6072 (16)	6041 (8)	8233 (12)
C(4)*B*	4918 (15)	6113 (8)	7768 (11)
C(5)*B*	4241 (17)	5602 (9)	7437 (13)
C(6)*B*	4779 (17)	4993 (9)	7544 (13)
C(7)*B*	7073 (13)	4058 (7)	7145 (10)
C(8)*B*	7957 (17)	4435 (9)	6815 (12)
C(9)*B*	8482 (19)	4270 (10)	5959 (14)
C(10)*B*	8059 (17)	3719 (9)	5473 (13)
C(11)*B*	7180 (19)	3381 (10)	5791 (14)
C(12)*B*	6658 (17)	3525 (9)	6642 (13)
C(13)*B*	6431 (14)	4215 (7)	8062 (10)
C(14)*B*	7225 (14)	4020 (7)	8977 (11)
H(2)*B*	7456	5385	8690
H(3)*B*	6550	6433	8510
H(5)*B*	3347	5650	7130
H(6)*B*	4318	4602	7272
H(8)*B*	8283	4830	7181
H(9)*B*	9171	4547	5697
H(11)*B*	6897	2973	5428
H(12)*B*	5973	3253	6879
H(13)*B*	5655	3945	8041

Table 2. *Interatomic distances* (Å) *and angles* (°), *with estimated standard deviations in parentheses, for compound* (I)

Cl(1)–C(4)	1·751 (10)	C(6)- C(1)	1·395 (12)
Cl(2)–C(10)	1·759 (10)	C(1)–C(13)	1·541 (12)
Cl(3)–C(14)	1·789 (10)	C(7)–C(8)	1·390 (13)
Cl(4)–C(14)	1·791 (10)	C(8)–C(9)	1·413 (15)
Cl(5)–C(14)	1·782 (9)	C(9)–C(10)	1·402 (14)
Cl(6)–C(13)	1·817 (8)	C(10)–C(11)	1·368 (14)
C(1)–C(2)	1·403 (13)	C(11)–C(12)	1·398 (14)
C(2)–C(3)	1·403 (13)	C(12)–C(7)	1·391 (14)
C(3)–C(4)	1·393 (14)	C(7)–C(13)	1·546 (12)
C(4)–C(5)	1·392 (14)	C(13)–C(14)	1·526 (13)
C(5)–C(6)	1·400 (13)		
C(2)–H(2)	1·08	C(8)–H(8)	1·09
C(3)–H(3)	1·05	C(9)–H(9)	1·05
C(5)–H(5)	1·06	C(11)–H(11)	1·08
C(6)–H(6)	1·07	C(12)–H(12)	1·08
Cl(1)–C(4)–C(3)	118·3 (8)	C(4)–C(5)–C(6)	118·0 (8)
Cl(1)–C(4)–C(5)	118·2 (8)	C(5)–C(6)–C(1)	120·2 (9)
Cl(2)–C(10)–C(9)	116·2 (8)	C(6)–C(1)–C(2)	120·3 (8)
Cl(2)–C(10)–C(11)	119·9 (8)	C(6)–C(1)–C(13)	118·1 (8)
Cl(3)–C(14)–Cl(4)	106·3 (5)	C(2)–C(1)–C(13)	121·6 (8)
Cl(3)–C(14)–Cl(5)	107·0 (6)	C(7)–C(8)–C(9)	121·7 (9)
Cl(3)–C(14)–C(13)	112·5 (7)	C(8)–C(9)–C(10)	115·9 (9)
Cl(4)–C(14)–Cl(5)	104·7 (6)	C(9)–C(10)–C(11)	123·8 (9)
Cl(4)–C(14)–C(13)	112·9 (7)	C(10)–C(11)–C(12)	118·7 (9)
Cl(5)–C(14)–C(13)	112·8 (6)	C(11)–C(12)–C(7)	120·2 (9)
Cl(6)–C(13)–C(1)	110·4 (6)	C(12)–C(7)–C(8)	119·7 (9)
Cl(6)–C(13)–C(7)	106·4 (6)	C(8)–C(7)–C(13)	116·4 (8)
Cl(6)–C(13)–C(14)	104·2 (6)	C(12)–C(7)–C(13)	123·6 (8)
C(1)–C(2)–C(3)	120·5 (8)	C(1)–C(13)–C(14)	109·9 (7)
C(2)–C(3)–C(4)	117·4 (9)	C(1)–C(13)–C(7)	110·3 (7)
C(3)–C(4)–C(5)	123·5 (9)	C(7)–C(13)–C(14)	115·4 (8)

The *E* maps revealed 16 of the 20 non-hydrogen atoms for (I) and 18 of the 19 for (II). Least-squares refinement reduced the *R* values from 0·36 to 0·067 for (I) and from 0·41 to 0·074 for (II). For both structures reflections with $\sigma(I)/I > 0{\cdot}3$ were omitted from the refinements. Unit weights were used.

For both compounds, positions for all H atoms were located from difference Fourier syntheses calculated towards the end of the refinement. These atoms were given the isotropic temperature factor equivalent of their attached C atoms, and were included in the calculations, but not refined.

The final positional parameters for both compounds are listed in Table 1.*

Discussion

Selected interatomic distances and bond angles are given in Tables 2 and 3. Numbering conventions follow the system adopted in all previous DDT-type structures (Figs. 1 and 2).

The Cl–C interatomic distances in (I) are similar to those of other chlorinated hydrocarbons. The mean

Table 3. *Interatomic distances* (Å) *and angles* (°), *with estimated standard deviations in parentheses, for compound* (II)

	A	*B*		*A*	*B*		*A*	*B*
Br(1)–C(14)	1·926 (15)	1·942 (15)	C(6)–C(1)	1·41 (2)	1·39 (2)	C(2)–H(2)	1·02	1·01
Br(2)–C(14)	1·957 (15)	1·969 (15)	C(1)–C(13)	1·51 (2)	1·55 (2)	C(3)–H(3)	1·02	1·03
Br(3)–C(14)	1·966 (15)	1·940 (15)	C(7)–C(8)	1·36 (2)	1·35 (2)	C(5)–H(5)	1·02	1·02
Cl(1)–C(4)	1·733 (16)	1·734 (17)	C(8)–C(9)	1·37 (3)	1·41 (3)	C(6)–H(6)	1·02	1·02
Cl(2)–C(10)	1·754 (19)	1·730 (19)	C(9)–C(10)	1·40 (3)	1·40 (3)	C(8)–H(8)	1·03	1·02
C(1)–C(2)	1·36 (2)	1·37 (2)	C(10)–C(11)	1·30 (3)	1·29 (3)	C(9)–H(9)	1·04	1·03
C(2)–C(3)	1·40 (3)	1·39 (3)	C(11)–C(12)	1·40 (3)	1·39 (3)	C(11)–H(11)	1·03	1·03
C(3)–C(4)	1·37 (3)	1·36 (3)	C(12)–C(7)	1·38 (3)	1·38 (3)	C(12)–H(12)	1·01	1·01
C(4)–C(5)	1·34 (3)	1·36 (3)	C(7)–C(13)	1·56 (2)	1·54 (2)	C(13)–H(13)	1·03	1·01
C(5)–C(6)	1·39 (3)	1·41 (3)	C(13)–C(14)	1·52 (2)	1·54 (2)			

	A	*B*		*A*	*B*
Br(1)–C(14)–Br(2)	107·4 (7)	106·9 (7)	C(6)–C(1)–C(2)	116·4 (14)	118·3 (15)
Br(1)–C(14)–Br(3)	105·9 (7)	106·6 (7)	C(6)–C(1)–C(13)	117·0 (13)	115·0 (13)
Br(2)–C(14)–Br(3)	107·8 (7)	107·9 (7)	C(2)–C(1)–C(13)	126·6 (13)	126·7 (13)
Br(1)–C(14)–C(13)	111·3 (10)	109·4 (10)	C(7)–C(8)–C(9)	120·9 (16)	119·3 (16)
Br(2)–C(14)–C(13)	109·8 (10)	108·8 (10)	C(8)–C(9)–C(10)	118·4 (16)	118·8 (17)
Br(3)–C(14)–C(13)	114·3 (10)	116·8 (10)	C(9)–C(10)–C(11)	121·0 (18)	120·3 (18)
Cl(1)–C(4)–C(3)	119·1 (13)	120·4 (13)	C(10)–C(11)–C(12)	122·2 (19)	122·2 (19)
Cl(1)–C(4)–C(5)	119·7 (13)	118·4 (13)	C(11)–C(12)–C(7)	117·3 (16)	118·8 (17)
Cl(2)–C(10)–C(9)	117·5 (14)	117·3 (15)	C(12)–C(7)–C(8)	120·3 (15)	120·6 (14)
Cl(2)–C(10)–C(11)	121·5 (15)	122·3 (16)	C(8)–C(7)–C(13)	120·4 (13)	122·3 (13)
C(1)–C(2)–C(3)	122·2 (16)	120·8 (15)	C(12)–C(7)–C(13)	119·2 (14)	117·0 (13)
C(2)–C(3)–C(4)	119·1 (16)	120·0 (16)	C(1)–C(13)–C(7)	110·2 (11)	109·0 (11)
C(3)–C(4)–C(5)	121·2 (16)	121·2 (16)	C(1)–C(13)–C(14)	118·2 (12)	116·8 (12)
C(4)–C(5)–C(6)	119·5 (16)	118·7 (17)	C(7)–C(13)–C(14)	112·3 (12)	112·6 (12)
C(5)–C(6)–C(1)	121·6 (15)	120·9 (16)			

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* Lists of structure factors and thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33604 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

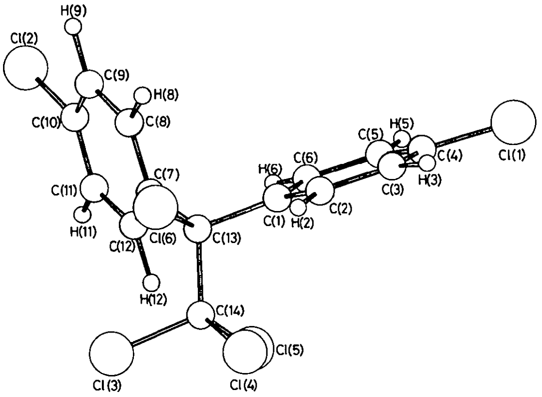

Fig. 1. 1,1,1,2-Tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (I) viewed perpendicular to the plane of C(1)–C(13)–C(14).

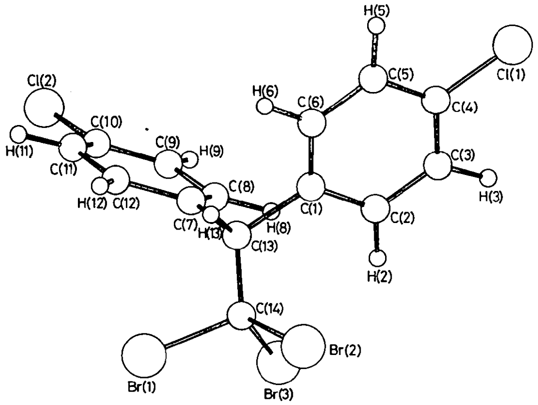

Fig. 2. 1,1,1-Tribromo-2,2-bis(*p*-chlorophenyl)ethane (II) viewed perpendicular to the plane of C(1)–C(13)–C(14).

Cl—C(sp^2) and Cl—C(sp^3) distances of 1·755 and 1·787 Å compare well with the average values found for 11 DDT-type compounds (1·736 and 1·782 Å respectively). The longer C(13)–Cl(6) distance [1·817 (8) Å] is also found for Cl substituents on the chlorocyclopentene and the dichlorotetrahydrofuran moieties in the cyclodiene insecticides heptachlor (Shields & Kennard, 1973) (1·82 Å) and isobenzan (Smith & Kennard, 1977) (1·84 Å). The molecular structure of (I) differs significantly from that observed for the closely related compound dicofol [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol] (Smith *et al.*, 1978) in the following aspects: (*a*) the angles about C(7) deviate significantly from the expected trigonal angle; (*b*) the dihedral angles between the planes of the benzene rings, and the angles between the benzene rings and the plane of C(1), C(13) and C(7) are 89, 34 and 75°, respectively, compared with 86, 52 and 58° in molecule *B* and 77, 35 and 86° in molecule *A* of dicofol.

The Newman projection of (I) down the C(14)–C(13) bond indicates a staggered conformation, as expected, for the three terminal Cl atoms with respect to the two phenyls and Cl(6). However, the torsion angles are slightly distorted in a manner similar to that found in other DDT analogues (Hovmöller *et al.*, 1977): the CCl_3 group is rotated about 10° away from the perfect staggered conformation, in order to avoid close contact between Cl(3) and the close phenyl atom H(12) of the most inclined phenyl group (*cf.* Fig. 1). The packing is illustrated in Fig. 3.

Interatomic distances and angles for (II) are similar to those for *p,p*-dichlorophenyltrichloroethanes. This structure is the first example of a brominated DDT analogue. The mean C—Br distance (1·950 Å) is consistent with the normal values observed for aliphatic

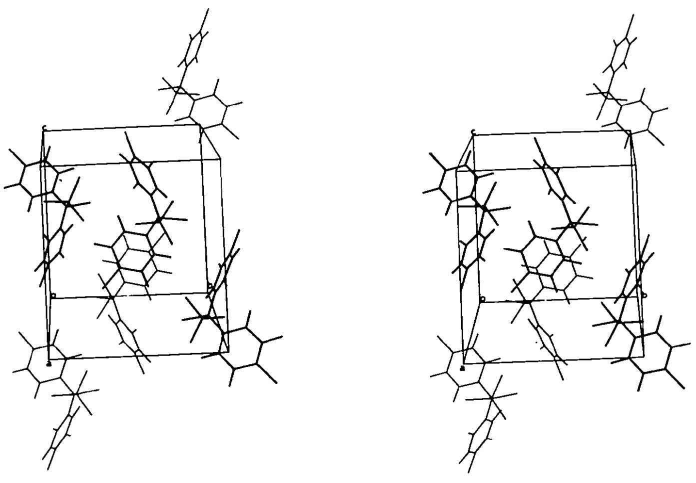

Fig. 3. Stereoscopic view of the packing of (I) in the unit cell viewed down the *a* axis.

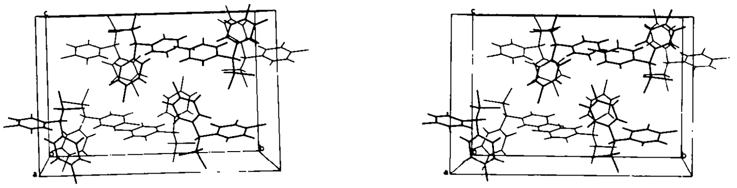

Fig. 4. Stereoscopic view of the packing of (II) in the unit cell viewed down the *a* axis.

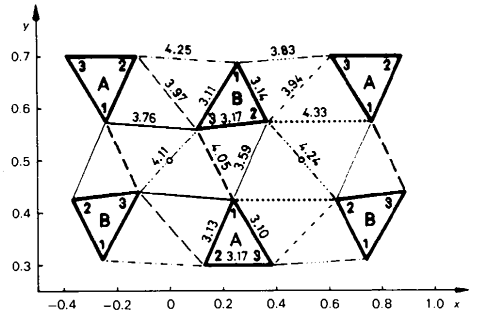

Fig. 5. The stacking of the Br_3 units in (II) shown as projections on to the *xy* plane, with the inter- and intramolecular Br—Br distances indicated.

Table 4. *Torsion angles of* (I), (II) *and dicofol*

It should be noted that all these molecules exist in two mirror-image conformations, since the space groups are centrosymmetric. Only one of the mirror-image conformations is listed, the other is easily derived from $\tau_1 = -\tau_2$ and $\tau_2 = -\tau_1$. Estimated standard deviations are 1°. The identity of each torsion angle is given for convenience in terms of the original numbering: 6—1—13—14 for example denotes C(6)—C(1)—C(13)—C(14).

Compound	τ_1			τ_2
(I)	6—1—13—14	+95°	−25°	12—7—13—14
(II)*A*	8—7—13—14	+88	−31	2—1—13—14
(II)*B*	8—7—13—14	+81	−36	2—1—13—14
Dicofol *A*	12—7—13—14	+90	−39	6—1—13—14
Dicofol *B*	12—7—13—14	+78	−1	6—1—13—14

C—Br bonds. Typical values reported for mono-, di- and tribromomethyl groups are 1·96 Å (Strieter & Templeton, 1962), 1·96 Å (Rendle & Trotter, 1975) and 1·92 Å (Voet & Lipscomb, 1964) respectively.

The bond lengths, valency angles and conformation of the two crystallographically independent molecules of (II) are very similar. The dihedral angles between the benzene planes, and the angles between the benzene rings and the C(1), C(13), C(7) plane are 82, 46 and 82°, respectively, for molecule *A*, and 79, 55 and 85° for molecule *B*. These angles are significantly different from those in similar active compounds such as *p,p'*-DDT (DeLacy & Kennard, 1972*b*) (65, 47, 84°) and methoxychlor (Smith *et al.*, 1976) (78, 42, 89°). The difference in activity could be due to the role of Br in (*a*) altering these conformational angles or (*b*) increasing the size of the trihalomethyl group which would be too large to act as a 'molecular wedge' to block the sodium gates of the nerve axon in the open position (Holan, 1969).

The molecules of (II) are stacked down the *a* axis in two columns, with close intermolecular Br interactions. Because the CBr_3 groups of molecules *A* and *B* both lie adjacent to $(x,\frac{1}{2},0)$, another pair of CBr_3 groups, related to these through the inversion operation, stack close to these (Figs. 4 and 5). Another column, related to the first through the symmetry operation $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, runs along $(x,0,\frac{1}{2})$.

The two crystallographically independent molecules of (II) have almost identical conformations (Fig. 4 and Table 4), and are related through non-crystallographic symmetry where the coordinates of molecule *B* are derived from those of molecule *A* by approximately $(x+\frac{1}{2}, y+\frac{1}{4}, z+\frac{1}{2})$ (Table 1). Because of this packing the *h*00 reflections are very weak for *h* odd.

The torsion angles around C(13) are quite similar in (I) and (II). If the torsion angles are named τ_1 and τ_2 as in Hovmöller *et al.* (1977), with τ_1 close to 90° and τ_2 close to −25°, the two molecules of (II) are similar to that of (I) and molecule *A* of dicofol, but molecule *B* of dicofol has a different conformation, with τ_2 almost 0°. The torsion angles are listed in Table 4.

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An X-ray Determination of the Crystal Structure of 1,12-Dimethylbenz[*a*]anthracene

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$C_{20}H_{16}$ is monoclinic, space group $P2_1$, with $Z = 2$, $a = 8{\cdot}432$ (14), $b = 8{\cdot}328$ (16), $c = 9{\cdot}963$ (14) Å, $\beta = 96{\cdot}65$ (15)°. Intensities collected from different single crystals on two different automatic diffractometers have been refined independently: set *A* to $R = 0{\cdot}081$ for 1164 reflexions, set *B* to 0·010 for 1457 reflexions. Half-normal probability plots for the two data sets suggest that apparent standard deviations for C atom positions, $\sigma_A = 0{\cdot}008$, $\sigma_B = 0{\cdot}010$ Å, are underestimated by a factor of two. As in other benz[*a*]anthracenes, the *K*-region bond C(5)–C(6) is short (1·33 Å), and the bond in the bay is long, C(13)–C(18) = 1·50 Å. In this novel bay region (with one methyl buttressed by a *peri* H atom), the methyl C atoms are 3·0 Å apart, with the 1-methyl C atom 0·4 Å below ring *A* and the 12-methyl C atom 0·5 Å above ring *C*. Individually, the benzene rings are fairly planar but overall molecular distortion is closer to that in the 5,6-epoxide of the highly carcinogenic 7,12-DMBA than to distortions in the 1- and 12-methylbenz[*a*]anthracenes.

Introduction

Although 1,12-dimethylbenz[*a*]anthracene (1,12-DMBA) is not thought to be carcinogenic, it is related to several carcinogenically active methylated benz[*a*]anthracenes: 1-methylbenz[*a*]anthracene (1-MBA) (Jones & Sowden, 1975), 12-methylbenz[*a*]anthracene (12-MBA) (Jones & Sowden, 1976), and the highly active 7,12-dimethylbenz[*a*]anthracene (7,12-DMBA), previously designated 9,10-dimethyl-1,2-benzanthracene (Iball, 1964). An arrangement with two bay (Bartle & Jones, 1967) methyl groups, 1 and 12, in which one of them is buttressed by a *peri* H atom on C(11), might be expected to cause molecular distortion in solution and in the solid state; this arrangement has not previously received crystallographic study.