

The Crystal Structure of 9,9,10,10-Tetrachloro-9,10-dihydroanthracene

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9,9,10,10-Tetrachloro-9,10-dihydroanthracene, $C_{14}H_8Cl_4$, crystallizes in the monoclinic space group $C2/m$. The unit-cell dimensions are $a=10.93$, $b=13.90$, $c=9.89$ Å, $\beta=116.2^\circ$. The crystal structure has been determined by three-dimensional X-ray analysis and refined to an R index of 13.0% by the method of least-squares.

The molecular packing is characterized by a dovetailed arrangement in which parallel pairs of crystallographically independent molecules assume orientations rotated with respect to each other by 90° . In general, the bond distances and angles of the independent molecules are identical within experimental error and are close to expected values. Intramolecular overcrowding between chlorine and hydrogen atoms forces the carbon framework of both molecules into essentially a planar configuration and hence into a strained conformation for the central cyclohexa-1,4-diene rings.

Introduction

As part of a program designed to characterize new organic semiconductors and photoconductors, the crystal structures of representative compounds prepared in these laboratories are being determined. 9,9,10,10-Tetrachloro-9,10-dihydroanthracene (TCA), synthesized in this regard, is also of inherent chemical interest with respect to the effect of halogen substitution on the conformation of the central cyclohexa-1,4-diene ring (Yannoni, Krukoni & Silverman, 1964).

Experimental

Cream-colored crystals prepared by the method of Meyer & Zahn (1913) provided the specimen selected for the X-ray analysis. This was rod-shaped, length 1.3 mm and average diameter 0.1 mm.

The chemical and crystallographic data are as follows:

$C_{14}H_8Cl_4$; $M=317.8$; m.p. 153–157°C.

Monoclinic:

$a=10.93 \pm 0.04$, $b=13.90 \pm 0.03$, $c=9.89 \pm 0.02$ Å,

$\beta=116.2 \pm 0.1$; $V=1348$ Å³; $Z=4$.

Density data: D_{calc} ($Z=4$) = 1.565 g.cm⁻³, D_{obs} = 1.55 g.cm⁻³ (flotation in CCl_4 , CS_2 mixtures).

Absent reflections, hkl when $h+k$ is odd; space group is $C2/m$ (No. 12); absorption coefficients for X-rays, $\mu(Cu K\alpha)=76.53$ cm⁻¹, $\mu(Mo K\alpha)=8.67$ cm⁻¹.

The intensity data were taken with Cu $K\alpha$ ($\lambda=1.5418$ Å) radiation using a Weissenberg camera in the equi-inclination geometry. Levels $hk0$ to $hk7$ were recorded on multiple films and intensities were measured by comparison with a calibrated standard. $h0l$ and $hk2h$ films obtained with the precession camera (Mo $K\alpha$ radiation, $\lambda=0.7107$ Å) were used for scaling the Weissenberg data as well as for measuring the unit cell parameters. The usual Lorentz and polarization factor corrections were applied. Cylindrical absorption corrections (*International Tables for X-Ray Crystallogra-*

phy, 1959, sec. 5.3.5.3.) were made. There were 780 observed reflections, 61% of the total possible on levels $hk0$ to $hk7$.

Structure determination

A sharpened three-dimensional Patterson function was calculated. The space group ambiguity among $C2/m$, $C2$, and Cm as well as an unusual occupancy of special positions complicated the structure solution. The latter effect resulted in the superposition of certain carbon-carbon vectors leading to peak heights in the Patterson function comparable to those of the heavy atom interactions. Inspection of the vector map and analysis of the possible special positions available for the heavy atoms in the three space groups finally yielded a trial structure in space group $C2/m$. This model placed the centers of the four molecules in two sets of twofold special positions: $2(a)$ ($000; \frac{1}{2}, \frac{1}{2}, 0$) and $2(c)$ ($00 \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), each of point group symmetry $2/m$. Fig. 1 gives the numbering scheme for the asymmetric unit and the caption summarizes the atomic occupancy of special positions. A three-dimensional Fourier map, phases calculated from chlorine atom contributions alone, yielded trial positions for all of the carbon atoms and the structure was refined using a full-matrix least-squares analysis.

Refinement was based on F_o and the quantity minimized was the weighted R index, $R=(\sum w(F_o - |F_c|)^2 / \sum w F_o^2)^{\frac{1}{2}}$. Scattering factors for carbon and chlorine atoms were taken from *International Tables for X-Ray Crystallography* (1962, p. 202).

Five cycles of refinement using 400 selected reflections with unit weights and individual isotropic temperature factors reduced the usual R index ($R=(\sum(F_o - |F_c|) / \sum F_o)$) from 24.4 to 16.0%. After five more least-squares cycles in the same mode on the full complement of observed data, 780 reflections, the R value converged to 19.7%. The ratio of observations to parameters was about 20. At this point, the weighting scheme was changed to one based upon standard devia-

Table 1. Final position parameters x , y , z in fractional coordinates, isotropic temperature factors, β (\AA^2) and final anisotropic thermal parameters

Anisotropic thermal parameters are based on the expression $T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$.

Standard deviations in parentheses refer to the last significant figure given.

Atom	x	y	z	β	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)-1	0.2605 (4)	0	-0.0201 (4)	4.0 (2)	0.0133 (4)	0.0060 (2)	0.0180 (8)	0	0.0126 (4)	0
Cl(2)-1	0.2613 (3)	0	0.2750 (4)	4.9 (2)	0.0113 (4)	0.0114 (3)	0.0102 (6)	0	0.0029 (3)	0
C(1)-1	0.072 (1)	0.2651 (7)	0.040 (1)	5.0 (5)	0.037 (3)	0.0043 (4)	0.026 (3)	-0.0037 (7)	0.025 (3)	-0.0033 (7)
C(2)-1	0.142 (1)	0.1807 (6)	0.073 (1)	4.6 (5)	0.022 (2)	0.0057 (5)	0.019 (2)	-0.0035 (7)	0.016 (2)	-0.0030 (7)
C(3)-1	0.0716 (8)	0.0925 (5)	0.039 (1)	3.4 (4)	0.012 (1)	0.0048 (4)	0.012 (1)	-0.0008 (4)	0.0077 (9)	-0.00011 (5)
C(4)-1	0.152 (1)	0	0.074 (1)	3.8 (6)	0.009 (1)	0.0055 (6)	0.012 (2)	0	0.006 (1)	0
Cl(1)-2	-0.0099 (3)	0.1839 (2)	0.3476 (6)	4.3 (1)	0.0133 (3)	0.0063 (2)	0.0162 (5)	0.0001 (1)	0.0075 (3)	0.0040 (2)
C(1)-2	0.3768 (9)	0.0498 (7)	0.661 (1)	4.2 (4)	0.011 (1)	0.0072 (5)	0.017 (2)	-0.0013 (6)	0.0038 (8)	-0.0012 (6)
C(2)-2	0.2543 (9)	0.0987 (7)	0.607 (1)	3.5 (4)	0.0109 (9)	0.0076 (6)	0.014 (2)	-0.0013 (5)	0.0069 (8)	-0.0024 (7)
C(3)-2	0.1325 (7)	0.0508 (6)	0.5573 (9)	3.0 (4)	0.0103 (8)	0.0055 (4)	0.008 (1)	0.0004 (4)	0.0049 (6)	0.0004 (4)
C(4)-2	0	0.1058 (8)	0.5	3.4 (6)	0.010 (1)	0.0059 (6)	0.011 (2)	0	0.007 (1)	0

tions: $\sigma = 0.15 F_o$ for all F_o . Four more cycles incorporating anisotropic thermal parameters completed the refinement. The final index was 13.05%; weighted R was 17.9%. The ratio of observations to parameters was about 9 and the final goodness of fit $(\sum w(F_o - |F_c|)^2 / (N_o - N_v))^{1/2}$, expected value unity, was 1.27. In the final refinement cycle, the changes in the coordinates were equal to or less than 1/60 of the standard deviations, and changes in the thermal parameters were no larger than 0.1σ . Table 1 presents the final position parameters and the anisotropic temperature factors as well as the isotropic thermal parameters at the conclusion of that portion of the refinement. A final difference Fourier map showed no features inconsistent with the proposed structure but did not locate conclusively the hydrogen atoms. Table 2 compares the observed and calculated structure factors.

Discussion

Fig. 2 presents a three-dimensional view of the contents of the unit cell. The molecules at 0, 0, 0 and 0, 0, $\frac{1}{2}$ are molecules 1 and 2 respectively of Fig. 1. Also shown are the C -centered translation equivalents of these two. Neighboring molecules are rotated with respect to each other by 90° about the c axis allowing for an efficient packing arrangement in which chlorine atoms 'nest' in the terminal benzene rings of adjacent molecules. Molecules 1 and 2 are crystallographically independent, each having point group symmetry $2/m$. However, to a fair approximation (see below) the molecules have identical dimensions, have mmm symmetry, and consequently are related in pairs by a pseudo 4_2 symmetry axis parallel to the c axis. The C -centered translations which involve the oblique a axis allow for a more efficient interleaving of molecular planes than would a tetragonal space group.

All intermolecular contacts are larger than the sum of the pertinent van der Waals radii. The closest contacts between molecular pairs related by the pseudo 4_2 axis are carbon-chlorine contacts. Between the chlorine atoms of molecule 2 and the outer ring carbon atoms of molecule 1, there are contacts of 3.71, 3.76, and 3.76 \AA ; and between the chlorine atoms on molecule 1 and the benzene rings to which they are adjacent, one finds shorter contacts of 3.52, 3.60, and 3.71 \AA on one side and contacts longer than 3.9 \AA on the other. The chlorine-chlorine contacts between pairs of dovetailed molecules are 4.21 and 4.08 \AA . The shortest contact between molecules related by the C -centered translation is a chlorine-carbon contact of 3.77 \AA . The chlorine atoms effectively separate the anthracene skeletons; the closest carbon-carbon contact is 3.77 \AA and occurs between carbon atoms on molecule 1 and the molecule at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Intermolecular packing effects involving the interleaving of molecule 1 with the molecules at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ are believed responsible for the slight twist from planarity of molecule 1 as described below.

Fig.3 shows the dimensions of molecules 1 and 2. Distances are uncorrected for thermal motion. The standard deviations as computed from the least-squares equations range from 0.01 to 0.03 Å for bond lengths and from 0.6 to 1.2° for the bond angles. With the

exception of the bond angles at the tetrahedral carbon atoms, there are no significant differences between the molecules; the dimensions of the outer rings do not differ within experimental error from those of benzene. The average of the three independent carbon-chlorine

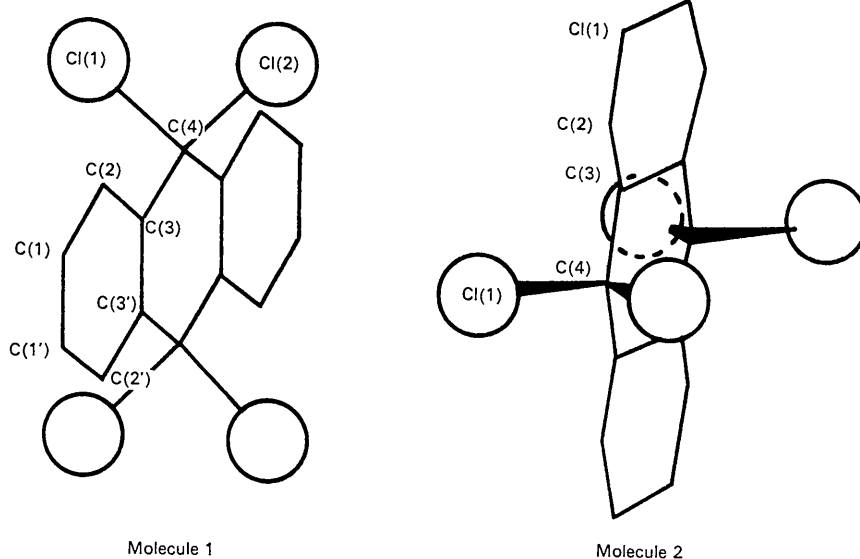


Fig.1. Numbering of independent atoms in the two crystallographically independent molecules. The pair as drawn corresponds in orientation to dovetailed pairs in Fig.2. In molecule 1 (center at 0,0,0), the chlorine atoms and attached carbon atoms lie in the $y=0$ mirror plane; *i.e.* Cl(1)-1, Cl(2)-1, C(4)-1 occupy special positions $4(i)$ ($x, 0, z$). In molecule 2 (center at $0, 0, \frac{1}{2}$), the tetrahedral carbon atoms lie on the $0, y, \frac{1}{2}$ line, *i.e.* C(4)-2 occupies special position $4(h)$ ($0, y, \frac{1}{2}$).

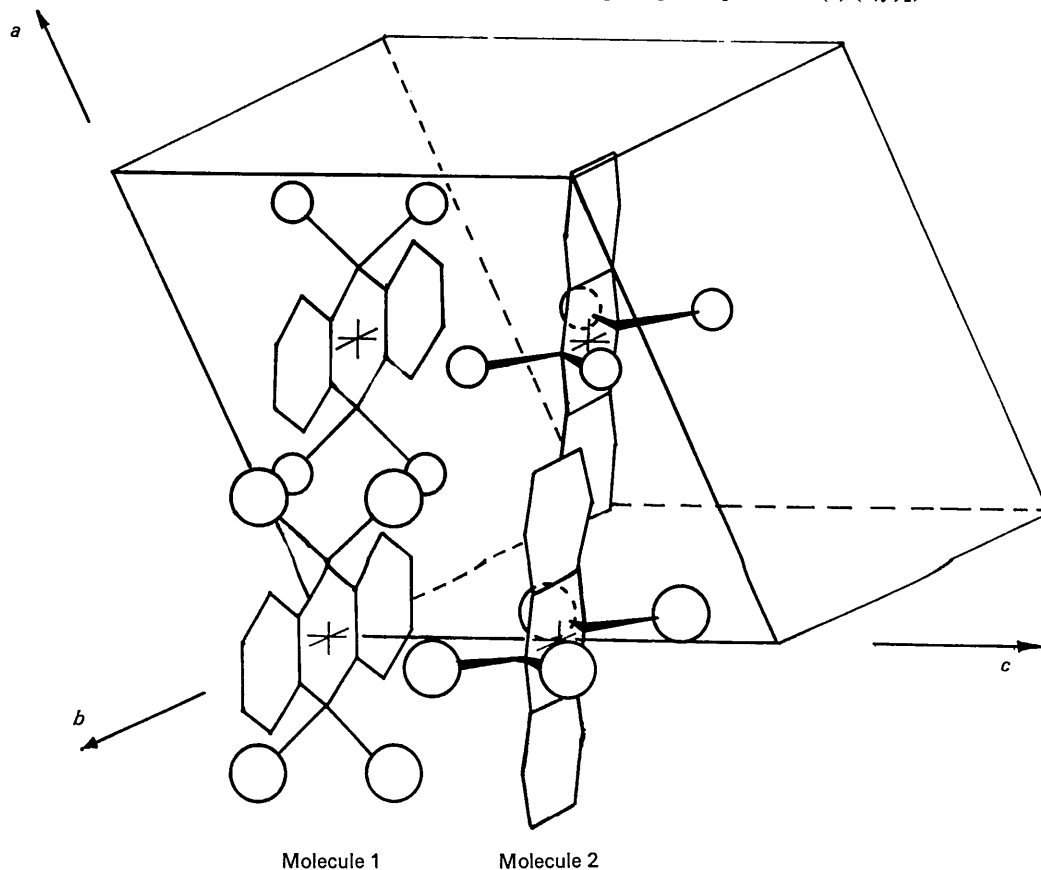


Fig.2. Packing arrangement of the four molecules in the unit cell.

bond distances is 1.81 Å as compared with the expected value of 1.77 Å (*International Tables for X-Ray Crystallography*, 1962). The bond angles involving chlorine atoms tend to be smaller than the tetrahedral value; not unexpectedly in view of the central ring angles of 117° and 119°. The composite molecule shown in Fig. 4 is obtained by averaging the benzene ring dimensions as well as corresponding dimensions on both molecules. Average deviations, computed for cases where more than two independent values are available, are given for purposes of comparison with the standard deviations of Fig. 3. Corresponding tetrahedral bond angles of both molecules are shown in Fig. 4 for completeness but the individual values of 109.4° and 106.6° for molecule 1 are significantly different and reflect the twist in this molecule described below. Also given for comparison are the dimensions

of 9,10-dihydro-1,2,5,6-dibenzanthracene determined from two-dimensional Fourier analysis (Iball & Young, 1958).

A review of the literature indicates that the structure of 9,10-dihydro-1,2,5,6-dibenzanthracene is the only other quantitative analysis available on a 9,10-saturated anthracene. The parent molecule, 9,10-dihydroanthracene, was studied by two-dimensional methods (Ferrier & Iball, 1954) and preliminary results indicated a folded conformation, *i.e.* a 'butterfly' shaped molecule with a dihedral angle of about 145°. On the other hand, the dibenzanthracene is essentially flat, although a careful analysis by Herbstein (1961) demonstrates that a slightly zigzag model (planes of naphthalene moieties about 0.18 Å apart are related by a center of symmetry in the molecule) gives a better fit to the experimental atomic coordinates. Tentative

Table 2. Comparison of observed and calculated structure factors
The three columns of each group refer to h , F_o , and F_c .

h00	h11	h20	h30	h40	h50	h60	h70	h80	h90	h100	h110	h120	h130	h140	h150	h160	h170	h180	h190	h200	h210	h220	h230	h240	h250	h260	h270	h280	h290	h300	h310	h320	h330	h340	h350	h360	h370	h380	h390	h400	h410	h420	h430	h440	h450	h460	h470	h480	h490	h500	h510	h520	h530	h540	h550	h560	h570	h580	h590	h600	h610	h620	h630	h640	h650	h660	h670	h680	h690	h700	h710	h720	h730	h740	h750	h760	h770	h780	h790	h800	h810	h820	h830	h840	h850	h860	h870	h880	h890	h900	h910	h920	h930	h940	h950	h960	h970	h980	h990	h1000	h1010	h1020	h1030	h1040	h1050	h1060	h1070	h1080	h1090	h1100	h1110	h1120	h1130	h1140	h1150	h1160	h1170	h1180	h1190	h1200	h1210	h1220	h1230	h1240	h1250	h1260	h1270	h1280	h1290	h1300	h1310	h1320	h1330	h1340	h1350	h1360	h1370	h1380	h1390	h1400	h1410	h1420	h1430	h1440	h1450	h1460	h1470	h1480	h1490	h1500	h1510	h1520	h1530	h1540	h1550	h1560	h1570	h1580	h1590	h1600	h1610	h1620	h1630	h1640	h1650	h1660	h1670	h1680	h1690	h1700	h1710	h1720	h1730	h1740	h1750	h1760	h1770	h1780	h1790	h1800	h1810	h1820	h1830	h1840	h1850	h1860	h1870	h1880	h1890	h1900	h1910	h1920	h1930	h1940	h1950	h1960	h1970	h1980	h1990	h2000	h2010	h2020	h2030	h2040	h2050	h2060	h2070	h2080	h2090	h2100	h2110	h2120	h2130	h2140	h2150	h2160	h2170	h2180	h2190	h2200	h2210	h2220	h2230	h2240	h2250	h2260	h2270	h2280	h2290	h2300	h2310	h2320	h2330	h2340	h2350	h2360	h2370	h2380	h2390	h2400	h2410	h2420	h2430	h2440	h2450	h2460	h2470	h2480	h2490	h2500	h2510	h2520	h2530	h2540	h2550	h2560	h2570	h2580	h2590	h2600	h2610	h2620	h2630	h2640	h2650	h2660	h2670	h2680	h2690	h2700	h2710	h2720	h2730	h2740	h2750	h2760	h2770	h2780	h2790	h2800	h2810	h2820	h2830	h2840	h2850	h2860	h2870	h2880	h2890	h2900	h2910	h2920	h2930	h2940	h2950	h2960	h2970	h2980	h2990	h3000	h3010	h3020	h3030	h3040	h3050	h3060	h3070	h3080	h3090	h3100	h3110	h3120	h3130	h3140	h3150	h3160	h3170	h3180	h3190	h3200	h3210	h3220	h3230	h3240	h3250	h3260	h3270	h3280	h3290	h3300	h3310	h3320	h3330	h3340	h3350	h3360	h3370	h3380	h3390	h3400	h3410	h3420	h3430	h3440	h3450	h3460	h3470	h3480	h3490	h3500	h3510	h3520	h3530	h3540	h3550	h3560	h3570	h3580	h3590	h3600	h3610	h3620	h3630	h3640	h3650	h3660	h3670	h3680	h3690	h3700	h3710	h3720	h3730	h3740	h3750	h3760	h3770	h3780	h3790	h3800	h3810	h3820	h3830	h3840	h3850	h3860	h3870	h3880	h3890	h3900	h3910	h3920	h3930	h3940	h3950	h3960	h3970	h3980	h3990	h4000	h4010	h4020	h4030	h4040	h4050	h4060	h4070	h4080	h4090	h4100	h4110	h4120	h4130	h4140	h4150	h4160	h4170	h4180	h4190	h4200	h4210	h4220	h4230	h4240	h4250	h4260	h4270	h4280	h4290	h4300	h4310	h4320	h4330	h4340	h4350	h4360	h4370	h4380	h4390	h4400	h4410	h4420	h4430	h4440	h4450	h4460	h4470	h4480	h4490	h4500	h4510	h4520	h4530	h4540	h4550	h4560	h4570	h4580	h4590	h4600	h4610	h4620	h4630	h4640	h4650	h4660	h4670	h4680	h4690	h4700	h4710	h4720	h4730	h4740	h4750	h4760	h4770	h4780	h4790	h4800	h4810	h4820	h4830	h4840	h4850	h4860	h4870	h4880	h4890	h4900	h4910	h4920	h4930	h4940	h4950	h4960	h4970	h4980	h4990	h5000	h5010	h5020	h5030	h5040	h5050	h5060	h5070	h5080	h5090	h5100	h5110	h5120	h5130	h5140	h5150	h5160	h5170	h5180	h5190	h5200	h5210	h5220	h5230	h5240	h5250	h5260	h5270	h5280	h5290	h5300	h5310	h5320	h5330	h5340	h5350	h5360	h5370	h5380	h5390	h5400	h5410	h5420	h5430	h5440	h5450	h5460	h5470	h5480	h5490	h5500	h5510	h5520	h5530	h5540	h5550	h5560	h5570	h5580	h5590	h5600	h5610	h5620	h5630	h5640	h5650	h5660	h5670	h5680	h5690	h5700	h5710	h5720	h5730	h5740	h5750	h5760	h5770	h5780	h5790	h5800	h5810	h5820	h5830	h5840	h5850	h5860	h5870	h5880	h5890	h5900	h5910	h5920	h5930	h5940	h5950	h5960	h5970	h5980	h5990	h6000	h6010	h6020	h6030	h6040	h6050	h6060	h6070	h6080	h6090	h6100	h6110	h6120	h6130	h6140	h6150	h6160	h6170	h6180	h6190	h6200	h6210	h6220	h6230	h6240	h6250	h6260	h6270	h6280	h6290	h6300	h6310	h6320	h6330	h6340	h6350	h6360	h6370	h6380	h6390	h6400	h6410	h6420	h6430	h6440	h6450	h6460	h6470	h6480	h6490	h6500	h6510	h6520	h6530	h6540	h6550	h6560	h6570	h6580	h6590	h6600	h6610	h6620	h6630	h6640	h6650	h6660	h6670	h6680	h6690	h6700	h6710	h6720	h6730	h6740	h6750	h6760	h6770	h6780	h6790	h6800	h6810	h6820	h6830	h6840	h6850	h6860	h6870	h6880	h6890	h6900	h6910	h6920	h6930	h6940	h6950	h6960	h6970	h6980	h6990	h7000	h7010	h7020	h7030	h7040	h7050	h7060	h7070	h7080	h7090	h7100	h7110	h7120	h7130	h7140	h7150	h7160	h7170	h7180	h7190	h7200	h7210	h7220	h7230	h7240	h7250	h7260	h7270	h7280	h7290	h7300	h7310	h7320	h7330	h7340	h7350	h7360	h7370	h7380	h7390	h7400	h7410	h7420	h7430	h7440	h7450	h7460	h7470	h7480	h7490	h7500	h7510	h7520	h7530	h7540	h7550	h7560	h7570	h7580	h7590	h7600	h7610	h7620	h7630	h7640	h7650	h7660	h7670	h7680	h7690	h7700	h7710	h7720	h7730	h7740	h7750	h7760	h7770	h7780	h7790	h7800	h7810	h7820	h7830	h7840	h7850	h7860	h7870	h7880	h7890	h7900	h7910	h7920	h7930	h7940	h7950	h7960	h7970	h7980	h7990	h8000	h8010	h8020	h8030	h8040	h8050	h8060	h8070	h8080	h8090	h8100	h8110	h8120	h8130	h8140	h8150	h8160	h8170	h8180	h8190	h8200	h8210	h8220	h8230	h8240	h8250	h8260	h8270	h8280	h8290	h8300	h8310	h8320	h8330	h8340	h8350	h8360	h8370	h8380	h8390	h8400	h8410	h8420	h8430	h8440	h8450	h8460	h8470	h8480	h8490	h8500	h851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results from a refinement of 9,10-dibromoanthrone (Silverman & Yannoni, 1963) indicate that the molecule has a bend of a few degrees in a butterfly configuration.

Herbstein (1959) in some qualitative calculations derived dihedral angles in agreement with experiment for the two dihydroanthracene molecules mentioned

above. The unstrained boat form of the cyclohexa-1,4-diene ring involves two types of hydrogen atom at the saturated positions, so-called 'lin' (equatorial) and 'perp' (axial) bonds (Beckett & Mulley, 1955). Substitution at the equatorial positions in 9,10-dihydroanthracene creates tight intramolecular contacts with hydrogen atoms on the 1,8 and 4,5 positions. In the

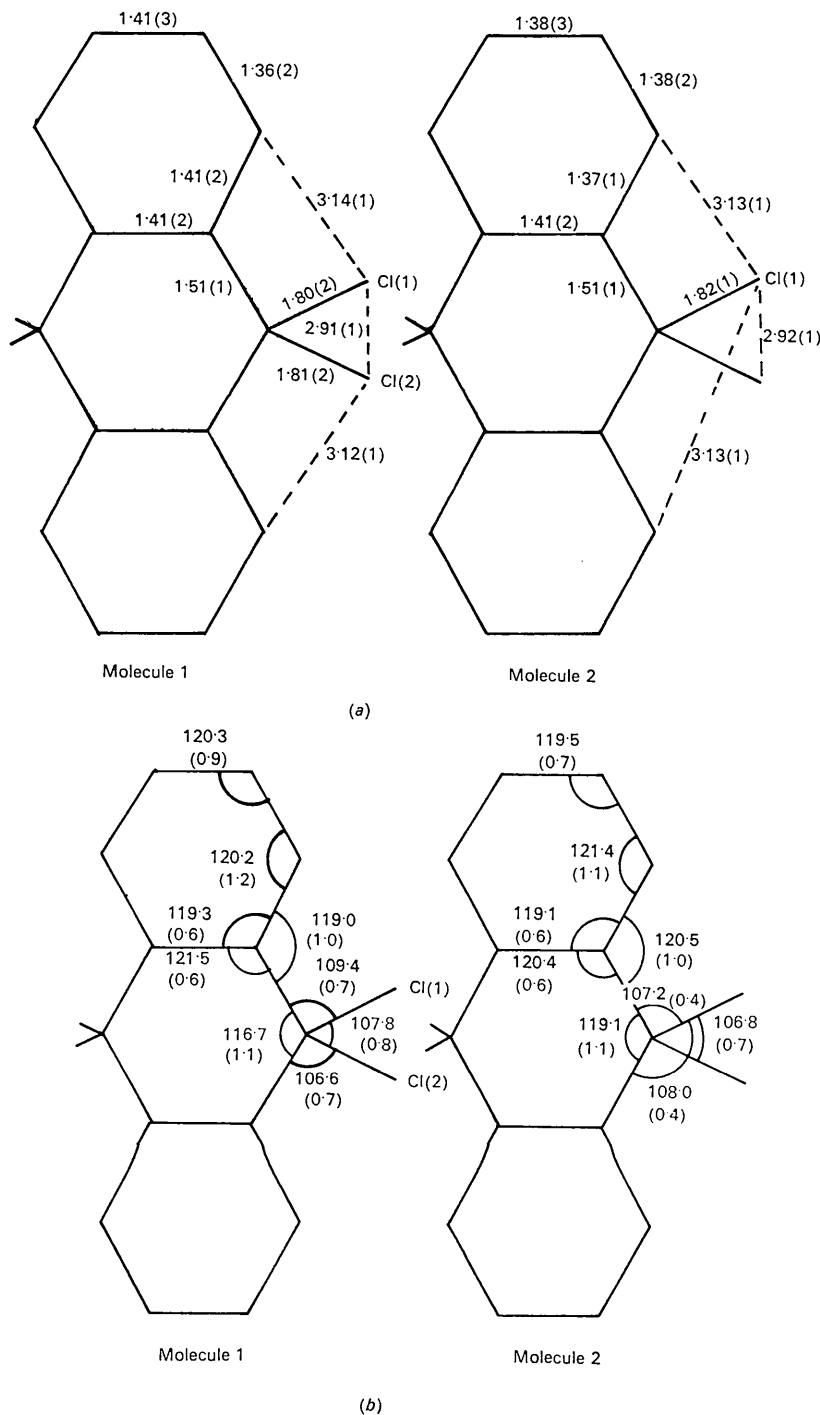


Fig. 3. The dimensions of molecules 1 and 2: (a) bond lengths in Å, standard deviations in units of 0·01 Å in parentheses; (b) bond angles in degrees, standard deviations in degrees in parentheses.

case of the dibenzanthracene molecule (Fig. 4), there are already close contacts with the hydrogen atom positions indicated by asterisks, even without substitution. These contacts are lengthened as the central ring flattens toward a strained planar conformation and the minimum potential energy involves a balance of the two strain conditions. For dibenzanthracene this minimum is a dihedral angle of about 180° (Herbstein, 1959). In TCA, because of the greater size of the

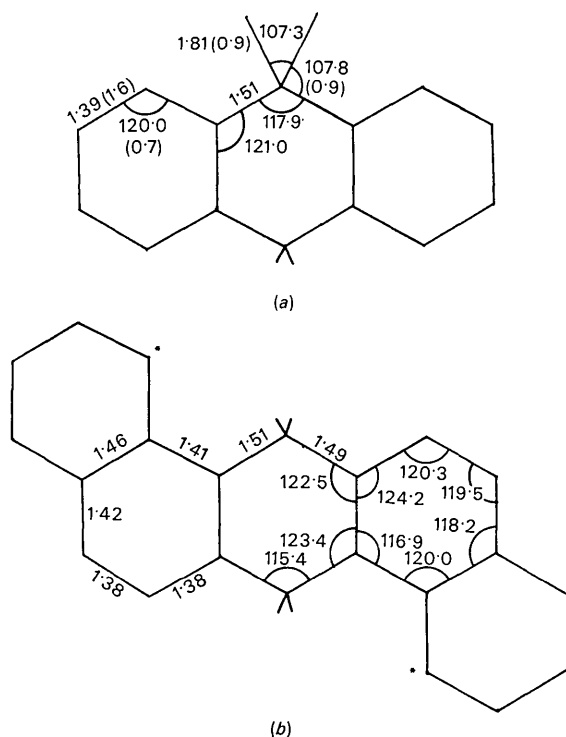


Fig. 4. Comparison of the dimensions of the composite molecule of (a) TCA with (b) those of 9,10-dihydro-1,2,5,6-dibenzanthracene. For the former, average deviations are given in parentheses in units of 0.01 \AA for bond distances and 1.0° for bond angles.

chlorine atoms, one would expect a considerably flatter conformation than that which is observed in 9,10-dihydroanthracene. Least-squares planes (Schomaker, Waser, Marsh & Bergman, 1959) passed through the carbon skeletons of each molecule verify that both are essentially planar (Table 3). As a consequence of this planar configuration, hydrogen atoms, postulated to lie in the plane at the 1,8,4, and 5 positions participate in chlorine-hydrogen contacts in the range of 2.9 \AA , only slightly shorter than 3.0 \AA , the sum of the van der Waals radii of the two atoms.

The results of Table 3 examined in conjunction with Fig. 2 reveal some interesting packing effects in the structure. For molecule 2, the equation of the least-squares plane is $-4.207x + 9.874z - 4.937 = 0$ with all atoms less than 0.01 \AA from the plane. The perpendicular to this plane lies in the $a-c$ plane and forms an angle of 3.6° with the c axis. The four chlorine atoms of molecule 2 form a rectangle which is parallel to the b axis (by symmetry) and makes a dihedral angle of 3.8° with the $b-c$ plane, *i.e.* the chlorine grouping follows quite closely the orientation of the carbon framework. For molecule 1, the equation of the least-squares plane reads $-5.009x + 9.892z = 0$ with a perpendicular lying in the $a-c$ plane at an angle of -1.1° to the c axis. However, the deviations from planarity here of up to 0.033 \AA or 2.5 are systematic and can be viewed in the following way. The chlorine atoms of molecule 1, which are restricted to the $a-c$ plane, lie almost exactly at the corners of a rectangle (not required by symmetry) whose sides turn out to be aligned perpendicular and parallel to the c -axis to within a few minutes of arc. The vector between the tetrahedral carbon atoms of molecule 1 is at 90.4° to the c axis. However, similar vectors from atom C(3') to C(3), C(2') to C(2) and C(1') to C(1) make angles of 87.0 , 88.7 , and 86.3° respectively with the c axis. The least-squares plane through one of the outer benzene rings is $-5.174x + 9.887z = 0$ and has a perpendicular which

Table 3. Deviations, Δ_\perp (\AA), from least-squares planes and the number of standard deviations ($|\Delta_\perp/\sigma_\perp|$) for each atom

Atoms in parentheses (and their symmetry-generated equivalents) were used in determining the least-squares planes. C(1), C(2), C(3) represent 4 atoms each, C(4) two atoms, for planes passed through the complete carbon skeleton of each molecule. For the benzene ring plane, C(1), C(2) and C(3) represent 2 atoms each.

Molecule 1			Molecule 2		
Atom	Δ_\perp	$ \Delta_\perp/\sigma_\perp $	Atom	Δ_\perp	$ \Delta_\perp/\sigma_\perp $
(C(1)-1)	0.003 \AA	2.3	(C(1)-2)	0.001 \AA	0.1
(C(2)-1)	0.007	0.5	(C(2)-2)	-0.009	0.8
(C(3)-1)	0.024	2.4	(C(3)-2)	0.008	0.9
(C(4)-1)	-0.033	2.5	(C(4)-2)	0.0 by symmetry	
Cl(1)-1	-1.50		Cl(1)-2	1.46	
Cl(2)-1	1.41				

Molecule 1 - benzene ring		
Atom	Δ_\perp	$ \Delta_\perp/\sigma_\perp $
(C(1)-1)	$\pm 0.021 \text{ \AA}$	1.5
(C(2)-1)	± 0.017	1.3
(C(3)-1)	± 0.012	1.2
C(4)-1	± 0.059	4.5
Cl(1)-1	-1.55	
Cl(2)-1	1.37	

makes an angle of -2.1° with the c axis. Deviations of the benzene ring carbon atoms from this plane are equal to or less than 1.5 while the tetrahedral carbon atoms lie ± 0.06 Å or 4.5 away from the plane. The twist of approximately 2° in the outer rings of molecule 1 is probably responsible for the significant difference between the two C–C–Cl bond angles for this molecule.

These results can be interpreted as follows. The rotation of 3.6° about the b axis by molecule 2 with respect to the chlorine framework of molecule 1 results in the two types of carbon–chlorine contact quoted above. Two of the four chlorine atoms on molecule 1 participate thereby in C–Cl contacts which approach the sum of the van der Waals radii, 3.5 Å. Dovetailed pairs of molecules are farther apart than they need be (considered as isolated pairs) in order to allow some interleaving of the hydrogen atoms of the molecules related by C -centered translations. The slight twist in molecule 1 helps to accommodate this interleaving. For example, the contact between the hydrogen atom on C(1)–1 (position estimated stereochemically) and a chlorine atom on its C -translated equivalent is 2.85 Å, somewhat shorter than the sum

Table 4. *R.M.S. displacements, $\mu(R_i)$, along the three principal axes of the thermal ellipsoid for each atom, and orientation of the principal axes 1,2,3 with respect to the c , b , and a^* axes (φ_c , φ_b , and φ_{a^*} respectively)*

Standard deviations (in units of 0.01 Å for μ and deg. for φ) are given in parentheses

Atom	R_i	$\mu(R_i)$	φ_c	φ_b	φ_{a^*}
Cl(1)–1	1	0.15 (1) Å	141 (2)°	90	51 (2)°
	2	0.24 (1)	90	0	90
	3	0.29 (1)	51 (2)	90	39 (2)
Cl(2)–1	1	0.20 (1)	36 (5)	90	54 (5)
	2	0.26 (1)	54 (5)	90	144 (5)
	3	0.33 (1)	90	180	90
C(1)–1	1	0.19 (2)	52 (31)	142 (32)	93 (13)
	2	0.21 (2)	43 (30)	54 (33)	111 (4)
	3	0.44 (2)	72 (3)	80 (3)	21 (3)
C(2)–1	1	0.19 (2)	23 (12)	91 (32)	113 (15)
	2	0.21 (2)	97 (33)	21 (5)	110 (15)
	3	0.35 (1)	68 (4)	69 (5)	31 (4)
C(3)–1	1	0.18 (2)	23 (8)	104 (17)	109 (12)
	2	0.21 (1)	85 (17)	26 (15)	115 (13)
	3	0.25 (1)	67 (8)	69 (11)	32 (11)
C(4)–1	1	0.19 (3)	130 (23)	90	40 (23)
	2	0.23 (2)	90	0	90
	3	0.23 (2)	40 (23)	90	50 (23)
Cl(1)–2	1	0.18 (1)	135 (2)	133 (2)	82 (2)
	2	0.25 (1)	91 (3)	101 (3)	169 (3)
	3	0.30 (1)	46 (2)	135 (2)	83 (3)
C(1)–2	1	0.22 (1)	79 (12)	113 (10)	26 (12)
	2	0.27 (2)	135 (60)	54 (54)	66 (17)
	3	0.28 (1)	133 (59)	136 (51)	99 (27)
C(2)–2	1	0.20 (3)	30 (18)	103 (15)	117 (27)
	2	0.22 (2)	108 (27)	63 (10)	146 (23)
	3	0.29 (1)	113 (7)	150 (8)	109 (7)
C(3)–2	1	0.17 (2)	5 (8)	85 (8)	91 (11)
	2	0.22 (1)	89 (11)	117 (28)	153 (29)
	3	0.24 (1)	85 (8)	152 (28)	63 (29)
C(4)–2	1	0.17 (3)	29 (15)	90	119 (15)
	2	0.23 (2)	119 (15)	90	151 (15)
	3	0.24 (2)	90	180	90

of the van der Waals radii, 3.0 Å. Without the twist of the outer rings, this contact would be still shorter.

R.M.S. components of thermal motion for each atom along the three principal axes of the anisotropic thermal ellipsoid as well as the directions of these axes are tabulated in Table 4.

Molecule 1 exhibits somewhat greater thermal motion than molecule 2. Atoms Cl(1)–1, Cl(2)–1 and especially C(1)–1 have highly anisotropic thermal motion. The directions of the principal axes for the chlorine atoms are physically reasonable. Directions of minimum motion are along C–Cl bonds and directions of high thermal motion are perpendicular to C–Cl bonds suggesting vibrational modes which alleviate the Cl–Cl repulsions (Cl–Cl intramolecular contacts are 2.91 and 2.92 Å; sum of van der Waals radii is 3.6 Å). The still greater repulsion of bromine atoms in 9,10-dibromoanthrone is possibly the cause of the apparent slight bend in this molecule.

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References

- BECKETT, A. H. & MULLEY, B. A. (1955). *Chem. and Ind.* p. 146.
- BUSING, W. R. & LEVY, H. A. (1959). ORXFE. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- FERRIER, W. G. & IBALL, J. (1954). *Chem. and Ind.* p. 1296.
- HERBSTEIN, F. H. (1959). *J. Chem. Soc.* p. 2292.
- HERBSTEIN, F. H. (1961). *Acta Cryst.* **14**, 77.
- IBALL, J. & YOUNG, D. W. (1958). *Acta Cryst.* **11**, 476.
- International Tables for X-Ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.
- International Tables for X-Ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- MEYER, K. H. & ZAHN, K. (1913). *Liebigs Ann.* **396**, 166.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
- SILVERMAN, J. & YANNONI, N. F. (1963). *Nature, Lond.* **200**, 64.
- SLY, W. G., SHOEMAKER, D. P. & VAN DEN HENDE, J. H. (1962). ERFR 2. Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.
- YANNONI, N. F., KRUKONIS, A. P. & SILVERMAN, J. (1964). *Science*, **148**, 231.