# 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 $a = 10\cdot93$, $b = 13\cdot90$, $c = 9\cdot89$ Å, $\beta = 116\cdot2°$. The crystal structure has been determined by three-dimensional X-ray analysis and refined to an $R$ index of $13\cdot0\%$ 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, Krukonis & 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 $1\cdot3$ mm and average diameter $0\cdot1$ mm.

The chemical and crystallographic data are as follows:

$C_{14}H_8Cl_4$; $M = 317\cdot8$; m.p. $153$–$157°C$.
Monoclinic:
$a = 10\cdot93 \pm 0\cdot04$, $b = 13\cdot90 \pm 0\cdot03$, $c = 9\cdot89 \pm 0\cdot02$ Å,
$\quad \beta = 116\cdot2 \pm 0\cdot1$; $V = 1348$ Å$^3$; $Z = 4$.
Density data: $D_{calc}$ $(Z=4) = 1\cdot565$ g.cm$^{-3}$, $D_{obs} = 1\cdot55$ 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 $K\alpha$) $= 76\cdot53$ cm$^{-1}$, $\mu$(Mo $K\alpha$) $= 8\cdot67$ cm$^{-1}$.

The intensity data were taken with Cu $K\alpha$ ($\lambda = 1\cdot5418$ 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, $\lambda = 0\cdot7107$ 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, $R = (\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{\frac{1}{2}}$. 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 ($R = \Sigma(F_o - |F_c|)/\Sigma F_o$) from $24\cdot4$ to $16\cdot0\%$. After five more least-squares cycles in the same mode on the full complement of observed data, 780 reflections, the $R$ value converged to $19\cdot7\%$. 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 (Å²) 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 | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 (6) | −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) | −0.0011 (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) |
| Cl(2)-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 $(\Sigma w(F_o - |F_c|)^2/(N_o - N_v))^{\frac{1}{2}}$, 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 $0.1\sigma$. 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, ½ 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 Å; 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 Å on one side and contacts longer than 3.9 Å on the other. The chlorine–chlorine contacts between pairs of dovetailed molecules are 4.21 and 4.08 Å. The shortest contact between molecules related by the C-centered translation is a chlorine–carbon contact of 3.77 Å. The chlorine atoms effectively separate the anthracene skeletons; the closest carbon–carbon contact is 3.77 Å and occurs between carbon atoms on molecule 1 and the molecule at ½, ½, ½. Intermolecular packing effects involving the interleaving of molecule 1 with the molecules at ½, ½, 0 and ½, ½, ½ 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



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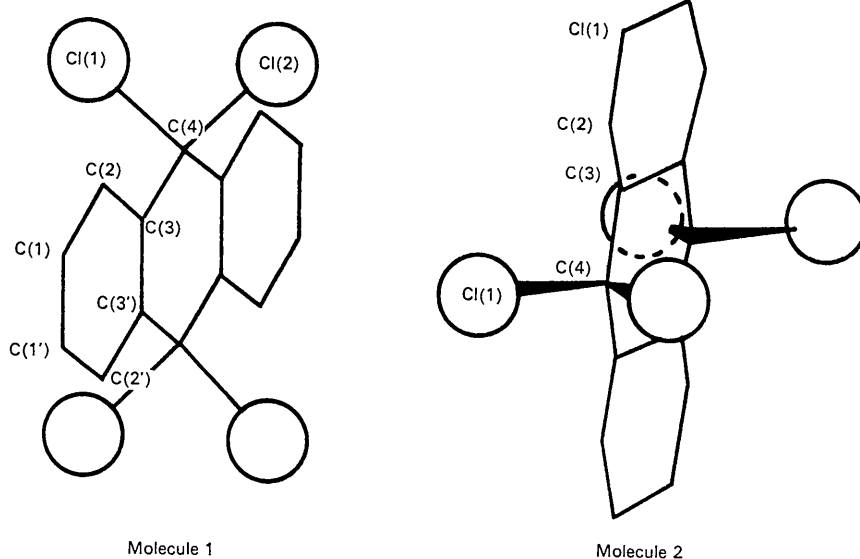
Fig. 1. Numbering of independent atoms in the two crystallographically independent molecules. The pair as drawn corresponds in orientation to dovetailed pairs in Fig. 2. In molecule 1 (center at 0,0,0), the chlorine atoms and attached carbon atoms lie in the $y=0$ mirror plane; i.e. Cl(1)–1, Cl(2)–1,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



Molecule 1              Molecule 2
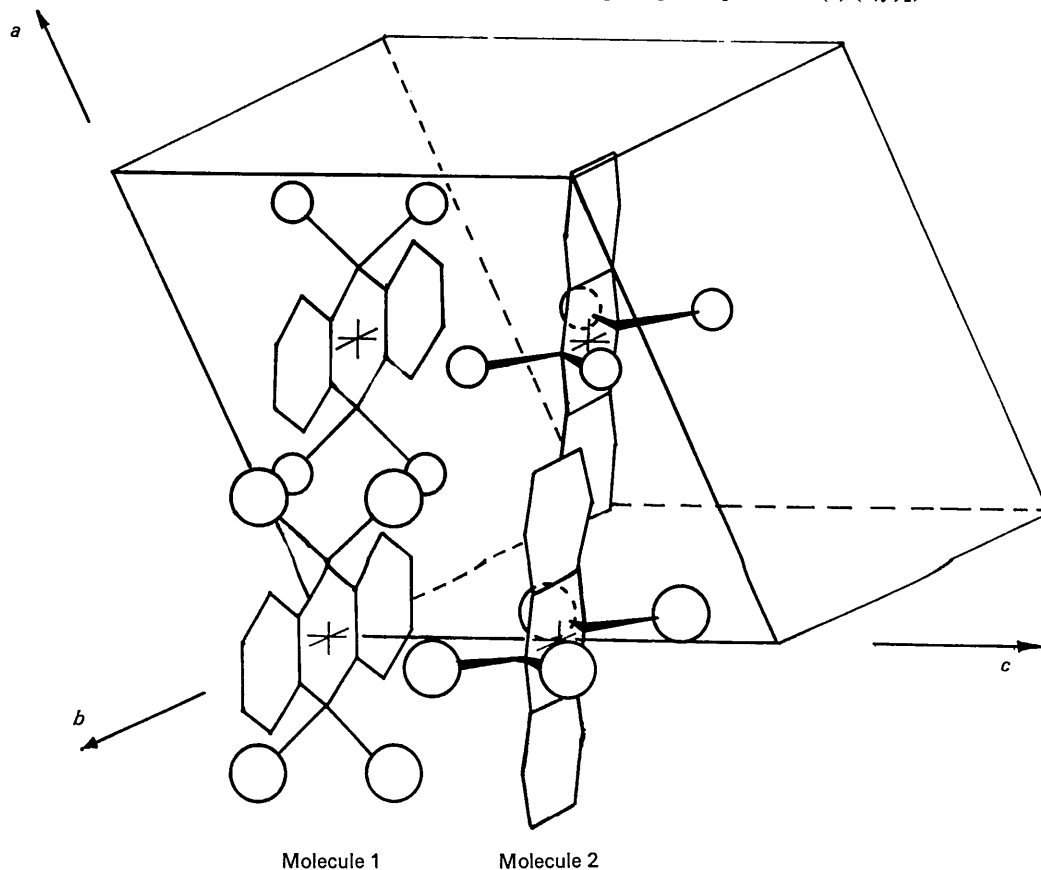
Fig. 2. Packing arrangement of the four molecules in the unit cell.

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 $F_c$.

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
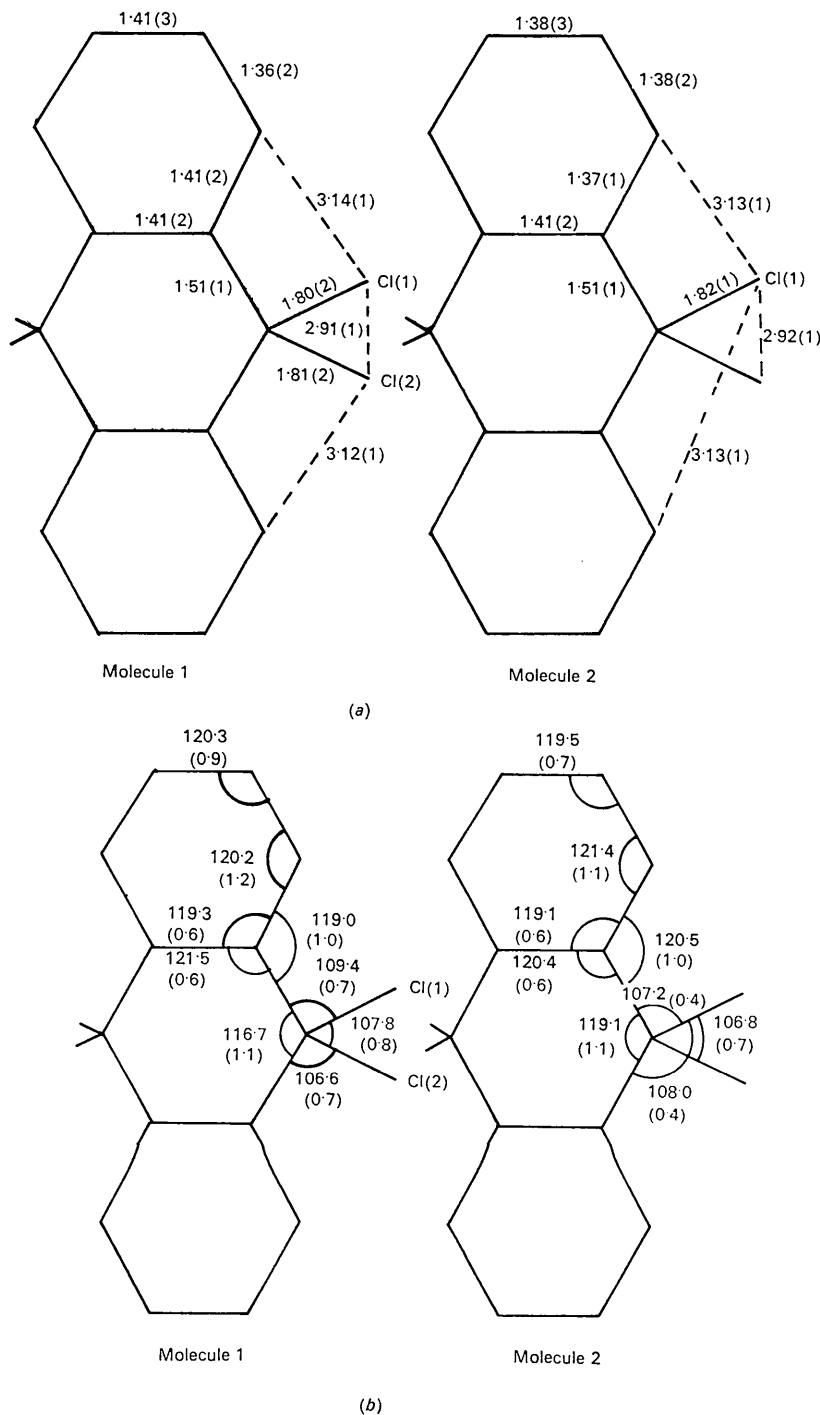


Fig. 3. The dimensions of molecules 1 and 2: (a) bond lengths in Å, standard deviations in units of 0·01 Å in parentheses; (b) bond angles in degrees, standard deviations in degrees in parentheses.

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
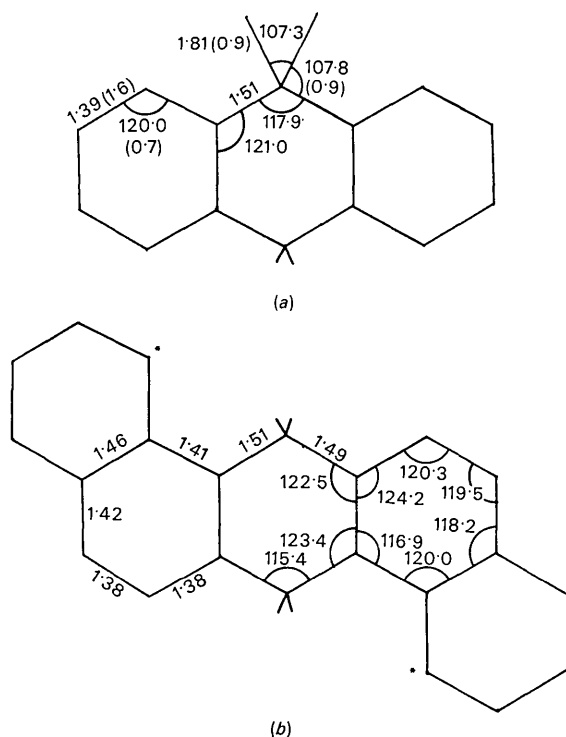


(a)



(b)

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 Å 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 Å, only slightly shorter than 3·0 Å, 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 $-4\cdot207x + 9\cdot874z - 4\cdot937 = 0$ with all atoms less than 0·01 Å 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 $-5\cdot009x + 9\cdot892z = 0$ with a perpendicular lying in the $a$–$c$ plane at an angle of $-1\cdot1°$ to the $c$ axis. However, the deviations from planarity here of up to 0·033 Å 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 $-5\cdot174x + 9\cdot887z = 0$ and has a perpendicular which

Table 3. Deviations, $\Delta_{\perp}$ (Å), 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 | $\Delta_{\perp}$ | $|\Delta_{\perp}/\sigma_{\perp}|$ | Atom | $\Delta_{\perp}$ | $|\Delta_{\perp}/\sigma_{\perp}|$ |
| (C(1)–1) | 0·003 Å | 2·3 | (C(1)–2) | 0·001 Å | 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 | $\Delta_{\perp}$ | $|\Delta_{\perp}/\sigma_{\perp}|$ |
|---|---|---|
| (C(1)–1) | ±0·021 Å | 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 $-2 \cdot 1°$ with the $c$ axis. Deviations of the benzene ring carbon atoms from this plane are equal to or less than $1 \cdot 5$ while the tetrahedral carbon atoms lie $\pm 0 \cdot 06$ Å or $4 \cdot 5$ 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 $3 \cdot 6°$ 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, $3 \cdot 5$ 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 $2 \cdot 85$ 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* ($\varphi_c$, $\varphi_b$, *and* $\varphi_{a*}$ *respectively*)

Standard deviations (in units of $0 \cdot 01$ Å for $\mu$ and deg. for $\varphi$) are given in parentheses

| Atom | $R_i$ | $\mu(R_i)$ | $\varphi_c$ | $\varphi_b$ | $\varphi_{a*}$ |
|---|---|---|---|---|---|
| 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, $3 \cdot 0$ 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 $2 \cdot 91$ and $2 \cdot 92$ Å; sum of van der Waals radii is $3 \cdot 6$ Å). The still greater repulsion of bromine atoms in 9,10-dibromoanthrone is possibly the cause of the apparent slight bend in this molecule.

### 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.