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The Crystal and Molecular Structure of
2,3,4,5-Tetrachlorotricyclo[4,2,2,0^{2,5}]deca-3,7-diene (C$_{10}$H$_8$Cl$_4$)

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The title compound crystallizes in space group $P2_1/c$ with $a = 7\cdot556$ (1), $b = 18\cdot545$ (2), $c = 8\cdot496$ (1) Å, $\beta = 113\cdot73$ (1)°, and $Z = 4$. The structure was determined by direct methods from data collected on a fully automated X-ray diffractometer. Full-matrix least-squares refinement of 128 parameters based on 3362 independent reflections [$\sin \theta/\lambda (\text{Mo } K\alpha) \le 0\cdot725$] yielded a final $R = 0\cdot045$. An unusually long C–C single bond ($1\cdot591$ Å) is observed in the highly strained junction between the cyclobutene ring and the bicyclohexene ring system.

Introduction

The reaction of 3*H*-pentachlorocyclobutene with potassium bases apparently (Scherer & Meyers, 1968, 1969) generates the unstable molecule tetrachlorocyclobutadiene (1) by β elimination of chloride ion from intermediate (2). Empirical evidence suggests that both (1) and (2) can be intermediates in subsequent reactions (Willcott & Cargle, 1967; Scherer & Meyers, 1969; Semmelhack & DeFranco, 1972).

(1)   (2)
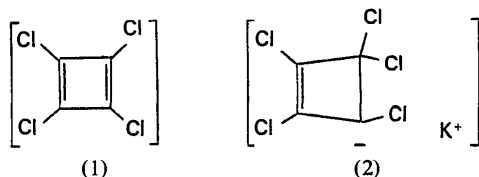
If (1) is the important intermediate, the product of the reaction between basic 3*H*-pentachlorocyclobutene and 1,3-cyclohexadiene would be (3) [2,3,4,5-tetra-

chlorotricyclo[4,2,2,0^{2,5}]deca-3,7-diene (TCTCDD)]; if intermediate (2) predominates, (4) would be the principal product.

(3)   (4)
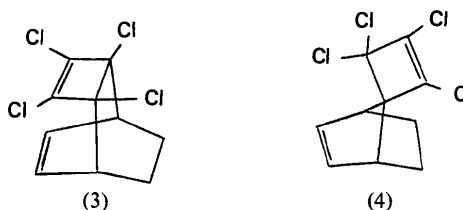
The present analysis proves that (3) is the principal product of this reaction. A complete summary of additional evidence pertaining to the possible intermediates (1) and (2) in this and related systems is given by Semmelhack & DeFranco (1972).

Experimental

Colorless crystals, which proved to be TCTCDD, were supplied by Drs M. F. Semmelhack and R. J. DeFranco of the Cornell University Department of Chemistry. The crystals turned yellow when exposed to X-rays in the open atmosphere; this effect was eliminated by sealing a crystal ($0\cdot7 \times 0\cdot5 \times 0\cdot5$ mm, $D_m = 1\cdot646$ g cm^{-3})

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inside a glass capillary. On the basis of diffraction symmetry and observed systematic extinctions $0k0$ $(k=2n+1)$ and $h0l$ $(l=2n+1)$, the structure was assigned the space group $P2_1/c$, No. 14.

Intensity data were collected on a fully automated Picker FACS-1 diffractometer using Zr-filtered Mo $K\bar{\alpha}$ radiation $(\lambda=0.71069)$. The lattice parameters were refined by least-squares analysis of the setting angles of 50 reflections and found to be: $a=7.556$ (1), $b=18.545$ (2), $c=8.496$ (1) Å, $\beta=113.73$ (1)°; with $Z=4$ and $D_c=1.645$ g cm^{-3}. Diffraction intensities were measured with a $\theta-2\theta$ scan mode, a scan rate of 1° min^{-1} and a base width that included a variable incre-

ment in angle above the minimum (1.1° at $2\theta=0$) to allow for dispersion. Initially stationary background counts of 40 s duration were measured at each end of the scan. Subsequently the background counting time was reduced to 20 s to minimize the exposure of the crystal to X-rays. Precisely 3362 reflections from a unique quadrant of reciprocal space, having $\sin\theta/\lambda$(Mo $K\alpha$)≤ 0.725, were examined. Of these, 205 were classified as unobserved by the criterion $F_o\leq 1.35\sigma_F$, where F_o and σ_F are the observed structure factor and its standard deviation, respectively, as defined by the following equations:

$$F_o=[(C-kB)/Lp]^{1/2}$$
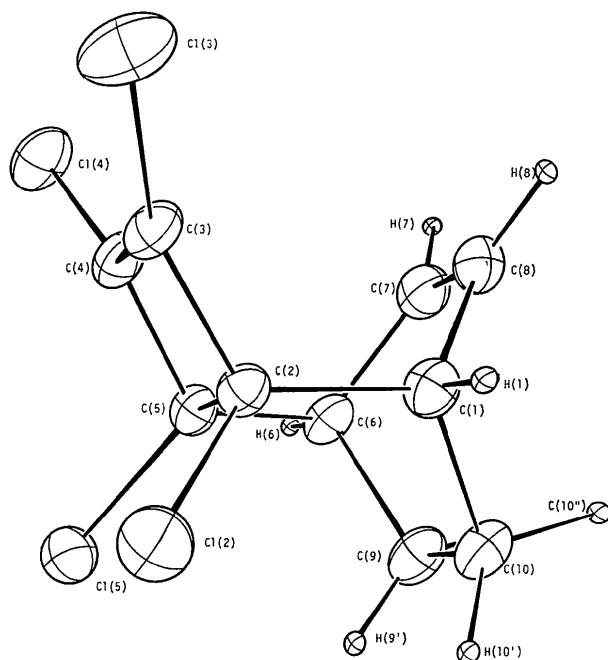$$\sigma_F=(C+k^2B)^{1/2}/(2F_oLp)+0.025F_o.$$

Fig. 1. The molecule showing labeling of the atoms. H(9''), attached to C(9), is obscured by C(10).

Table 1. *Final atomic fractional coordinates* ($\times 10^4$)

The estimated standard deviations in parentheses apply to the last significant digit. The numbering of Cl and H atoms corresponds to the C to which they are attached.

	x	y	z
C(1)	6349 (3)	1787 (1)	6607 (3)
C(2)	7831 (3)	1269 (1)	7864 (3)
C(3)	8984 (3)	1514 (1)	9677 (3)
C(4)	8091 (3)	1087 (1)	10370 (3)
C(5)	6766 (3)	753 (1)	8703 (3)
C(6)	4599 (3)	945 (1)	7964 (3)
C(7)	4414 (4)	1740 (2)	8234 (3)
C(8)	5313 (4)	2169 (1)	7553 (3)
C(9)	3805 (4)	816 (2)	5992 (3)
C(10)	4828 (4)	1317 (1)	5191 (3)
Cl(2)	9261 (1)	848 (0)	6895 (1)
Cl(3)	10653 (1)	2176 (0)	10447 (1)
Cl(4)	8169 (1)	996 (0)	12386 (1)
Cl(5)	7124 (1)	−191 (0)	8597 (1)
H(1)	7000	2100	6000
H(6)	4027	616	8571
H(7)	3750	1900	9000
H(8)	5503	2709	7601
H(9')	4000	300	5750
H(9'')	2438	978	5780
H(10')	5318	1065	4390
H(10'')	4011	1758	4667

Table 2. *Thermal parameters* (Å^2)

The estimated standard deviations in parentheses apply to the last significant digit. The anisotropic B_{ij} (Å^2) are related to the dimensionless β_{ij} employed during the least-squares refinement by $B_{ij}=4\beta_{ij}/a_i^*a_j^*$ where β_{ij} is given by the expression:

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\right].$$

The isotropic thermal parameters are calculated from $B=4[V^2\det(\beta_{ij})]^{1/3}$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B
C(1)	2.78 (9)	3.09 (9)	2.37 (8)	−0.04 (7)	0.95 (7)	0.32 (7)	2.74
C(2)	2.24 (8)	3.05 (9)	2.17 (7)	−0.06 (7)	0.96 (6)	−0.13 (6)	2.43
C(3)	2.12 (8)	3.54 (10)	2.55 (8)	−0.25 (7)	0.56 (7)	−0.33 (7)	2.77
C(4)	2.56 (9)	3.52 (10)	1.97 (7)	0.35 (7)	0.69 (7)	0.03 (7)	2.66
C(5)	2.44 (8)	2.72 (8)	2.13 (7)	−0.02 (7)	0.89 (6)	0.12 (6)	2.42
C(6)	2.23 (8)	3.68 (10)	2.47 (8)	−0.28 (7)	0.95 (7)	0.03 (7)	2.71
C(7)	2.62 (9)	4.23 (12)	3.01 (10)	0.73 (9)	1.05 (8)	−0.36 (9)	3.15
C(8)	2.98 (10)	3.19 (10)	2.94 (9)	0.57 (8)	0.69 (8)	−0.17 (8)	3.11
C(9)	2.55 (9)	4.06 (12)	2.63 (9)	−0.54 (8)	0.54 (7)	−0.21 (8)	3.11
C(10)	3.20 (10)	3.83 (11)	2.08 (8)	−0.20 (9)	0.63 (7)	0.10 (7)	3.05
Cl(2)	3.24 (3)	5.20 (4)	3.58 (3)	0.56 (2)	2.06 (2)	−0.17 (2)	3.53
Cl(3)	3.64 (3)	5.57 (4)	4.35 (3)	−1.99 (3)	1.08 (3)	−1.26 (3)	4.25
Cl(4)	4.70 (3)	5.81 (4)	2.05 (2)	0.06 (3)	1.23 (2)	0.08 (2)	3.83
Cl(5)	4.41 (3)	2.76 (2)	3.41 (3)	0.22 (2)	1.31 (2)	0.21 (2)	3.52

In these equations C and B are, respectively, the total scan and background counts and k is the ratio of scan time to total background counting time. Corrections were made for Lorentz and polarization effects but not for absorption since the linear absorption coefficient μ is small (10 cm^{-1}). Atomic scattering factors were calculated for C and Cl from the coefficients of Cromer & Mann (1968) and for H from parameters derived from data in *International Tables for X-ray Crystallography* (1962).

Structure determination

The structure was solved by direct methods (Karle & Karle, 1966) using the Fortran program *FAME* (Dewar & Stone, 1968a) to generate the normalized structure factors (E's); *MAGIC* (Dewar & Stone, 1968b) was then used to systematically assign symbols to 211 reflections. Three signs were arbitrarily selected to determine the origin and two sets of signs for the remainder of the starting reflections resulted in two relatively probable sets of phases for the 211 reflections. In the E map derived from the less probable of the two there were three Cl atom positions that were entirely consistent with the Patterson synthesis. A difference Fourier map based on this assignment of three-eighths of the electrons in the unit cell clearly revealed the positions of the remaining chlorine atom and all of the C atoms. After further refinement, H atoms were located in eight regions of relatively high electron density and, for consistency, were placed 1·01 Å from adjacent C atoms. Full-matrix least-squares (Busing, Martin & Levy, 1962) refinement, in which positional and anisotropic thermal parameters of all nonhydrogen atoms, a scale factor, and finally a secondary extinction correction (Zachariasen, 1968) were varied, resulted in standard residuals $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.045$ and $R' = \{\sum||F_o| - |F_c||^2/\sum|F_o|^2\}^{1/2} = 0.048$.* The data to parameter ratio was 24·7. The final value of the extinction coefficient was 5.81×10^{-6} and the smallest related correction factor c in $F_o/c = F_{corr}$ was 0·843 for the 230 reflection. A final difference map displayed no electron density greater than 0·35 e Å^{-3}.

Results and discussion

Fig. 1 is an illustration of the molecule depicting the thermal ellipsoids of the atoms (Johnson, 1970). The atom designations are consistent, wherever possible, with IUPAC convention. Final atomic positional parameters are presented in Table 1. Anisotropic thermal parameters (B_{ij}) and the equivalent isotropic parameters appear in Table 2.

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* Tables of structure factors, thermal motion parameters and deviations from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31344 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances* (Å) *and bond angles* (°)

The estimated standard deviations in parentheses apply to the last significant digit. Corresponding distances and angles across the molecular pseudo mirror plane appear opposite each other. The figures in brackets apply to the last significant digit and represent positive increments derived from correction for rigid-body thermal motion. They have not been included in the bond distances to which they are appended.

C–C single bonds

C(1)–C(2)	1·535 (3) [4]	C(5)–C(6)	1·541 (3) [5]
C(1)–C(8)	1·505 (3) [5]	C(6)–C(7)	1·506 (4) [4]
C(1)–C(10)	1·554 (3) [4]	C(6)–C(9)	1·554 (3) [3]
C(2)–C(3)	1·503 (3) [4]	C(4)–C(5)	1·500 (3) [4]
C(2)–C(5)	1·591 (3) [5]		
C(9)–C(10)	1·532 (4) [5]		

C–C double bonds

C(3)–C(4)	1·322 (3) [5]	
C(7)–C(8)	1·322 (4) [4]	

C–Cl bonds

C(2)–Cl(2)	1·780 (2) [4]	C(5)–Cl(5)	1·779 (3) [5]
C(3)–Cl(3)	1·691 (2) [4]	C(4)–Cl(4)	1·698 (2) [4]

C(2)–C(1)–C(8)	108·3 (2)	C(5)–C(6)–C(7)	108·2 (2)
C(2)–C(1)–C(10)	107·0 (2)	C(5)–C(6)–C(9)	106·8 (2)
C(8)–C(1)–C(10)	107·2 (2)	C(7)–C(6)–C(9)	107·2 (2)
C(1)–C(2)–C(3)	118·9 (2)	C(4)–C(5)–C(6)	119·0 (2)
C(1)–C(2)–C(5)	109·2 (2)	C(2)–C(5)–C(6)	108·9 (2)
C(3)–C(2)–C(5)	84·9 (2)	C(2)–C(5)–C(4)	84·8 (2)
C(1)–C(2)–Cl(2)	111·2 (2)	C(6)–C(5)–Cl(5)	111·4 (2)
C(3)–C(2)–Cl(2)	113·4 (2)	C(4)–C(5)–Cl(5)	113·4 (2)
C(5)–C(2)–Cl(2)	117·0 (2)	C(2)–C(5)–Cl(5)	117·0 (2)
C(2)–C(3)–C(4)	94·9 (2)	C(3)–C(4)–C(5)	95·3 (2)
C(2)–C(3)–Cl(3)	130·6 (2)	C(5)–C(4)–Cl(4)	130·6 (2)
C(4)–C(3)–Cl(3)	134·2 (2)	C(3)–C(4)–Cl(4)	133·8 (2)
C(1)–C(8)–C(7)	114·8 (2)	C(6)–C(7)–C(8)	115·3 (2)
C(1)–C(10)–C(9)	110·1 (2)	C(6)–C(9)–C(10)	109·9 (2)

Table 3 is a listing of intramolecular bond distances and bond angles with their standard deviations (Busing, Martin & Levy, 1964). A tabulation of relevant thermal motion parameters (Schomaker & Trueblood, 1968) is available.* Calculated increments to be added to the bond lengths as corrections for rigid-body thermal motion appear in square brackets in Table 3. The bond length corrections are slightly greater than one standard deviation; all bond angle corrections were negligible.

The free molecule might be expected to exhibit the symmetry m; indeed, in the crystal structure, the approximation to that symmetry is excellent despite the fact that the atoms occupy only general positions in the space group. From Table 3 it is clear that corresponding angles and distances across the pseudo mirror plane are virtually identical. A further measure of this molecular symmetry was obtained from a least-squares analysis of the deviations from perfect superposition after reflecting each pseudo equivalent pair; an average deviation of 0·01 Å was found for the seven pairs of related non-hydrogen atoms. The pseudo mirror plane indicates that the molecular geometry is largely determined by intramolecular rigidity rather than by inter-

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* See previous footnote.

molecular packing forces. This conclusion is supported by the fact that all intermolecular contact distances fall within the normal ranges of van der Waals distances for the types of atoms involved.

With the exception of the unusually long (1·591 Å) single C–C bond, C(2)–C(5), all of the bond lengths in the molecule are remarkably typical of the respective types of bonds (Sutton, 1965). Though uncommon, long (1·575–1·623 Å) C–C single bonds are found in a few other compounds. These are generally associated with highly strained cyclobutane rings that are fused on opposite sides to adjacent four-, five-, or six-membered ring systems (Margulis, 1965; Camerman, Weinblum & Nyberg, 1969; Camerman & Nyberg, 1969; Barnett & Davis, 1970; Brown, Towns & Trefonas, 1971). Long bonds are also found in strained cage compounds (Beisler, Silverton, Pentilla, Horn & Fales, 1971). In the present case, it appears to result from the considerable strain that is inherent in the cyclobutene ring and, to a lesser extent, in the fused cyclohexene ring.

Quantitative measures of the planarity of selected rings and atomic groupings within the molecule are available* along with dihedral angles that further describe the detailed molecular geometry. No deviation from planarity is greater than 0·004 Å in the three least-squares planes that are determined respectively by C(1), C(6) and an adjacent pair of C atoms, and which intersect (approximately) along the line between C(1) and C(6). Similarly, the deviation is less than 0·002 Å for each of the three planes that are determined respectively by C(2), C(5), and an adjacent pair of C or Cl atoms, and which intersect along the bond between C(2) and C(5). The sp^2 bond system at C(3)–C(4) deviates about 6° from planarity. It appears that intermolecular interactions displace the Cl atoms slightly in the direction of the cyclohexene ring.

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* See footnote on p. 1214.

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