acids can be put together. A rule in so doing is that there must be either an odd number of *A* conformers or an even number of *S* conformers in a loop. This is because *A* conformers effect 180° turns in the direction of helix propagation and *S* conformers cause 90° turns. One example of a possible model for a five-nucleotide loop is shown in Fig. 5.

## Discussion

These seven conformations can be considered as model basic conformations of nucleic acids. They are by no means rigid. Indeed, small changes in the sugar pucker and/or $\psi$, $\psi'$, $\varphi$, $\varphi'$, $\chi$ and $\chi'$ can give quite noticeable structural differences in a polymerized form. This is most clearly seen when one compares polyUpA [Fig. 4(*e*)] with RNA11 (Arnott, Dover & Wonacott, 1969) [Fig. 4(*f*)] which are both $P_3$ polymers. However, the gross features, as defined by Table 1, of both structures are similar, and differ quite markedly from those of the other six conformers. We hope that these conformers, as we have defined them, will be particularly useful in model fitting of low resolution Fourier maps of nucleic acids.

We wish to thank Alexander Rich, Jenny Glusker, Walter Hamilton and Joel Sussman for their encouragement and criticism and L. Katz, Director of the Graphics Facility for Interactive Displays for the use of the computer.

This research was supported in part by U.S.P.H.S. grants CA-06927, CA-10925, CA-04186, RR-05539, 3P07RR00442 and a Training Grant in Biophysics 5T01GM02012 from the National Institutes of Health; by grants GB-15754 and GB-18421 from the National Science Foundation; by grant E-247B from the American Cancer Society; by the Atomic Energy Commission and by an appropriation from the Commonwealth of Pennsylvania.

## References

ARNOTT, S. (1970). *Prog. Biophys. Molec. Biol.* **21**, 265–319.
ARNOTT, S., DOVER, S. D. & WONACOTT, A. J. (1969). *Acta Cryst.* B**25**, 2192–2206.
DONOHUE, J. & TRUEBLOOD, K. N. (1960). J. *Mol. Biol.* **2**, 363–371.
MARVIN, D. A., SPENCER, M., WILKINS M. H. F. & HAMILTON, L. D. (1961). J. *Mol. Biol.* 3, 547–565.
NEWTON, M. (1973). J. *Amer. Chem. Soc.* In the press.
OLSON, W. & FLORY, P. (1972). *Biopolymers*, **11**, 1–23, 25–56, 57–66.
RUBIN, J., BRENNAN, T. & SUNDARALINGAM, M. (1972). *Biochemistry*, **11**, 3112–3128.
SEEMAN, N. C., SUSSMAN, J. L., BERMAN, H. M. & KIM, S.-H. (1971). *Nature, New Biol.* **233**, 90–92.
SUNDARALINGAM, M. (1969). *Biopolymers*, **7**, 821–860.
SUSSMAN, J. L., SEEMAN, N. C., KIM, S.-H. & BERMAN, H. M. (1972). *J. Mol. Biol.* **66**, 403–421.
T'SO, P., KONDO, N., SCHWEIZER, M. & HALLES, D. (1969). *Biochemistry*, **8**, 997–1028.
WATSON, J. D. & CRICK, F. M. C. (1953). *Nature, Lond.* **171**, 737–738.

*Acta Cryst.* (1973). B**29**, 710

# The Crystal and Molecular Structure of Octachloro-2,4-dihydropentalene

BY GRETCHEN MANDEL AND JERRY DONOHUE

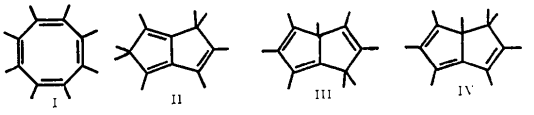
*Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania* 19104, *U.S.A.*

(*Received* 8 *August* 1972; *accepted* 18 *November* 1972)

The unit cell of octachloro-2,4-dihydropentalene ($\varepsilon$-$C_8Cl_8$) is orthorhombic, space group *Pnma* ($D_{2h}^{16}$), with lattice constants $a=10{\cdot}170\pm0{\cdot}007$, $b=7{\cdot}284\pm0{\cdot}006$, and $c=17{\cdot}281\pm0{\cdot}010$ Å. With $Z=4$, the calculated density is 1·75 g cm$^{-3}$. Three-dimensional data were collected at 21 °C on an automated diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation by the $\theta$–$2\theta$ scan technique. Direct phasing methods were used to obtain the trial structure. The final $R$ value was 8·8%. The average carbon–chlorine bond distance is $1{\cdot}79\pm0{\cdot}01$ Å for aliphatic chlorine atoms and $1{\cdot}69\pm0{\cdot}02$ Å for vinyl chlorine atoms. The shortest intermolecular distance is a 3·51 Å chlorine–chlorine contact.

## Introduction

The series of structures generated by dimerization and subsequent rearrangement of perchlorobutenyne has been studied by Roedig, Helm, West & Smith (1969). One of the reactions involves the thermal rearrangement at 180° of $\gamma$-$C_8Cl_8$ (m. p. 172°), (believed to be I on the basis of ultraviolet, infrared and n.q.r. spectra), into $\delta$-$C_8Cl_8$ (m. p. 86°) and $\varepsilon$-$C_8Cl_8$ (m. p. 111°). The $\delta$-$C_8Cl_8$ was thought to be II and the structure of $\varepsilon$-$C_8Cl_8$ to be III or IV.



The compounds $\delta$-$C_8Cl_8$ and $\varepsilon$-$C_8Cl_8$ undergo a variety of transformations, including those to carbonyl derivatives. In order to deduce the correct structures for these derivatives, it was important to determine the structures of $\delta$-$C_8Cl_8$ and $\varepsilon$-$C_8C_{18}$ unequivocally.

For this reason, and in the hope of finding interesting intermolecular chlorine–chlorine distances, the structure determination of $\varepsilon$-$C_8Cl_8$ was undertaken. The structure of $\varepsilon$-$C_8Cl_8$ was determined to be II, contrary to the one originally proposed.

Table 1. *Observed and calculated structure factors*

| h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 0 2 | 51.4 | 52.8 | 1 2 10 | 13.1 | 12.3 | 2 1 9 | 39.6 | 39.3 | 3 0 5 | 18.4 | 21.1 | 3 7 9 | 7.9 | 7.8 | 4 4 7 | 9.5 | 9.7 | 5 4 6 | 16.0 | 17.0 | 6 4 5 | 5.2 | 5.2 | 8 1 7 | 17.9 | 17.7 |
| 0 0 4 | 76.9 | 76.3 | 1 2 11 | 31.1 | 27.4 | 2 1 10 | 21.5 | 20.9 | 3 0 6 | 0.0 | 1.8 | 3 7 7 | 0.0 | 0.5 | 4 4 8 | 9.5 | 9.7 | 5 4 7 | 7.2 | 8.1 | 6 4 6 | 15.5 | 14.7 | 8 1 8 | 8.7 | 3.4 |
| 0 0 6 | 137.3 | 138.5 | 1 2 12 | 5.1 | 4.9 | 2 1 11 | 22.0 | 22.2 | 3 0 7 | 22.2 | 22.2 | 3 7 8 | 9.4 | 9.1 | 4 4 9 | 10.1 | 11.3 | 5 4 8 | 18.8 | 19.1 | 6 4 7 | 5.0 | 4.2 | 8 1 10 | 20.4 | 20.4 |
| 0 0 8 | 35.2 | 33.4 | 1 2 13 | 13.7 | 12.5 | 2 1 12 | 19.9 | 19.6 | 3 0 8 | 99.2 | 104.5 | 3 7 9 | 9.4 | 10.0 | 4 4 10 | 10.1 | 11.3 | 5 4 10 | 8.8 | 9.1 | 6 4 8 | 9.0 | 8.0 | 8 1 11 | 8.1 | 7.9 |
| 0 0 10 | 12.2 | 10.7 | 1 2 14 | 5.3 | 5.3 | 2 1 13 | 14.8 | 15.4 | 3 0 9 | 49.8 | 52.4 | 4 0 1 | 12.9 | 12.4 | 4 4 11 | 8.5 | 8.0 | 5 4 11 | 8.4 | 9.3 | 6 4 9 | 5.2 | 5.3 | 8 1 12 | 15.4 | 14.2 |
| 0 0 12 | 125.5 | 115.1 | 1 2 15 | 26.0 | 25.5 | 2 1 14 | 20.5 | 21.7 | 3 0 10 | 33.5 | 37.1 | 4 0 2 | 9.0 | 9.4 | 5 4 1 | 12.9 | 12.4 | 5 4 12 | 8.4 | 8.2 | 6 4 10 | 5.2 | 5.9 | 8 1 13 | 8.1 | 5.9 |
| 0 0 14 | 10.1 | 7.4 | 1 2 16 | 13.1 | 12.8 | 2 1 15 | 28.6 | 31.4 | 3 0 11 | 20.1 | 22.3 | 4 0 3 | 50.0 | 5.4 | 5 4 2 | 9.0 | 2.4 | 5 7 1 | 15.3 | 17.1 | 7 0 1 | 11.1 | 11.3 | 8 1 14 | 5.1 | 5.8 |
| 0 0 16 | 51.2 | 46.4 | 1 2 17 | 5.4 | 2.1 | 2 1 16 | 5.8 | 6.8 | 3 0 12 | 15.8 | 15.5 | 4 0 4 | 12.9 | 13.5 | 5 4 3 | 12.9 | 13.5 | 5 7 2 | 7.3 | 5.7 | 7 0 2 | 15.4 | 15.4 | 9 1 1 | 7.0 | 7.0 |
| 0 0 18 | 30.2 | 28.5 | 1 2 18 | 3.2 | 0.9 | 2 1 17 | 5.7 | 4.8 | 3 0 13 | 4.5 | 12.1 | 4 0 5 | 27.7 | 28.2 | 5 4 4 | 8.1 | 8.4 | 5 7 3 | 5.2 | 5.8 | 7 0 3 | 3.1 | 1.0 | 9 1 2 | 29.2 | 28.9 |
| 1 0 1 | 3.8 | 2.5 | 1 2 19 | 3.2 | 2.1 | 2 1 18 | 20.0 | 21.9 | 3 0 14 | 4.5 | 5.1 | 4 0 6 | 20.1 | 22.8 | 5 4 5 | 10.0 | 12.8 | 5 7 4 | 10.2 | 12.8 | 7 0 4 | 10.1 | 9.4 | 9 1 3 | 24.0 | 24.2 |
| 1 0 3 | 9.2 | 9.4 | 1 3 1 | 31.1 | 26.3 | 2 1 19 | 20.0 | 21.9 | 3 0 15 | 49.5 | 52.4 | 4 0 7 | 21.6 | 23.3 | 5 4 6 | 5.1 | 1.7 | 5 7 5 | 1.5 | 3.2 | 7 0 5 | 5.6 | 5.8 | 9 1 4 | 37.8 | 37.2 |
| 1 0 5 | 15.9 | 17.6 | 1 3 2 | 15.4 | 16.0 | 2 2 1 | 15.8 | 18.0 | 3 0 16 | 5.1 | 2.6 | 4 0 8 | 3.1 | 2.1 | 5 4 7 | 12.5 | 10.1 | 6 0 1 | 12.5 | 10.1 | 7 0 6 | 5.1 | 5.8 | 9 1 5 | 70.4 | 70.4 |
| 1 0 7 | 9.1 | 8.9 | 1 3 3 | 88.1 | 78.5 | 2 2 2 | 34.4 | 39.1 | 3 0 17 | 21.7 | 25.3 | 4 0 9 | 16.4 | 17.2 | 5 4 8 | 18.0 | 26.4 | 6 0 2 | 37.1 | 40.6 | 7 0 7 | 7.7 | 2.0 | 9 1 6 | 25.4 | 26.8 |
| 1 0 9 | 5.6 | 5.1 | 1 3 4 | 57.6 | 57.0 | 2 2 3 | 12.4 | 10.6 | 3 0 18 | 9.8 | 10.5 | 4 0 10 | 15.8 | 15.7 | 5 0 1 | 9.2 | 9.2 | 6 0 3 | 20.1 | 18.0 | 7 0 8 | 5.1 | 5.2 | 9 1 7 | 38.1 | 37.0 |
| 1 0 11 | 23.0 | 22.3 | 1 3 5 | 9.2 | 9.5 | 2 2 4 | 6.3 | 8.2 | 3 0 19 | 8.1 | 9.7 | 4 0 11 | 15.2 | 17.0 | 5 0 2 | 3.8 | 3.8 | 6 0 4 | 8.1 | 8.4 | 7 0 9 | 8.1 | 7.4 | 9 1 8 | 27.6 | 27.6 |
| 1 0 13 | 24.5 | 25.1 | 1 3 6 | 29.1 | 29.0 | 2 2 5 | 29.1 | 29.0 | 3 1 1 | 5.1 | 2.6 | 4 0 12 | 10.8 | 15.1 | 5 0 3 | 10.8 | 1.0 | 6 0 5 | 10.8 | 9.1 | 7 0 10 | 10.4 | 28.5 | 9 1 9 | 30.6 | 28.8 |
| 1 0 15 | 3.5 | 0.0 | 1 3 7 | 77.2 | 75.0 | 2 2 6 | 32.5 | 33.8 | 3 1 2 | 3.1 | 4.6 | 4 0 13 | 5.4 | 4.6 | 5 0 4 | 59.0 | 61.9 | 6 0 6 | 115.4 | 104.2 | 7 0 11 | 13.0 | 11.9 | 9 1 10 | 17.0 | 19.0 |
| 1 0 17 | 31.1 | 32.9 | 1 3 8 | 11.3 | 13.7 | 2 2 7 | 144.7 | 151.5 | 3 1 3 | 39.1 | 40.6 | 4 0 14 | 19.1 | 21.2 | 5 0 5 | 68.5 | 83.8 | 6 0 7 | 95.1 | 92.8 | 7 0 12 | 12.1 | 13.0 | 9 2 9 | 15.3 | 19.7 |
| 1 0 19 | 21.2 | 23.3 | 1 3 9 | 66.7 | 61.7 | 2 2 8 | 66.7 | 61.7 | 3 1 4 | 7.8 | 8.2 | 4 0 15 | 9.4 | 9.3 | 5 0 6 | 42.6 | 76.3 | 6 0 8 | 42.6 | 76.3 | 7 0 13 | 5.1 | 2.1 | 9 2 10 | 20.1 | 21.8 |
| 1 2 0 | 181.4 | 182.0 | 1 3 10 | 40.5 | 43.0 | 2 2 9 | 32.7 | 31.6 | 3 1 5 | 7.8 | 9.2 | 4 0 16 | 8.7 | 7.0 | 5 0 7 | 29.3 | 21.5 | 6 0 9 | 6.6 | 5.1 | 7 0 14 | 5.7 | 5.1 | 9 2 11 | 23.4 | 22.9 |
| 1 2 2 | 172.4 | 172.4 | 1 3 11 | 10.5 | 5.4 | 2 2 10 | 3.5 | 2.4 | 3 1 6 | 32.7 | 32.5 | 4 0 17 | 32.7 | 33.5 | 5 0 8 | 15.4 | 19.2 | 6 0 10 | 15.4 | 19.2 | 7 0 15 | 14.0 | 14.0 | 9 2 12 | 1.5 | 1.9 |
| 1 2 4 | 169.1 | 174.0 | 1 3 12 | 28.4 | 31.1 | 2 2 11 | 37.5 | 23.8 | 3 1 7 | 32.4 | 32.0 | 4 0 18 | 5.7 | 0.6 | 5 0 9 | 17.1 | 11.7 | 6 0 11 | 34.3 | 12.4 | 7 1 1 | 9.1 | 7.4 | 9 2 13 | 27.9 | 26.7 |
| 1 2 6 | 17.4 | 18.4 | 1 3 13 | 76.1 | 74.0 | 2 2 12 | 19.4 | 18.7 | 3 1 8 | 19.2 | 33.0 | 4 0 19 | 33.7 | 33.0 | 5 0 10 | 43.5 | 37.2 | 6 0 12 | 23.1 | 79.1 | 7 1 2 | 32.1 | 29.2 | 9 3 0 | 8.1 | 6.0 |
| 1 2 8 | 19.1 | 18.3 | 1 3 14 | 13.0 | 14.1 | 2 2 13 | 51.0 | 49.2 | 3 1 9 | 19.2 | 31.9 | 4 0 20 | 20.9 | 24.5 | 5 0 11 | 7.8 | 8.0 | 6 0 13 | 23.2 | 26.8 | 7 1 3 | 24.8 | 23.8 | 9 3 1 | 10.0 | 9.1 |
| 1 2 10 | 179.5 | 172.1 | 1 3 15 | 5.4 | 10.0 | 2 2 14 | 5.1 | 3.7 | 3 1 10 | 4.5 | 5.1 | 5 0 1 | 12.7 | 5.2 | 5 0 12 | 12.8 | 15.0 | 6 0 14 | 18.1 | 15.0 | 7 1 4 | 24.8 | 24.8 | 9 3 2 | 9.1 | 9.6 |
| 1 2 12 | 9.0 | 5.1 | 1 3 16 | 21.6 | 24.5 | 2 2 15 | 5.1 | 5.4 | 3 1 11 | 2.5 | 1.4 | 5 0 2 | 43.5 | 37.8 | 5 0 13 | 6.6 | 8.0 | 6 0 15 | 43.5 | 37.8 | 7 1 5 | 16.5 | 15.4 | 9 3 3 | 5.1 | 4.6 |
| 1 2 14 | 71.1 | 64.4 | 1 3 17 | 10.7 | 10.5 | 2 2 16 | 11.1 | 11.0 | 3 1 12 | 16.4 | 18.0 | 5 0 3 | 58.1 | 100.3 | 5 0 14 | 12.5 | 11.3 | 6 0 16 | 2.5 | 4.8 | 7 1 6 | 45.4 | 40.2 | 9 3 4 | 5.2 | 0.1 |
| 1 2 16 | 79.1 | 66.0 | 1 3 18 | 5.4 | 10.0 | 2 2 17 | 5.4 | 5.8 | 3 1 13 | 16.4 | 18.0 | 5 0 4 | 58.1 | 100.3 | 5 0 15 | 4.5 | 5.8 | 6 0 17 | 8.1 | 8.4 | 7 1 7 | 8.1 | 8.4 | 9 3 5 | 25.0 | 25.0 |
| 1 2 18 | 3.0 | 0.9 | 1 3 19 | 29.4 | 28.0 | 2 2 18 | 0.0 | 1.0 | 3 1 14 | 10.3 | 10.5 | 5 0 5 | 10.3 | 10.1 | 5 0 16 | 10.4 | 8.4 | 6 0 18 | 16.5 | 51.4 | 7 1 8 | 35.8 | 4.3 | 9 3 6 | 1.5 | 1.7 |
| 1 2 20 | 3.0 | 0.9 | 1 4 1 | 11.8 | 11.1 | 2 2 19 | 11.8 | 11.1 | 3 1 15 | 2.4 | 0.7 | 5 0 6 | 66.6 | 51.4 | 5 0 17 | 3.1 | 7.0 | 6 0 19 | 8.1 | 8.4 | 7 1 9 | 4.5 | 4.8 | 9 3 7 | 28.4 | 27.1 |
| 1 3 1 | 13.5 | 12.1 | 1 4 2 | 52.3 | 46.3 | 2 2 20 | 12.1 | 13.7 | 3 1 16 | 22.2 | 20.8 | 5 1 1 | 2.4 | 0.7 | 5 0 18 | 4.5 | 3.4 | 6 1 1 | 5.9 | 4.7 | 7 1 10 | 11.6 | 12.4 | 9 3 8 | 2.5 | 3.1 |
| 1 3 3 | 15.5 | 16.1 | 1 4 3 | 3.0 | 3.0 | 2 3 0 | 100.3 | 92.7 | 3 1 17 | 5.7 | 2.5 | 5 1 2 | 13.2 | 15.4 | 5 0 19 | 5.6 | 2.3 | 6 1 2 | 35.2 | 36.8 | 7 1 11 | 8.6 | 9.0 | 9 3 9 | 5.1 | 5.7 |
| 1 3 5 | 9.5 | 5.2 | 1 4 4 | 29.1 | 27.1 | 2 3 1 | 39.1 | 52.6 | 3 1 18 | 1.5 | 1.1 | 5 1 3 | 80.5 | 65.6 | 5 0 17 | 3.1 | 7.0 | 6 1 3 | 37.4 | 35.3 | 7 1 12 | 14.5 | 10.4 | 9 3 10 | 0.4 | 0.1 |
| 1 3 7 | 22.0 | 23.0 | 1 4 5 | 12.4 | 13.6 | 2 3 2 | 12.1 | 13.6 | 3 1 19 | 5.7 | 2.5 | 5 1 4 | 12.3 | 34.0 | 5 1 1 | 12.3 | 20.9 | 6 1 4 | 32.1 | 34.0 | 7 1 13 | 3.1 | 0.5 | 9 3 11 | 8.4 | 9.0 |
| 1 3 11 | 15.1 | 16.6 | 1 4 6 | 24.8 | 25.6 | 2 3 3 | 3.5 | 0.3 | 3 2 1 | 53.4 | 56.5 | 5 1 5 | 4.1 | 0.1 | 5 1 2 | 5.8 | 7.7 | 6 1 5 | 0.1 | 0.1 | 7 1 14 | 13.0 | 9.7 | 9 3 12 | 8.4 | 7.8 |
| 1 3 13 | 3.7 | 3.7 | 1 4 7 | 31.0 | 32.7 | 2 3 4 | 87.2 | 87.2 | 3 2 2 | 19.1 | 19.1 | 5 1 6 | 19.1 | 19.1 | 5 1 3 | 5.8 | 7.7 | 6 1 6 | 24.9 | 25.6 | 7 1 15 | 12.8 | 15.1 | 9 4 0 | 4.8 | 2.8 |
| 1 3 15 | 15.3 | 16.1 | 1 4 8 | 22.0 | 22.7 | 2 3 5 | 28.0 | 31.7 | 3 2 3 | 27.8 | 25.1 | 5 1 7 | 27.8 | 25.1 | 5 1 4 | 5.8 | 7.7 | 6 1 7 | 28.6 | 31.0 | 7 2 1 | 8.4 | 7.0 | 9 4 1 | 28.4 | 28.4 |
| 1 3 17 | 4.3 | 2.1 | 1 4 10 | 9.7 | 7.2 | 2 3 6 | 40.0 | 40.7 | 3 2 4 | 15.5 | 15.5 | 5 1 8 | 15.5 | 15.5 | 5 1 5 | 11.6 | 14.1 | 6 1 8 | 15.7 | 15.6 | 7 2 2 | 20.0 | 17.0 | 9 4 2 | 26.1 | 26.2 |
| 1 4 0 | 240.4 | 220.0 | 1 4 11 | 30.1 | 31.5 | 2 3 7 | 5.3 | 0.6 | 3 2 5 | 19.5 | 19.6 | 5 1 9 | 19.5 | 19.6 | 5 1 6 | 11.6 | 14.1 | 6 1 9 | 26.4 | 28.1 | 7 2 3 | 5.1 | 2.0 | 9 4 3 | 2.5 | 3.3 |
| 1 4 2 | 77.3 | 59.3 | 1 4 12 | 29.5 | 29.1 | 2 3 8 | 29.5 | 29.1 | 3 2 6 | 18.9 | 19.4 | 5 1 10 | 3.9 | 8.0 | 5 1 7 | 5.8 | 8.3 | 6 1 10 | 17.4 | 18.9 | 7 2 4 | 41.8 | 39.5 | 9 4 4 | 28.3 | 30.5 |
| 1 4 4 | 37.1 | 38.0 | 1 4 13 | 37.1 | 35.9 | 2 3 9 | 40.4 | 40.0 | 3 2 7 | 18.4 | 18.2 | 5 1 11 | 3.9 | 8.0 | 5 1 8 | 18.1 | 18.2 | 6 1 11 | 5.1 | 4.1 | 7 2 5 | 15.8 | 15.4 | 9 4 5 | 2.6 | 2.1 |
| 1 4 6 | 102.5 | 98.1 | 1 4 14 | 8.5 | 9.5 | 2 3 10 | 40.4 | 40.0 | 3 2 8 | 18.4 | 20.5 | 5 1 12 | 8.1 | 9.1 | 5 1 9 | 15.7 | 8.9 | 6 1 12 | 41.3 | 22.7 | 7 2 6 | 0.0 | 0.9 | 9 4 6 | 21.4 | 24.4 |
| 1 4 8 | 35.4 | 38.4 | 1 4 15 | 3.4 | 3.0 | 2 3 11 | 10.2 | 1.0 | 3 2 9 | 17.5 | 17.6 | 5 1 13 | 8.1 | 9.1 | 5 1 10 | 10.4 | 8.4 | 6 1 13 | 8.1 | 8.4 | 7 2 7 | 9.1 | 7.4 | 9 4 7 | 5.1 | 5.7 |
| 1 4 10 | 36.4 | 38.4 | 1 4 16 | 4.6 | 3.5 | 2 3 12 | 40.8 | 35.3 | 3 2 10 | 8.3 | 5.3 | 5 1 14 | 5.3 | 0.5 | 5 1 11 | 8.1 | 8.1 | 6 1 14 | 0.0 | 0.6 | 7 2 8 | 7.2 | 3.7 | 9 4 8 | 1.2 | 1.3 |
| 1 4 12 | 29.4 | 29.2 | 1 4 17 | 10.2 | 10.5 | 2 3 13 | 10.6 | 10.3 | 3 2 11 | 12.7 | 12.5 | 5 1 15 | 12.7 | 12.5 | 5 1 12 | 45.3 | 45.6 | 6 1 15 | 26.8 | 21.4 | 7 2 9 | 23.8 | 20.1 | 9 4 9 | 10.4 | 10.4 |
| 1 4 14 | 9.1 | 10.1 | 1 4 18 | 8.2 | 9.5 | 2 3 14 | 10.6 | 10.3 | 3 2 12 | 55.4 | 46.3 | 5 2 1 | 10.2 | 12.5 | 5 1 13 | 5.8 | 6.1 | 6 1 16 | 33.7 | 33.3 | 7 2 10 | 23.8 | 20.1 | 9 4 10 | 5.1 | 4.9 |
| 1 4 16 | 2.8 | 2.4 | 1 5 1 | 20.7 | 20.8 | 2 3 15 | 33.4 | 33.4 | 3 2 13 | 9.4 | 9.4 | 5 2 2 | 93.8 | 92.5 | 5 1 14 | 2.6 | 3.9 | 6 1 17 | 33.7 | 33.3 | 7 2 11 | 18.3 | 17.8 | 9 4 11 | 15.0 | 15.3 |
| 1 4 18 | 2.8 | 2.4 | 1 5 2 | 85.7 | 80.1 | 2 3 16 | 12.8 | 12.0 | 3 2 14 | 9.4 | 9.4 | 5 2 3 | 93.8 | 92.5 | 5 1 15 | 2.6 | 3.9 | 6 1 18 | 36.1 | 30.4 | 7 2 12 | 3.1 | 3.0 | 9 5 0 | 4.8 | 5.1 |
| 1 5 1 | 1.1 | 2.3 | 1 5 3 | 4.1 | 3.1 | 2 3 17 | 8.0 | 9.3 | 3 2 15 | 4.6 | 5.1 | 5 2 4 | 4.1 | 5.7 | 5 1 16 | 8.6 | 8.1 | 6 2 1 | 33.8 | 33.9 | 7 2 13 | 5.2 | 3.0 | 9 5 1 | 4.0 | 2.6 |
| 1 5 3 | 1.1 | 2.3 | 1 5 4 | 17.3 | 19.3 | 2 3 18 | 17.3 | 19.3 | 3 2 16 | 4.6 | 5.1 | 5 2 5 | 4.1 | 5.7 | 5 1 17 | 8.6 | 8.9 | 6 2 2 | 33.8 | 33.9 | 7 2 14 | 5.2 | 1.7 | 9 5 2 | 4.0 | 2.6 |
| 1 5 5 | 7.1 | 9.7 | 1 5 5 | 38.2 | 34.7 | 2 3 19 | 13.5 | 18.3 | 3 2 17 | 13.5 | 18.3 | 5 2 6 | 38.6 | 38.1 | 5 2 1 | 9.0 | 9.7 | 6 2 3 | 52.1 | 45.9 | 7 2 15 | 2.0 | 1.1 | 9 5 3 | 9.0 | 5.9 |
| 1 5 7 | 7.1 | 9.7 | 1 5 6 | 40.4 | 44.4 | 2 4 1 | 10.6 | 10.3 | 3 2 18 | 10.6 | 10.3 | 5 2 7 | 38.6 | 38.1 | 5 2 2 | 9.0 | 9.7 | 6 2 4 | 52.1 | 45.9 | 7 3 1 | 18.1 | 10.1 | 9 5 4 | 2.6 | 2.1 |
| 1 5 9 | 12.8 | 15.4 | 1 5 8 | 11.5 | 14.4 | 2 4 2 | 10.6 | 10.3 | 3 2 19 | 1.6 | 2.3 | 5 2 8 | 30.2 | 30.3 | 5 2 3 | 78.7 | 88.1 | 6 2 5 | 14.8 | 19.8 | 7 3 2 | 41.3 | 40.1 | 9 5 5 | 2.6 | 2.0 |
| 1 5 11 | 19.4 | 21.0 | 1 5 9 | 36.1 | 37.1 | 2 4 3 | 30.2 | 30.3 | 3 3 1 | 90.4 | 90.2 | 5 2 9 | 30.2 | 30.3 | 5 2 4 | 78.7 | 88.1 | 6 2 6 | 14.8 | 19.8 | 7 3 3 | 41.3 | 40.1 | 9 5 6 | 1.5 | 1.0 |
| 1 5 13 | 4.1 | 2.0 | 1 5 10 | 9.4 | 12.0 | 2 4 4 | 38.4 | 38.0 | 3 3 2 | 90.4 | 90.2 | 5 2 10 | 5.2 | 1.4 | 5 2 5 | 15.8 | 0.6 | 6 2 7 | 33.8 | 33.2 | 7 3 4 | 17.9 | 15.1 | 9 6 0 | 8.1 | 8.7 |
| 1 5 15 | 17.1 | 17.3 | 1 5 11 | 5.1 | 5.2 | 2 4 5 | 38.4 | 38.0 | 3 3 3 | 7.7 | 7.4 | 5 2 11 | 10.7 | 11.4 | 5 2 6 | 48.6 | 46.1 | 6 2 8 | 33.8 | 33.2 | 7 3 5 | 8.2 | 8.1 | 9 6 1 | 8.1 | 8.7 |
| 1 5 17 | 24.0 | 25.3 | 1 5 12 | 11.1 | 9.2 | 2 4 6 | 30.5 | 40.0 | 3 3 4 | 7.7 | 7.4 | 5 2 12 | 10.7 | 10.0 | 5 2 7 | 48.6 | 46.1 | 6 2 9 | 52.1 | 43.5 | 7 3 6 | 8.2 | 5.5 | 9 6 2 | 8.2 | 8.7 |
| 1 5 19 | 26.0 | 22.8 | 1 5 13 | 24.1 | 24.8 | 2 4 7 | 29.5 | 29.8 | 3 3 5 | 27.5 | 25.4 | 5 2 13 | 27.5 | 27.3 | 5 2 8 | 36.1 | 34.8 | 6 2 10 | 52.1 | 43.5 | 7 3 7 | 10.8 | 9.8 | 9 6 3 | 1.5 | 1.1 |
| 1 5 21 | 40.4 | 44.4 | 1 5 14 | 8.2 | 8.0 | 2 4 8 | 32.1 | 32.0 | 3 3 6 | 27.5 | 25.4 | 5 2 14 | 27.5 | 27.3 | 5 2 9 | 36.1 | 34.8 | 6 2 11 | 14.2 | 12.4 | 7 3 8 | 10.8 | 9.8 | 9 6 4 | 1.5 | 1.1 |
| 1 5 23 | 4.3 | 3.6 | 1 5 15 | 33.0 | 38.8 | 2 4 9 | 8.5 | 9.1 | 3 3 7 | 7.6 | 0.9 | 5 2 15 | 10.7 | 14.5 | 5 2 10 | 81.6 | 73.2 | 6 2 12 | 14.2 | 12.4 | 7 3 9 | 11.8 | 9.7 | 9 6 5 | 18.5 | 19.2 |
| 1 6 0 | 8.1 | 8.4 | 1 5 16 | 12.0 | 15.1 | 2 4 10 | 28.6 | 29.0 | 3 3 8 | 7.6 | 0.9 | 5 2 16 | 10.7 | 14.5 | 5 2 11 | 81.6 | 73.2 | 6 2 13 | 10.5 | 7.4 | 7 3 10 | 11.8 | 9.7 | 9 6 6 | 2.5 | 2.1 |
| 1 6 2 | 51.0 | 35.4 | 1 5 17 | 8.0 | 5.2 | 2 4 11 | 9.0 | 8.2 | 3 3 9 | 19.5 | 19.8 | 5 2 17 | 11.0 | 12.3 | 5 2 12 | 4.5 | 4.7 | 6 2 14 | 40.0 | 40.0 | 7 3 11 | 6.1 | 3.1 | 9 6 7 | 4.5 | 4.7 |
| 1 6 4 | 5.1 | 5.0 | 1 5 18 | 20.4 | 17.2 | 2 4 12 | 3.7 | 4.1 | 3 3 10 | 19.5 | 19.8 | 5 2 18 | 11.0 | 12.3 | 5 2 13 | 4.1 | 7.2 | 6 2 15 | 40.0 | 37.0 | 7 3 12 | 40.1 | 37.0 | 9 6 8 | 39.1 | 41.1 |
| 1 6 6 | 2.6 | 1.0 | 1 5 19 | 4.0 | 0.1 | 2 4 13 | 19.6 | 19.1 | 3 3 11 | 19.1 | 18.4 | 5 2 19 | 11.6 | 12.3 | 5 2 14 | 4.1 | 4.1 | 6 2 16 | 51.7 | 50.6 | 7 3 13 | 5.1 | 5.6 | 9 6 9 | 5.1 | 5.7 |
| 1 6 8 | 7.1 | 2.7 | 1 6 1 | 8.4 | 8.6 | 2 4 14 | 19.6 | 19.1 | 3 3 12 | 19.1 | 18.4 | 5 3 1 | 3.1 | 3.2 | 5 2 15 | 2.7 | 2.1 | 6 2 17 | 51.7 | 50.6 | 7 3 14 | 5.1 | 5.6 | 9 6 10 | 29.0 | 32.0 |
| 1 6 10 | 7.1 | 2.6 | 1 6 2 | 7.6 | 10.7 | 2 4 15 | 4.5 | 5.2 | 3 3 13 | 3.1 | 3.2 | 5 3 2 | 3.1 | 3.2 | 5 2 16 | 25.3 | 24.7 | 6 2 18 | 23.8 | 24.5 | 7 3 1 | 4.1 | 4.8 | 9 6 11 | 29.0 | 32.0 |
| 1 6 12 | 5.1 | 5.2 | 1 6 3 | 33.1 | 13.9 | 2 4 16 | 4.5 | 5.2 | 3 3 14 | 3.1 | 3.2 | 5 3 3 | 3.1 | 3.2 | 5 3 1 | 29.3 | 32.0 | 6 3 1 | 23.8 | 24.5 | 7 3 2 | 32.8 | 28.7 | 9 6 12 | 2.5 | 2.1 |
| 1 6 14 | 25.4 | 33.1 | 1 6 4 | 0.0 | 1.4 | 2 4 17 | 13.8 | 14.8 | 3 3 15 | 3.1 | 0.4 | 5 3 4 | 3.1 | 3.2 | 5 3 2 | 29.3 | 32.0 | 6 3 2 | 17.0 | 18.1 | 7 3 3 | 32.8 | 28.7 | 9 6 13 | 5.1 | 5.2 |
| 1 6 16 | 26.0 | 27.4 | 1 6 5 | 0.0 | 1.4 | 2 4 18 | 18.1 | 18.1 | 3 3 16 | 1.7 | 0.4 | 5 3 5 | 3.1 | 3.2 | 5 3 3 | 36.1 | 34.6 | 6 3 3 | 17.0 | 18.1 | 7 3 4 | 27.9 | 28.4 | 9 10 0 | 23.0 | 21.0 |
| 1 6 18 | 22.4 | 22.4 | 1 6 6 | 10.0 | 10.1 | 2 5 0 | 18.1 | 18.1 | 3 3 17 | 10.1 | 11.4 | 5 3 6 | 36.1 | 34.6 | 5 3 4 | 29.4 | 27.0 | 6 3 4 | 36.1 | 34.6 | 7 3 5 | 27.9 | 28.4 | 9 10 1 | 23.0 | 21.0 |
| 1 6 20 | 18.6 | 19.0 | 1 6 7 | 8.1 | 10.2 | 2 5 1 | 7.5 | 7.0 | 3 3 18 | 10.1 | 11.4 | 5 3 7 | 29.4 | 27.0 | 5 3 5 | 29.4 | 27.0 | 6 3 5 | 93.8 | 40.1 | 7 3 6 | 7.6 | 8.2 | 9 10 2 | 4.1 | 5.1 |
| 1 6 22 | 10.2 | 10.7 | 1 6 8 | 11.2 | 11.2 | 2 5 2 | 7.5 | 7.0 | 3 3 19 | 32.1 | 32.2 | 5 3 8 | 29.4 | 27.0 | 5 3 6 | 29.4 | 27.0 | 6 3 6 | 93.8 | 40.1 | 7 3 7 | 7.6 | 8.2 | 9 10 3 | 3.6 | 3.9 |
| 1 7 1 | 27.1 | 27.2 | 1 6 9 | 20.4 | 21.7 | 2 5 3 | 13.3 | 13.3 | 3 4 0 | 20.7 | 24.1 | 5 3 9 | 29.4 | 27.0 | 5 3 7 | 29.4 | 27.0 | 6 3 7 | 11.6 | 12.8 | 7 3 8 | 10.1 | 11.5 | 9 11 1 | 21.1 | 21.1 |
| 1 7 3 | 1.4 | 0.4 | 1 6 10 | 2.6 | 2.6 | 2 5 4 | 13.3 | 13.3 | 3 4 1 | 20.7 | 24.1 | 5 3 10 | 10.4 | 11.1 | 5 3 8 | 11.6 | 12.8 | 6 3 8 | 11.6 | 12.8 | 7 3 9 | 10.1 | 11.5 | 9 11 2 | 22.2 | 22.2 |
| 1 7 5 | 31.4 | 29.6 | 1 7 1 | 4.4 | 0.1 | 2 5 5 | 51.1 | 55.6 | 3 4 2 | 8.1 | 11.3 | 5 3 11 | 10.4 | 11.1 | 5 3 9 | 20.7 | 20.4 | 6 3 9 | 20.7 | 20.4 | 7 3 10 | 20.4 | 20.5 | 9 11 3 | 15.1 | 15.4 |
| 1 7 7 | 42.4 | 48.8 | 1 7 2 | 17.3 | 21.6 | 2 5 6 | 51.1 | 55.6 | 3 4 3 | 8.1 | 11.3 | 5 3 12 | 10.4 | 11.1 | 5 3 10 | 20.7 | 20.4 | 6 3 10 | 18.2 | 17.8 | 7 3 11 | 5.1 | 5.6 | 9 11 4 | 15.1 | 15.4 |
| 1 7 9 | 62.1 | 64.7 | 1 7 3 | 28.6 | 30.0 | 2 5 7 | 7.9 | 9.9 | 3 4 4 | 29.1 | 30.0 | 5 3 13 | 10.4 | 11.1 | 5 3 11 | 18.2 | 17.8 | 6 3 11 | 18.2 | 17.8 | 7 3 12 | 2.1 | 2.8 | 9 11 5 | 19.7 | 19.7 |
| 1 7 11 | 5.0 | 3.8 | 1 7 4 | 10.8 | 11.6 | 2 5 8 | 28.0 | 29.8 | 3 4 5 | 29.1 | 30.0 | 5 3 14 | 20.7 | 20.7 | 5 3 12 | 8.8 | 7.5 | 6 3 12 | 15.3 | 13.1 | 7 3 13 | 4.1 | 2.8 | 9 11 6 | 19.7 | 19.7 |
| 1 7 13 | 7.8 | 7.8 | 1 7 5 | 10.8 | 11.6 | 2 5 9 | 28.0 | 29.8 | 3 4 6 | 10.1 | 5.0 | 5 3 15 | 20.7 | 20.7 | 5 3 13 | 8.8 | 7.5 | 6 3 13 | 15.3 | 13.1 | 7 3 14 | 4.1 | 2.8 | 9 11 7 | 15.7 | 15.2 |
| 1 7 15 | 7.8 | 7.8 | 1 7 6 | 12.8 | 14.1 | 2 5 10 | 5.0 | 5.4 | 3 4 7 | 10.1 | 5.0 | 5 3 16 | 20.7 | 20.7 | 5 3 14 | 8.8 | 7.5 | 6 3 14 | 10.1 | 5.0 | 7 4 1 | 42.5 | 38.0 | 9 11 8 | 15.7 | 15.2 |
| 1 7 17 | 10.4 | 9.4 | 1 7 7 | 22.0 | 24.6 | 2 5 11 | 20.3 | 19.2 | 3 4 8 | 15.5 | 15.8 | 5 4 1 | 2.3 | 3.1 | 5 3 15 | 3.1 | 3.2 | 6 3 15 | 10.1 | 5.0 | 7 4 2 | 42.5 | 38.0 | 9 11 9 | 25.2 | 25.8 |
| 1 7 19 | 10.4 | 9.4 | 1 7 8 | 9.0 | 5.0 | 2 5 12 | 20.3 | 19.2 | 3 4 9 | 15.5 | 15.8 | 5 4 2 | 2.3 | 3.1 | 5 3 16 | 3.1 | 3.2 | 6 3 16 | 3.1 | 3.2 | 7 4 3 | 5.1 | 3.0 | 9 11 10 | 25.2 | 25.8 |
| 1 7 21 | 38.4 | 40.0 | 1 7 9 | 12.8 | 21.1 | 2 5 13 | 7.8 | 8.4 | 3 4 10 | 20.3 | 19.8 | 5 4 3 | 18.7 | 21.1 | 5 4 1 | 2.3 | 3.1 | 6 3 17 | 3.1 | 3.2 | 7 4 4 | 5.1 | 3.0 | 9 11 11 | 21.5 | 20.0 |
| 1 7 23 | 4.1 | 4.3 | 1 7 10 | 10.8 | 10.4 | 2 5 14 | 7.8 | 8.4 | 3 4 11 | 20.3 | 19.8 | 5 4 4 | 0.0 | 5.6 | 5 4 2 | 2.3 | 3.1 | 6 3 18 | 3.1 | 3.2 | 7 4 5 | 2.1 | 2.1 | 9 11 12 | 21.5 | 20.0 |
| 1 8 0 | 10.1 | 7.7 | 1 8 1 | 12.2 | 14.3 | 2 5 15 | 21.3 | 21.8 | 3 4 12 | 11.5 | 11.8 | 5 4 5 | 0.0 | 5.6 | 5 4 3 | 2.3 | 3.1 | 6 4 1 | 4.8 | 5.6 | 7 4 6 | 2.1 | 2.1 | 9

## Experimental

The sample of $\varepsilon$-$C_8Cl_8$ (octachloro-2,4-dihydropentalene) was prepared by Professor Robert West of the University of Wisconsin. Suitable light-yellow crystals were grown by slow evaporation from acetone at 6 °C. Two crystal habits appeared. One took the form of hexagonal plates exhibiting threefold symmetry. The other consisted of hexagonal rods with angularly truncated ends. The hexagonal rods were rarer, but much better formed. The one used for the data collection was a rod approximately 0·30 mm long with a mean diameter of 0·13 mm. The $b$ axis was along the rod axis and the $a$ axis parallel to the Petri dish as the crystals grow.

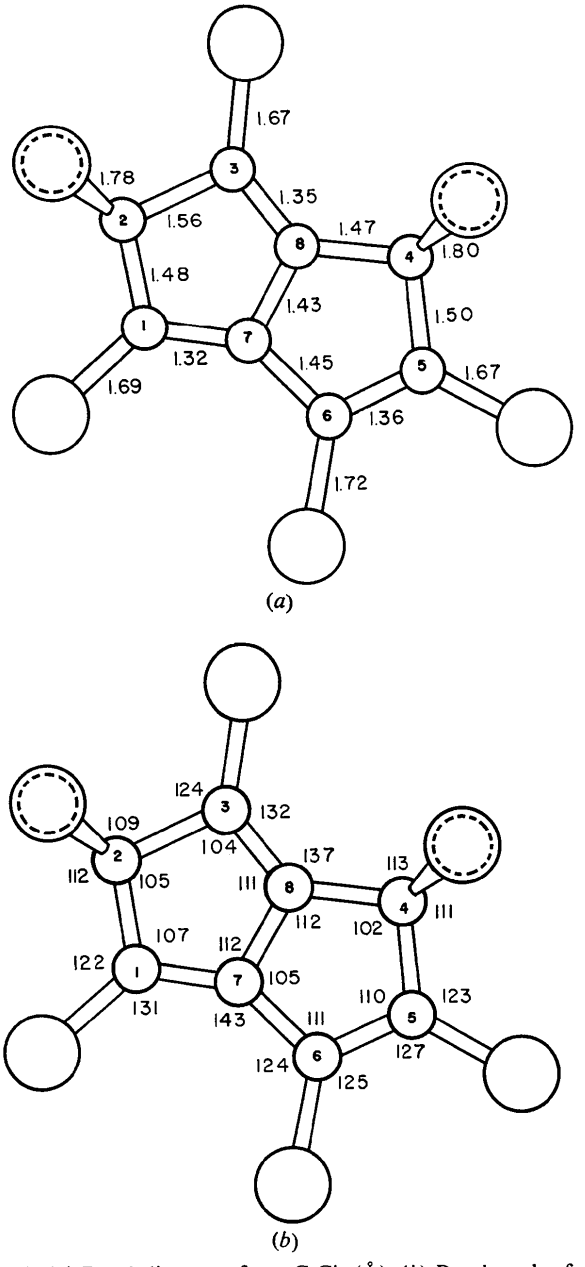



Fig. 1. (a) Bond distances for $\varepsilon$-$C_8Cl_8$ (Å). (b) Bond angles for $\varepsilon$-$C_8Cl_8$ (°).

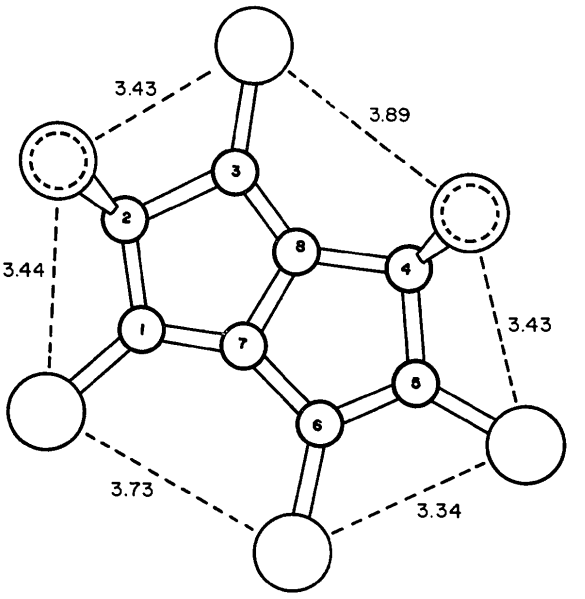



Fig. 2. Non-bonded intramolecular distances.

Diffraction symmetry proved the crystals to be orthorhombic, with refined lattice constants of:

$$a = 10{\cdot}170 \pm 0{\cdot}007 \text{ Å}$$
$$b = 7{\cdot}284 \pm 0{\cdot}006$$
$$c = 17{\cdot}281 \pm 0{\cdot}010,$$

as obtained from least-squares treatment of nine observed values of $2\theta$ above 25° centered on a Picker FACS-I automated diffractometer, using Cu $K\alpha$ radiation.

The systematic extinctions were $0kl$, $k+l=2n+1$ and $hk0$, $h=2n+1$. These extinctions indicate two possible space groups, $Pnma(D_{2h}^{16})$ or $Pn2_1a(C_{2v}^{9})$. The calculated density with $Z=4$ is 1·75 g cm$^{-3}$. With $Z=4$ and space group $Pn2_1a$, no assumptions of molecular geometry need be made. In $Pnma$, the four molecules must contain either a mirror plane or a center of symmetry.

There were several experimental problems encountered during the preliminary photographic analysis. The orthorhombic cell exhibited pseudohexagonal spacings giving rise to three orientations of a cell with the same lattice constants, only one of which had the correct orthorhombic symmetry. This peculiar geometry allows the multiple diffraction phenomenon to become a problem. Another difficulty with the crystals was that they reacted with the mounting glue, Ambroid. Crystals which were mounted and not exposed to X-rays developed the same powdery appearance. These crystals

decomposed rapidly when exposed to X-rays. The data were collected from a crystal mounted in Araldite, an epoxide glue. This crystal also decomposed on exposure to X-rays, but the decay rate was considerably slower. The intensities of several reflections were carefully checked after the crystal was aligned on the diffractometer to ensure that the orientation matrix of the crystal was correct. The crystal axes were deliberately set away from the diffractometer axes in order to reduce the effect of multiple diffraction (Coppens, 1968).

The data were collected at room temperature by the $\theta$–$2\theta$ scan technique with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The scan speed was 2° per min, take-off angle 2·5°, and base width 1·7°. Aluminum attenuators and a graphite monochromator were used. Three standard reflections were re-collected every 50 reflections. There was an overall variation in intensity of 12%.

The data were reduced in the usual manner. Since the linear absorption coefficient was 159·8 $cm^{-1}$, absorption corrections were made using the program *ABSTMA*, written by J. de Meulenaer, H. Tompa and N. Alcock. The maximum transmission factor was 0·284 and the minimum 0·127.

The 1052 reflections in the data set are listed in Table 1. The 197 reflections with intensities less than 2·33 $\sigma(I)$ were taken as unobserved and are denoted by * in the Table.

### Structure determination and refinement

The $N(z)$ plot indicated that the space group was the centric *Pnma*. Straightforward application of centric direct phasing methods led to the structure. The refinement by the UCLA full-matrix least-squares program proceeded smoothly to a final $R$ value of 8·8% and weighted $R$ of 8·4% based on the observed reflections only. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The function minimized was the usual $\sum_h w_h[F_o(h) - (1/k)F_c(h)]^2$, where $w_h$ is defined by $\sqrt{w_h} = 1/\sigma_h = 1/\{[F_o^2 + \sigma(I)]^{1/2} - F_o\}$. Final coordinates, anisotropic thermal parameters, and their estimated standard deviations are given in Table 2.

### The discussion of the structure

The bond distances and angles are given in Fig. 1. Table 3 gives a summary of the carbon bond lengths and angles from this structure determination, together with comparable values determined by the electron diffraction investigations of cyclopentadiene (Schomaker & Pauling, 1939) and cyclopentene (Davis & Muecke, 1970). The bond distances C(7)–C(8) and C(6)–C(7) are not strictly comparable with the values in the isolated cyclopentene molecule, as they are both conjugated, and resonance effects shorten this type of central bond. The value of Sutton (1965) for this type of carbon–carbon single bond is 1·465 Å. Apparently the C(1)–C(2) and C(8)–C(4) bonds are also shortened by additional resonance in this ring system. The difference between the C(4)–C(8)–C(7) angle in the two structures doubtless arises because carbons (7) and (8) are bridgeheads of the bicyclo system.

The vinyl carbon–chlorine bonds are shorter (aver-

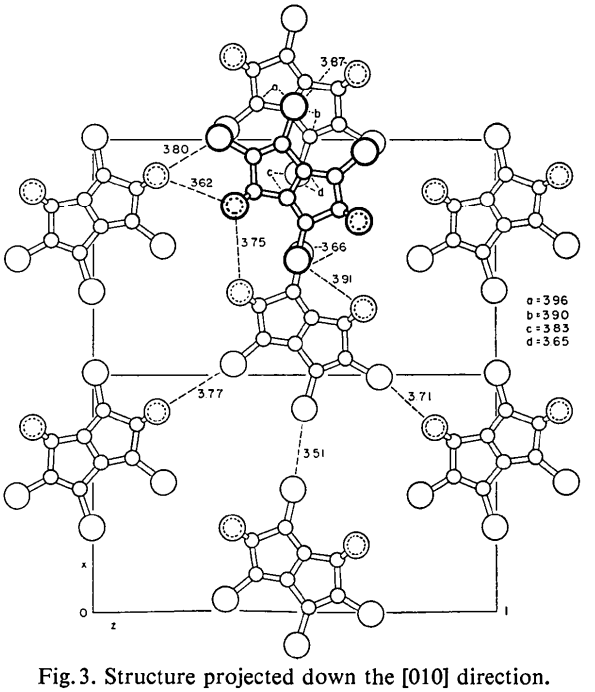



Fig. 3. Structure projected down the [010] direction.

Table 3. *Comparison of bond distances and angles*

| | Cyclopentadiene This work | S & P | | Cyclopentene This work | D & M |
|---|---|---|---|---|---|
| C(1)–C(2) | 1·48 Å | 1·53 Å | C(7)–C(8) | 1·43 Å | 1·55 Å |
| C(2)–C(3) | 1·56 | 1·53 | C(8)–C(4) | 1·47 | 1·55 |
| C(3)–C(8) | 1·35 | 1·35 | C(4)–C(5) | 1·50 | 1·52 |
| C(8)–C(7) | 1·43 | 1·46 | C(5)–C(6) | 1·36 | 1·34 |
| C(1)–C(7) | 1·32 | 1·35 | C(6)–C(7) | 1·40 | 1·52 |
| C(7)–C(1)–C(2) | 107° | 109° | C(8)–C(7)–C(6) | 105° | 103° |
| C(1)–C(2)–C(3) | 105 | 101 | C(7)–C(6)–C(5) | 111 | 111 |
| C(2)–C(3)–C(8) | 104 | 109 | C(6)–C(5)–C(4) | 110 | 111 |
| C(3)–C(8)–C(7) | 111 | 110 | C(5)–C(4)–C(8) | 102 | 103 |
| C(8)–C(7)–C(1) | 112 | 110 | C(4)–C(8)–C(7) | 112 | 104 |

age 1·69 ± 0·02 Å) than the aliphatic carbon–chlorine bonds (average 1·79 ± 0·01 Å). Sutton (1965) gives the average value of such vinyl bonds as 1·719 ± 0·005 Å and these aliphatic bonds as 1·767 ± 0·005 Å.

Fig. 2 shows the non-bonded chlorine···chlorine intramolecular contacts. The Cl(2)···Cl(2) (2·89 Å) and Cl(4)···Cl(4) (2·88 Å) distances are the same as the 2·89 Å chlorine···chlorine contacts in carbon tetrachloride (Bartell, Brockway & Schwendeman, 1955). The Cl(5)···Cl(6) contact (3·34 Å) is slightly longer than the value of 3·25 Å in *cis*-1,2-dichloroethane (Hoffman, 1958), as is expected. Twice the van der Waals (Pauling, 1960) radius for chlorine is 3·60 Å. Thus, the short C(1)···Cl(2), Cl(2)···Cl(3), and Cl(4)···Cl(5) distances imply repulsive interactions.

Intermolecular distances less than 4·0 Å are shown in the packing of the cell down the [010] direction, Fig. 3. There is only one kind of chlorine···chlorine contact less than twice the van der Waals radius (Pauling, 1960), the 3·51 Å contact between atoms Cl(3) and Cl(6). The molecules pack such that the Cl(6) site is above and below the centers of carbon ring systems of neighboring molecules. This situation gives rise to several short intermolecular carbon···chlorine distances. Pauling (1960) gives the effective thickness of a double-bonded carbon atom in an aromatic ring system as 3·4 Å. Thus carbon···chlorine distances of less than 3·5 Å indicate interpenetration of the electron clouds. There are no such distances in this structure.

This work was supported by the National Science Foundation, grant GH-33633. We thank Professor R. West for the sample used.

### References

BARTELL, L. S., BROCKWAY, L. O. & SCHWENDEMAN, R. H. (1955). *J. Chem. Phys.* **23**, 1854–1859.
COPPENS, P. (1968). *Acta Cryst.* A**24**, 253–257.
DAVIS, M. I. & MUECKE, T. W. (1970). *J. Phys. Chem.* **74**, 1104–1108.
HOFFMAN, C. W. (1958). Ph. D. Dissertation, Purdue University, Lafayette, Indiana.
*International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.
PAULING, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
ROEDIG, A., HELM, R., WEST, R. & SMITH, R. M. (1969). *Tetrahedron Lett.* **26**, 2137–2139.
SCHOMAKER, V. & PAULING, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769–1780.
SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18. London: The Chemical Society.

*Acta Cryst.* (1973). B**29**, 714

# Structural Studies of Analgesics and Their Interactions. I. The Crystal and Molecular Structure of Antipyrine

BY T. P. SINGH AND M. VIJAYAN

*Department of Physics, Indian Institute of Science, Bangalore-12, India*

(*Received* 14 *September* 1972; *accepted* 21 *November* 1972)

Antipyrine, $C_{11}H_{12}N_2O$, one of the best known pyrazole derivatives used as pain-relieving medicines, crystallizes in the monoclinic space group $C2/c$, with eight molecules in a unit cell of dimensions $a=16{\cdot}919$, $b=7{\cdot}425$, $c=17{\cdot}796$ Å and $\beta=117{\cdot}03°$. Three-dimensional intensity data from the crystal were collected on a 4-circle diffractometer. The structure was solved by the symbolic addition method and the atomic parameters, including those of the hydrogen atoms, were refined to an $R$ value of 0·060 for 1775 reflexions. The molecular geometry of antipyrine in this structure differs substantially from that observed in some metal–antipyrine complexes. First, the differences in the dimensions of the pyrazolone ring suggest that antipyrine is considerably less polar in the free state than in the complexes. Secondly, the two nitrogen atoms in the pyrazolone ring are more pyramidal in free antipyrine than in its complexes. Consequently, the conformation of the molecule is significantly different in the two cases. The molecular structure of antipyrine is also compared with that of 3-methyl-3-pyrazolin-5-one. Antipyrine is one of the few molecules without internal symmetry which crystallize in the space group $C2/c$. The molecular packing in the structure can be most adequately described as consisting of layers of molecules parallel to the $(20\bar{4})$ plane. The molecular coordination number in this arrangement is 11.

## Introduction

Several synthetic chemicals, including the derivatives of salicylic acid, pyrazole and acetanilide are extensively used as pain-relieving medicines. Most of them have varying degrees of antipyretic and anti-inflammatory properties as well. Many of these non-narcotic analgesics have been in use for several decades and a great deal of research has been carried out on their pharmacological properties when administered individually and in combination. However, the molecular basis of their interactions and their mode of action