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AN X-RAY DETERMINATION OF THE STRUCTURE OF 1,2,3,4-TETRACHLORO-5,6-DI-n-PROPYLCALICENE

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Recently several derivatives of cyclopropenylidene cyclopentadiene (calicene) (I) have been synthesized (1-10) and studied from the theoretical and organic point of view. However, the detailed molecular structure of this system has not been analysed so far. As one of the stable derivatives of this system, 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene (II) has been synthesized independently at two laboratories (11,12).

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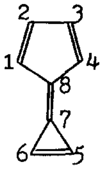
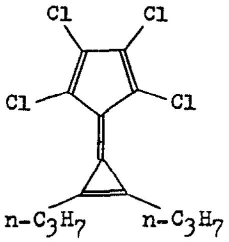


I



II

The present investigation was undertaken in order to reveal the molecular geometry of such a new system by X-ray analysis.

This compound crystallizes in an orthorhombic unit cell with dimensions: a=23.056Å, b=9.150Å, and c=7.017Å. The space group is $Pna2_1$ or Pnam. Since intensity statistics and pyroelectricity test showed the existence of a center of symmetry, it was decided that the space group was the latter. While in this space group the number of general positions is eight, there are four molecules in the unit cell. Therefore, the molecule should lie on a crystallographic mirror plane perpendicular to the c axis.

The cell dimensions and the relative intensities were measured with a proportional counter on a General Electric XRD-5 diffractometer, MoKα radiation being used. Size of the crystal mounted on a 'goniostat' was 0.06 × 0.15 × 0.20mm. The independent reflections from 1,747 planes were observed within the range of $\theta \leq 27^\circ$.

The structure was solved by the direct sign-determination methods (13); the Harker-Kasper inequality and the Sayre's relation were applied to F(hk0)'s. The positional and thermal parameters of the non-hydrogen atoms so obtained were refined by the least-squares method. Anisotropic temperature factors were applied for the chlorine atoms, while the carbon atoms were treated as undergoing isotropic thermal motions. After two cycles of refinement the discrepancy factor, $R=\Sigma\left||F_o|-|F_c|\right|/\Sigma|F_o|$, was reduced to 0.13. The electron density projection along the c axis is shown in Fig. 1. The molecule is completely planar from a crystallographic requirement stated above. The bond lengths and angles at this stage are shown in Fig. 2. The bond lengths in the five-membered ring and that between the two rings are very close to the predicted values for calicene itself (I) (14,15), but those in the three-membered ring are considerably shorter than the theoretical values.

Further refinements are in progress. A detailed account of this work will be presented in the near future.

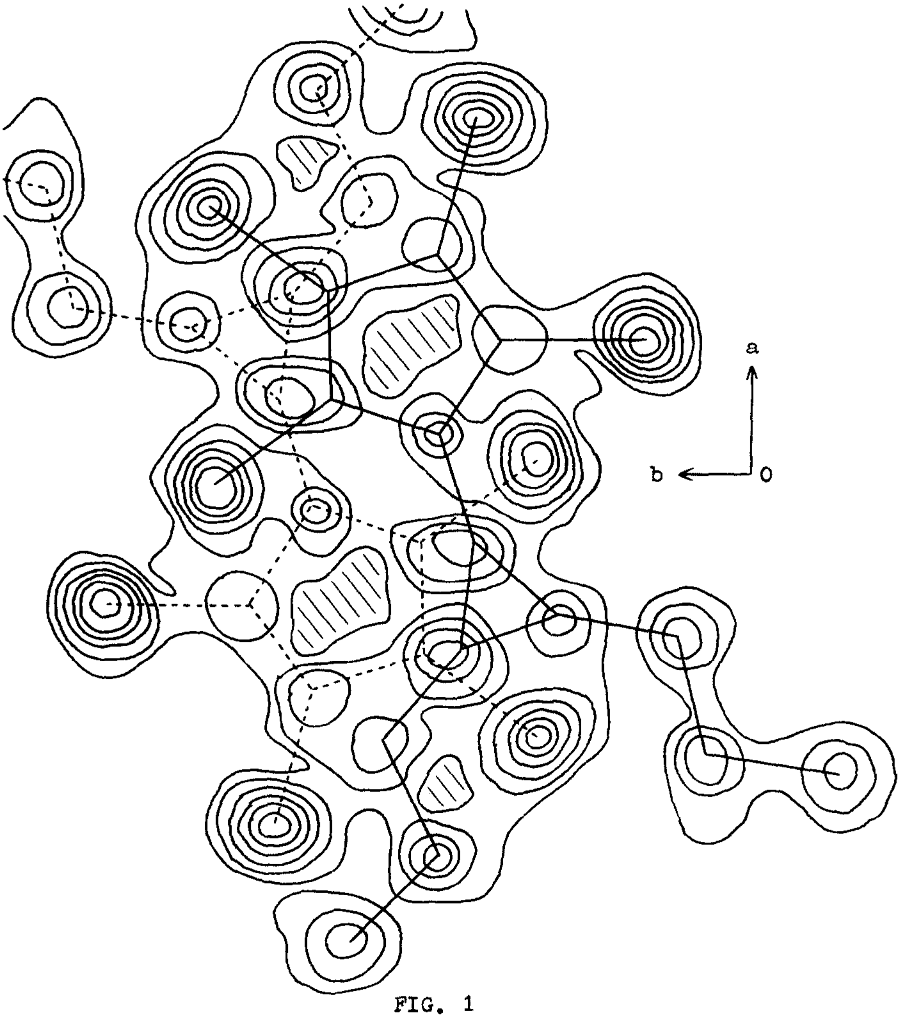


FIG. 1

The Electron Density Projection on (001).

Contours of carbon atoms are drawn at intervals of 2.0 $e.\mathring{A}^{-2}$, the lowest being at 2.0 $e.\mathring{A}^{-2}$. Contours of chlorine atoms are drawn at intervals of 4.0 $e.\mathring{A}^{-2}$ from 4.0 $e.\mathring{A}^{-2}$, the lowest being at 2.0 $e.\mathring{A}^{-2}$. The molecule drawn with broken lines lies down half-period of the c axis.

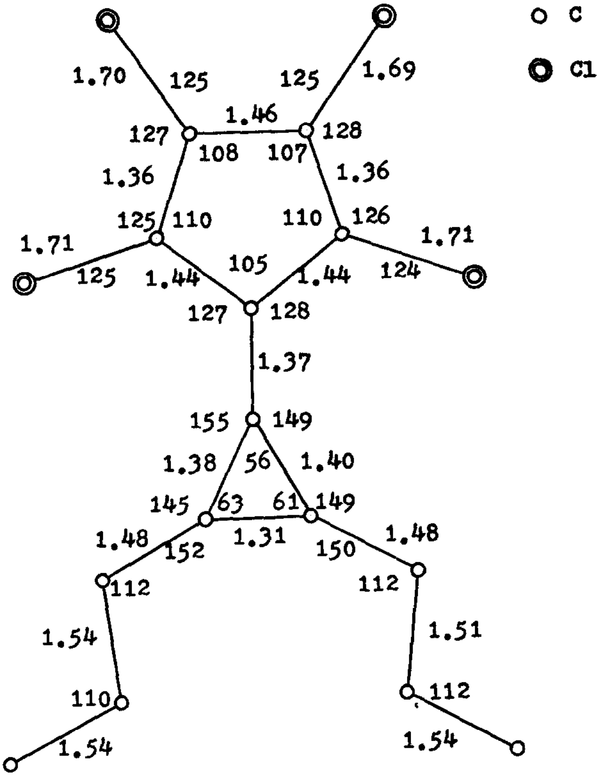


FIG. 2

Bond Lengths (Å) and Angles (deg.)

e.s.d.(C-C) =0.02Å

e.s.d.(C-Cl)=0.02Å

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