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# MOLECULAR AND CRYSTAL STRUCTURE OF 1,2,3,4-TETRACHLORO-5,6-DIPHENYLCALICENE

by

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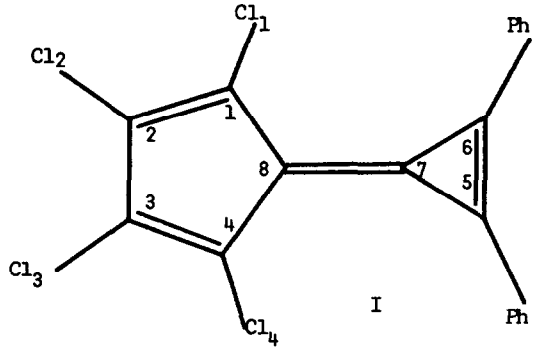
Over the past two years successful attempts have been made to prepare stable derivatives of the cyclopropenylidene-cyclopentadiene (calicene) system. This paper presents the preliminary results of an X-ray crystallographic study of 1,2,3,4-tetrachloro-5,6-diphenylcalicene (I) using crystals kindly supplied by Mr. I. Agranat of the Department of Organic Chemistry, Hebrew University, Jerusalem. These were prepared, together with hexaphenyl calicene (hexaphenyltripentafulvalene), but only the tetrachloro compound proved suitable for X-ray analysis. The compound has been fully described by Bergmann and Agranat[1a,b] and by Murata and co-workers[1c,d].




I

Crystal Data:- $C_{20}H_{10}Cl_4$: Orthorhombic. Needles, elongated c.

a = 11.588±0.002, b = 21.158±0.004, c = 7.020±0.002Å. Z = 4. CuKα radiation λ = 1.5418. Space group $P2_12_12_1$ from absences.

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The cell dimensions and intensities of 1836 reflexions were measured from a crystal of size 0.02 x 0.04 x 0.70 mm. using a Picker automatic diffractometer in the 2θ scan mode. The structure was solved by the heavy-atom technique. Two cycles of full-matrix isotropic and two cycles of anisotropic least-squares calculations have reduced the discrepancy index R to 7.3%. The bond distances are shown in Fig. 1. Comparable values, found by Shimanouchi et. al.[2] in 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene are given in parentheses.

The standard deviation of a carbon-carbon bond distance is estimated as 0.01Å in the present work while Shimanouchi et. al. quote 0.02Å for the stage of refinement reached at the time of publication. The maximum deviation between the two sets of bond values is 0.032Å or less than three standard deviations. The agreement between chemically equivalent bonds, e.g. C(1)-C(2) and C(3)-C(4) is also well within the estimated standard deviation.

A similar close agreement is obtained for the comparable bond angles. The large external and small internal angles found by Shimanouchi et. al. for the three membered ring system is confirmed. The observed bond angles are listed in Table I.

Table I.

| Apex | End | End | Angle° | Apex | End | End | Angle° |
|---|---|---|---|---|---|---|---|
| C(1) | Cl(1) | C(2) | 125.28 | C(8) | C(1) | C(4) | 102.79 |
| C(1) | Cl(1) | C(8) | 123.38 | C(8) | C(1) | C(7) | 127.56 |
| C(1) | C(2) | C(8) | 111.22 | C(8) | C(4) | C(7) | 129.59 |
| C(2) | Cl(2) | C(1) | 127.26 | C(7) | C(8) | C(5) | 155.55 |
| C(2) | Cl(2) | C(3) | 125.44 | C(7) | C(8) | C(6) | 146.90 |
| C(2) | C(1) | C(3) | 107.19 | C(7) | C(5) | C(6) | 56.94 |
| C(3) | Cl(3) | C(2) | 123.02 | C(5) | C(7) | C(6) | 60.73 |
| C(3) | Cl(3) | C(4) | 128.04 | C(5) | C(7) | C(15) | 152.67 |
| C(3) | C(2) | C(4) | 108.64 | C(5) | C(6) | C(15) | 146.58 |
| C(4) | Cl(4) | C(3) | 125.02 | C(6) | C(7) | C(5) | 62.33 |
| C(4) | Cl(4) | C(8) | 124.89 | C(6) | C(7) | C(9) | 151.55 |
| C(4) | C(3) | C(8) | 109.94 | C(6) | C(5) | C(9) | 146.10 |

C-C-C average in benzene ring = 120.0°

Both X-ray determinations confirm the calculations of Dewar and Gleicher[3] which predict strong bond fixation and lack of aromatic character in the calicene system.

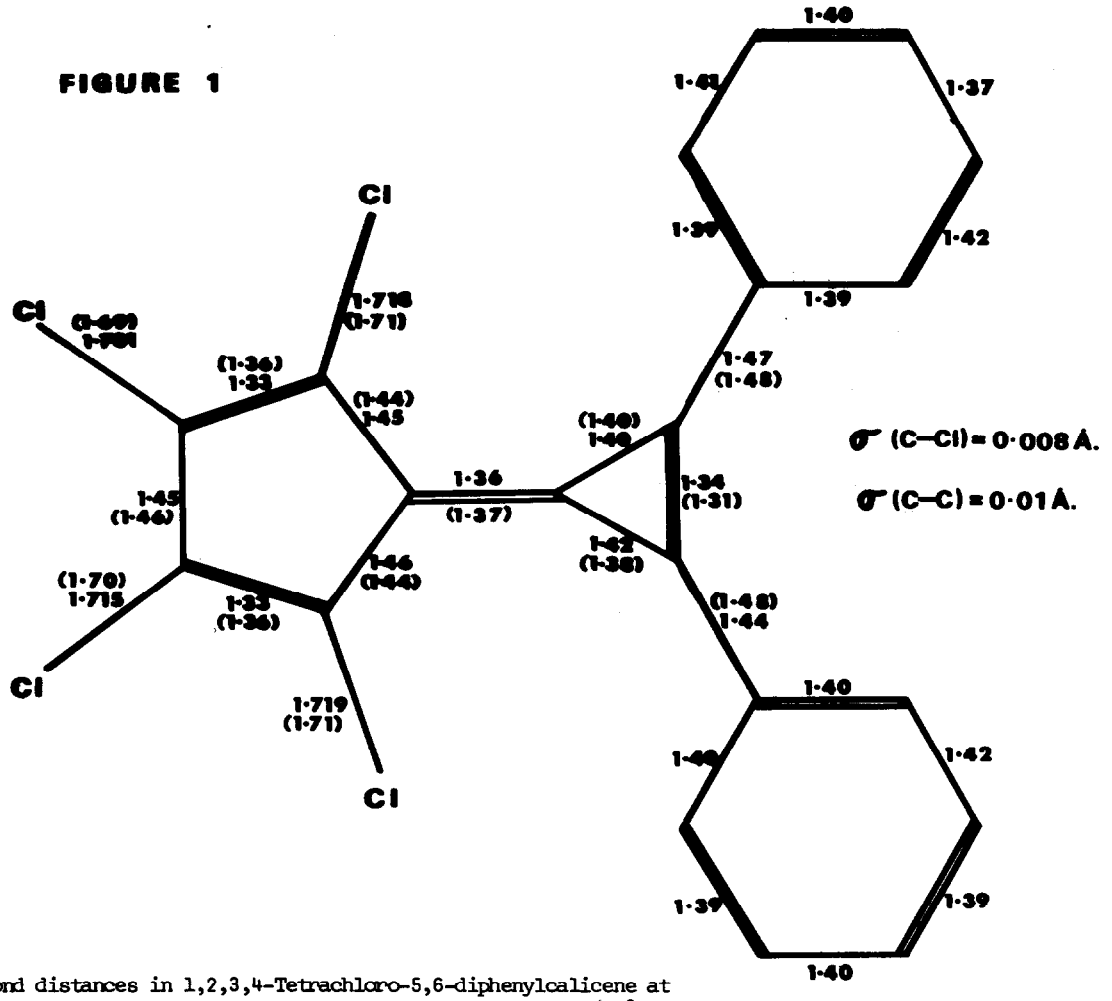
Further refinement of the structure is in progress and full details of the analysis and discussion of the results will be published later.

Acknowledgements: We would like to thank Professor Bergmann and Dr. Agranat for provision of the crystals, Professor Lord Todd for his interest in the work and the Directors and Staff of the Computer Units of Imperial College, London and the Science Research Council, Chilton for their help with computing.

References:-

1a. E. D. Bergmann and I. Agranat, Chemical Communications, 21, 512, 1965.

**FIGURE 1**




Bond distances in 1,2,3,4-Tetrachloro-5,6-diphenylcalicene at R = 7.2%. Comparable values found by Shimanouchi et. al.[2] in 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene at R = 13% are given in parentheses.


1b. E. D. Bergmann and I. Agranat, Tetrahedron, 22, 1275, 1966.

1c. I. Murata, M. Ueno and Y. Kitahara, Tetrahedron Letters, 1831, 1966.

1d. M. Ueno, I. Murata and Y. Kitahara, Tetrahedron Letters, 2967, 1965.

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