Tetrahedron Letters No. 21, pp 2081 - 2084, 1972. Pergamon Press. Printed in Great Britain.

THE CRYSTAL STRUCTURE OF A REARRANGEMENT PRODUCT OF A PERCHLORINATED CAGE AMINE

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(Received in USA 22 November 1971; received in UK for publication 17 April 1972)

I wish to report the molecular structure of the methyl ester of 4-Z-(chlorocyanomethylene) -1,2,3,6-tetrachlorobicyclo[3.1.0]hex-2-ene-6-syn-carboxylic acid produced by the unusual room temperature degradation of 4-aminononachlorohomocubane in alkaline t-butanol.[1]

Colorless crystals of $C_{10}H_4Cl_5NO_2$, grown by sublimation, and kindly supplied by Professor K. V. Scherer, were mounted on thin-walled glass capillary tubes. Crystallographic data: Triclinic; space group P1 or $P\bar{1}$, a = 8.43 Å, b = 13.28 Å, c = 6.24 Å, α = 97.5°, β = 106.3°, γ = 95.4°. One complete hemisphere of data, totalling 1312 reflections, was collected on a Nonius CAD-3 automated diffractometer with Mo Kα radiation. A zero-moment test[2] performed on the data indicated that the space group was probably $P\bar{1}$.

Initially, attempts were made to solve the phase problem by using Long's program[3] which utilizes a reiterative application of Sayre's equation.[4] Direct use of this program did not lead to a successful solution, however, because the crucial choice of a starting set of signs (in this case, seven) was not made correctly. To solve the problem, it was necessary to apply the symbolic addition procedure[5] manually to the starting set of 146 reflections (with E > 1.5), using only interactions having probabilities greater than 0.95. In this way, it was possible to express the signs of 94 reflections in terms of 4 symbols. Long's program was now rerun using 4 carefully chosen reflections as variables, and this resulted in a rapid convergence to the correct solution (2 cycles, consistency index 0.993).[3] An E-map based on this solution revealed the positions of the five chlorine atoms very clearly, and the rest of the non-hydrogen atom positions were obtained from a difference Fourier map phased by the five chlorine atoms. A series

of least-squares refinement cycles (in which anisotropic temperature factors were assigned to the chlorine atoms) resulted in a final R factor of 7.4%.[6]

The geometry of the molecule is shown in Figure 1, and the bond lengths and angles are given in Table 1. The molecule is based on a [3,1,0] bicyclic framework. Double bonds are inferred to exist between C_2 and C_3, and between C_4 and C_7 because of their bond lengths (1.318 Å and 1.320 Å resp.) and because of the near-planarity of the $C_1C_2C_3C_4C_5C_7C_8NCl_2Cl_3Cl_4$ fragment. The crystal is racemic, each unit cell containing two mirror-related molecules.

I would like to thank the Petroleum Research Fund (Grant #2059-G3, administered by the American Chemical Society), the National Institutes of Health (Biomedical Sciences Support Grant #FR-07012-04) and the Research Corporation for supporting this research. The help of the University of Southern California Computing Center, in making available its IBM 360/65 computer, is also gratefully acknowledged.

REFERENCES

1. K. V. Scherer, accompanying communication.
2. E. R. Howells, D. C. Phillips and D. Rogers, Acta Cryst., 3, 210 (1950).
3. R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.
4. D. Sayre, Acta Cryst., 5, 60 (1952).
5. I. L. Karle and J. Karle, Acta Cryst., 16, 969 (1963).
6. The following computer programs were used in this work:
   (a) Symbolic addition interaction list:
   SIGMA 2, by R. Destro, California Institute of Technology
   (b) Reiterative application of Sayre's equation:
   REL, by R. E. Long, U.C.L.A.
   (c) Fourier maps, least squares refinement, geometry:
   CRYM, by R. E. Marsh, California Institute of Technology
   (d) Thermal elliposoid plots:
   ORTEP, by C. K. Johnson, Oak Ridge National Laboratory.

TABLE I

Bond Lengths (Å) (Standard Deviations in Parentheses)

C_1-C_2	1.475 (12)	C_1-C_5	1.510 (12)	C_1-C_6	1.501 (12)
C_2-C_3	1.318 (13)	C_3-C_4	1.448 (12)	C_4-C_5	1.502 (12)
C_4-C_7	1.320 (13)	C_5-C_6	1.526 (12)	C_6-C_9	1.535 (12)
C_7-C_8	1.422 (14)				
C_1-Cl_2	1.713 (9)	C_2-Cl_2	1.698 (9)	C_3-Cl_3	1.730 (9)
C_6-Cl_5	1.728 (8)	C_7-Cl_4	1.733 (10)		
C_8-N	1.140 (16)	C_9-O_1	1.209 (12)	C_9-O_2	1.312 (12)
C_{10}-O_2	1.415 (14)				

Bond Angles (deg.)
(Standard deviations in parenthesis)

Cl_1-C_1-C_2	117.2 (6)	Cl_5-C_6-C_1	118.2 (6)
Cl_1-C_1-C_5	124.0 (6)	Cl_5-C_6-C_5	116.6 (6)
Cl_1-C_1-C_6	120.8 (6)	Cl_5-C_6-C_9	110.1 (6)
C_2-C_1-C_5	104.8 (7)	C_1-C_6-C_5	59.8 (6)
C_2-C_1-C_6	116.3 (7)	C_1-C_6-C_9	121.3 (7)
C_5-C_1-C_6	60.9 (6)	C_5-C_6-C_9	122.8 (7)
Cl_2-C_2-C_1	122.2 (7)	Cl_4-C_7-C_4	125.6 (7)
Cl_2-C_2-C_3	126.1 (7)	Cl_4-C_7-C_8	112.3 (8)
C_1-C_2-C_3	111.5 (8)	C_4-C_7-C_8	122.0 (9)
Cl_3-C_3-C_2	123.0 (7)	N-C_8-C_7	177.2 (12)
Cl_3-C_3-C_4	125.0 (7)	O_1-C_9-O_2	123.2 (9)
C_2-C_3-C_4	111.9 (8)	O_1-C_9-C_6	125.4 (8)
C_3-C_4-C_5	106.0 (7)	O_2-C_9-C_6	111.3 (7)
C_3-C_4-C_7	133.4 (8)	C_9-O_2-C_{10}	118.6 (8)
C_5-C_4-C_7	120.6 (8)		
C_1-C_5-C_4	105.7 (7)		
C_1-C_5-C_6	59.3 (6)		
C_4-C_5-C_6	117.1 (7)		

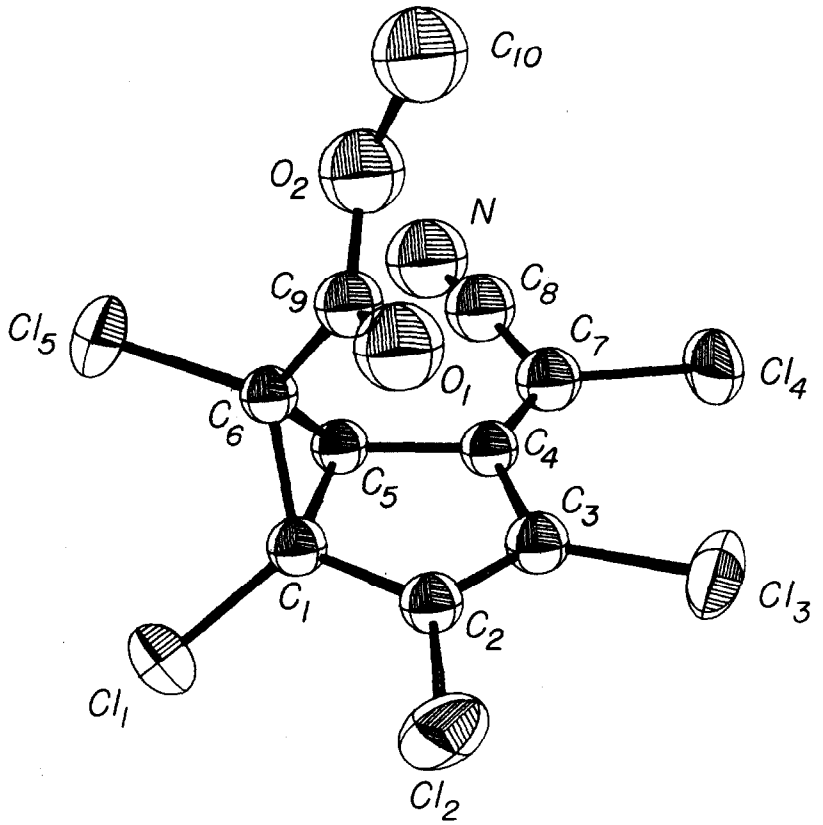

Fig. 1: The molecular geometry of methyl-4-Z-(chlorocyanomethylene)-1,2,3,6,-tetrachlorobicyclo[3.1.0]hex-2-ene-6-syn-carboxylate (the hydrogen atoms are not shown).