

# Organic and Biological Chemistry

## The Crystal and Molecular Structure of Perchloro[4]radialene

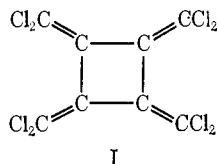
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**Abstract:** The crystal and molecular structure of perchloro[4]radialene,  $C_8Cl_8$ , has been determined by a single-crystal three-dimensional X-ray diffraction study. This compound crystallizes in space group  $Pbcn$  with lattice parameters  $a = 14.719 \pm 0.007$ ,  $b = 9.156 \pm 0.003$ , and  $c = 9.923 \pm 0.005$  Å, giving a calculated density  $\rho = 1.885$  g  $cm^{-3}$  for  $Z = 4$ . The intensities of 1528 unique reflections were measured using the  $\theta$ - $2\theta$  scan mode of a Picker automatic diffractometer (Mo  $K\alpha$  radiation). The structure was solved by reiterative application of Sayre's equation and refined by full-matrix least-squares to a final discrepancy index  $R_1 = 0.042$  for 1034 reflections above background. All atoms were assigned anisotropic thermal parameters. The molecule is found to be highly nonplanar and to conform very closely to molecular  $D_{2d}$  symmetry, although only a single twofold axis is required by the space group. Deformation of the molecule from a planar geometry is achieved largely by bending the four-membered ring to a dihedral angle of  $153.5 \pm 0.6^\circ$ . As a result the intramolecular  $Cl \cdots Cl$  contacts are increased to values ranging from 3.308 to 3.338 Å, and the planes of the four chlorines above and the four chlorines below the central ring are separated by 2.454 Å. The bond distances give no evidence of conjugation. The distances in the ring (1.446, 1.494, and 1.486 Å) are normal for single bonds between  $sp^2$  hybridized carbons, and the  $C=C$  (1.329 and 1.326 Å) and  $C-Cl$  bonds (1.708, 1.716, 1.708, and 1.712 Å) compare well with literature values.

The  $[n]$ radialenes are carbocyclic systems containing  $n$ -cross-conjugated exocyclic double bonds. The high symmetry of these compounds makes them of considerable spectroscopic and theoretical interest, and several have now been synthesized.<sup>1-3</sup> The ultraviolet spectra show unusual low-energy transitions, which, in the even ( $n = 2, 4, 6, \dots$ ) radialenes, have been attributed to reduction of the molecular symmetry from planar  $D_{nh}$  to  $D_{(n/2)d}$  via either strong bending modes or permanent deformation.<sup>4</sup>

The synthesis of perchloro[4]radialene (I), the chloro-



radinated derivative of tetramethylenecyclobutane, by thermal dimerization of perchlorobutatriene, has recently been reported by Heinrich and Roedig.<sup>5</sup> Steric repulsions between the chlorine atoms in perchloro[4]radialene clearly rule out a planar  $D_{4h}$  structure; these interactions can be relieved either by twisting the  $C-C$  double bonds to a  $D_4$  geometry or by puckering the central ring to  $D_{2d}$ .

We present below the results of an X-ray diffraction study which gives direct proof of the structure of perchloro[4]radialene, and is believed to be the first crystallographic report of the molecular structure of a [4]radialene.<sup>6</sup>

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(3) G. Köbrich and H. Heineman, *Angew. Chem.*, **77**, 590 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

(4) E. Heilbronner, *Theor. Chim. Acta*, **4**, 64 (1966).

(5) B. Heinrich and A. Roedig, *Angew. Chem.*, **80**, 367 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 375 (1968).

### Experimental Section

**Data Collection.** Two samples of perchloro[4]radialene obtained (A) by sublimation at low pressure<sup>5</sup> and (B) by recrystallization from a mixture of chloroform and ethanol were kindly supplied by Professor A. Roedig of the Institut für Organische Chemie der Universität Würzburg (Germany). The crystals of A (mp  $164^\circ$ ) were platelike and appeared almost glassy. Their cell parameters, determined from oscillation and Weissenberg photographs using  $Cu K\alpha$  radiation ( $\lambda$  1.5418 Å), are  $a = 8.77$ ,  $b = 12.19$ ,  $c = 12.99$  Å, and  $\beta = 107^\circ 43'$ . The unit cell volume is 1322 Å<sup>3</sup>; for four molecules of  $C_8Cl_8$  per unit cell the calculated density would be 1.91 g  $cm^{-3}$ . Systematic absences, occurring for the  $h0l$  reflections when  $l = 2n + 1$  and for the  $0k0$  reflections when  $k = 2n + 1$ , indicate unambiguously the space group  $P2_1/c$ . X-Ray diffraction photographs of numerous crystals were taken but no crystals suitable for intensity measurements were found. Sample B consisted of colorless needles (mp  $164^\circ$ ) yielding excellent diffraction patterns belonging to the orthorhombic system. The systematic absences in the reciprocal lattice, surveyed on Weissenberg photographs taken with  $Cu K\alpha$  radiation, were consistent with space group  $Pbcn$  ( $0kl$ ,  $k = 2n + 1$ ;  $h0l$ ,  $l = 2n + 1$ ; and  $hk0$ ,  $h + k = 2n + 1$ ).

A needlelike crystal, of hexagonal cross section, with minimum radius 0.11 mm and length 1.4 mm, was sealed in a 0.3 mm thin-wall glass capillary tube. Careful centering along the  $c$  (needle) axis on a Picker automatic four-circle diffractometer gave  $\phi$  independence of the  $00l$  reflections to  $\pm 6.1\%$ . Lattice constants were calculated from a least-squares refinement of the setting angles of ten reflections with Mo  $K\alpha$  radiation ( $\lambda$  0.71069 Å). The cell parameters,  $a = 14.719 \pm 0.007$ ,  $b = 9.156 \pm 0.003$ , and  $c = 9.923 \pm 0.005$  Å, give a unit cell volume of 1337.3 Å<sup>3</sup> and a calculated density  $\rho = 1.885$  g  $cm^{-3}$  for  $C_8Cl_8$  with  $Z = 4$ . A direct measurement of the density by flotation in  $NaI-H_2O$  solutions gave  $\rho = 1.880 \pm 0.005$ , in good agreement. With four molecules per cell, the molecules are required to lie on centers of symmetry or on the twofold axes parallel to the  $y$  axis.

Intensity data were collected using the  $\theta$ - $2\theta$  scan mode of the diffractometer with Zr filtered molybdenum radiation. The take-off angle of the tube was  $2^\circ$ , and a counter aperture 4.0 (vertical)

(6) Structures of [3]radialenes have been reported by J. D. Dunitz and A. Mugnoli, *Helv. Chim. Acta*, **49**, 1680 (1966); H. Dietrich and H. Dierks, *Angew. Chem.*, **80**, 487 (1968); and E. A. Dorko, J. L. Hencher, and S. H. Bauer, *Tetrahedron*, **24**, 2425 (1968).

× 6.0 mm (horizontal) was placed 32 cm from the crystal. Angles ranging between 2.00 and 2.36° of  $2\theta$  were scanned at a speed of 2°/min, and two stationary-crystal stationary-counter background counts of 15 sec were taken at each end of the scan. The reciprocal lattice was recorded out to the limits of the Cu K $\alpha$  sphere ( $\sin \theta = 0.461$ ) and a total of 1528 independent reflections was measured. Three test reflections (420, 521, and 911), recorded every 55 reflections, showed that no decomposition occurred. The net intensity,  $I = N_o - kN_b$ , for each reflection was assigned an error  $\sigma(I) = [(0.02I)^2 + N_o + k^2N_b]^{1/2}$ , where  $N_o$  is the gross count,  $N_b$  the background count, and  $k$  the ratio of scan time to background time. These  $\sigma$ 's were used to calculate the weights  $w = 4F^2/\sigma^2(F^2)$  for the least-squares refinement, where the quantity  $\sum w(|F_o| - |F_c|)^2$  was minimized. The intensities of 494 measured reflections for which  $\sigma(I)/I > 0.3$  were considered to be absent, and were omitted from the analysis. The intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient  $\mu$  for Mo K $\alpha$  is 16.34 cm $^{-1}$ ; a partial absorption correction was made by assuming a cylindrical crystal with a radius of 0.011 cm. A correction was also made for change in diffracting volume as a function of crystal orientation. Finally, an absolute scale factor and an overall temperature factor were computed by Wilson's method.

### Structure Determination and Refinement

**Structure Determination.** The structure was solved by iterative application of Sayre's<sup>7</sup> equation in three dimensions. This equation is

$$s(E_a) = s\left(\sum_{a=b+c} E_b E_c\right)$$

where  $s$  means "sign of,"  $a, b, c$  are the vectors ( $hkl$ ) for the reflections  $a, b, c$ , and  $E_a, E_b$ , and  $E_c$  are normalized structure factors for  $a, b, c$ . Input to the computer program<sup>8</sup> comprised a set of 172 reflections having  $|E| \geq 1.5$ . Table IA lists the starting sets of seven phases each used for the application of Sayre's equa-

tion. In Table IB we have assembled the number of cycles, and the number of positive and negative phases, together with the consistency index,  $C$ , for the 16 starting sets. It is this index where the sums are over

$$C = \frac{\langle |E_a \sum_{a=b+c} E_b E_c| \rangle}{\langle |E_a| \sum_{a=b+c} |E_b| |E_c| \rangle}$$

all pairs of  $b$  and  $c$  for which  $b + c = a$  and where the average is over all values of  $a$ , which is used to indicate which of the generated solutions is most likely to be the true one. The last two columns of Table IB give the starting phases for the four symbolic phases being cycled, and the predicted phases for these four after the last cycle. Solutions 9, 11, 14, and 15 are found to be identical with 13 as is suggested by the fact that the iteration gives predicted phases for starting sets of solutions 9, 11, 14, and 15 which are the same as the solution 13 starting set. An  $E$  map<sup>9</sup> calculated from 13 showed the 8 atoms of the asymmetric unit unambiguously, and the complete molecule could easily be generated by a twofold axis. A review of the phases after the least-squares refinement showed that all of the 172 signs predicted by this solution are correct.

**Structure Refinement.** Five cycles of full-matrix least-squares refinement<sup>10</sup> on the positions and isotropic temperature factors of the atoms found in the  $E$  map reduced

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

from 0.26 to 0.16. The introduction of anisotropic temperature factors had a pronounced effect on  $R_1$  which dropped to 0.067 after one further cycle. Two additional cycles of full-matrix least-squares in which all positional and anisotropic thermal parameters were varied reduced  $R_1$  to 0.055 and

$$R_2 = \{\sum w[F_o - F_c]^2 / \sum wF_o^2\}^{1/2}$$

to 0.068. A difference map revealed very diffuse peaks, some as high as 0.75 e/Å<sup>3</sup>, randomly distributed over the asymmetric unit. The largest background (negative) peaks were less than 0.5 e/Å<sup>3</sup>. At this point it was clear that 15 strong low order reflections, systematically less intense than their calculated values, showed severe secondary extinction. Their corrected intensity was obtained from the equation  $I_o(\text{cor}) = I_o(1 + 2gI_c)$  with  $g = 2.868 \times 10^{-4}$  (electrons) $^{-2}$ , where  $I_o$  is the observed intensity and  $I_c$  the scaled calculated intensity.<sup>11</sup> After introduction of these corrected values additional refinement on all parameters converged in three more cycles of full-matrix least-squares to the final discrepancy indices of  $R_1 = 0.042$  and of  $R_2 = 0.048$ . In the final refinement cycle the changes of atomic parameters were less than 0.006 of their estimated standard deviations.

(9) Fourier calculations were performed using program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and Van den Hende's ERFR-2, by J. Gvildys.

(10) (a) Least-squares and structure factor calculations were performed using a program written for the IBM 1130 by the authors for isotropic thermal parameters, and using ANL-FLS-14E, J. Gvildys' version of Busing, Martin, and Levy's OR-FLS for anisotropic thermal parameters. (b) Atomic scattering factors were taken from "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

(11) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 411.

Table I

A. Starting Sets for Application of Sayre's Relation						
$h$	$k$	$l$	$E$			
11	1	3	+3.59			
7	2	8	+3.83			
9	3	6	+3.38			
1	1	3	±2.42			
2	3	8	±3.56			
9	5	0	±3.43			
2	6	3	±2.44			
B. Consistency Indices for Cycled Phase Sets						
Set	Cycles	No. +	No. -	$C^a$	Initial	Predicted
1	10	80	91	0.599	++++	+--+
2	17	84	83	0.459	++++	++++
3	15	94	76	0.491	++-+	+--+
4	17	88	79	0.494	++--	+--+
5	17	83	87	0.623	+--+	+--+
6	10	97	74	0.742	+--+	+--+
7	14	83	86	0.580	+--+	+--+
8	17	87	81	0.472	+--+	+--+
9	8	96	75	0.760	-+++	-+++
10	11	83	88	0.711	-+++	-+++
11	11	96	75	0.716	-+++	-+++
12	12	86	83	0.593	-+++	-+++
13	7	96	75	0.811	---+	---+
14	12	96	75	0.769	---+	---+
15	7	96	75	0.763	---+	---+
16	17	86	77	0.518	-----	-----

<sup>a</sup>  $C$  = consistency index.

(7) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

(8) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1965.

**Table II.** Final Structure Parameters<sup>a</sup> and Estimated Standard Deviations<sup>b</sup>

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
Cl(1)	0.4004 (1)	0.4805 (1)	0.1696 (2)	63 (1)	95 (1)	224 (2)	19 (1)	-17 (1)	9 (2)
Cl(2)	0.2713 (1)	0.2596 (1)	0.2443 (1)	30 (1)	181 (2)	188 (2)	12 (1)	-0 (1)	-29 (2)
Cl(3)	0.3315 (1)	0.0239 (1)	0.4807 (1)	48 (1)	190 (2)	106 (1)	-19 (1)	28 (1)	-17 (1)
Cl(4)	0.4506 (1)	-0.2072 (1)	0.4000 (1)	65 (1)	103 (1)	100 (1)	-17 (1)	-2 (1)	14 (1)
C(1)	0.4513 (2)	0.2201 (4)	0.2652 (4)	33 (2)	91 (5)	83 (4)	-2 (2)	1 (3)	-14 (4)
C(2)	0.4567 (2)	0.0591 (4)	0.2884 (3)	31 (2)	90 (5)	68 (4)	-5 (3)	-4 (2)	-10 (4)
C(3)	0.3834 (3)	0.3104 (4)	0.2357 (4)	34 (2)	100 (5)	126 (6)	5 (3)	-4 (3)	-29 (5)
C(4)	0.4166 (2)	-0.0305 (4)	0.3750 (4)	36 (2)	109 (5)	74 (4)	-11 (2)	1 (2)	-17 (4)

<sup>a</sup> The anisotropic thermal parameters are in the form  $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ . <sup>b</sup> Estimated standard deviations are given in parentheses.

Final atomic parameters and their standard deviations as calculated in the last least-squares cycle are listed in Table II. A table of observed and calculated structure factors is available on request.<sup>12</sup> Intramolecular distances and angles with standard deviations obtained from the least-squares variance-covariance matrix<sup>13</sup> are given in Table III. The amplitudes and

**Table III.** Bond Lengths and Angles<sup>a,b</sup>

A. Bond Distances, Å					
Carbon-chloride bonds					
	C(3)-Cl(1)		1.708 (4)		
	C(3)-Cl(2)		1.716 (4)		
	C(4)-Cl(3)		1.708 (4)		
	C(4)-Cl(4)		1.712 (4)		
Exocyclic carbon-carbon bonds					
	C(1)-C(3)		1.329 (5)		
	C(2)-C(4)		1.326 (5)		
Endocyclic carbon-carbon bonds					
	C(1)-C(2)		1.494 (5)		
	C(1)-C(1)'		1.466 (7)		
	C(2)-C(2)'		1.486 (7)		
B. Bond angles, deg					
Vertex	Atom 1	Atom 2		Atom 1	Atom 2
C(1)	C(2)	C(1)'	88.8 (0.2)	C(3)	C(1)
	C(2)	C(3)	133.5 (0.3)	C(1)	Cl(1)
	C(3)	C(1)'	133.6 (0.3)	C(1)	Cl(2)
C(2)	C(1)	C(2)'	88.1 (0.2)	C(4)	C(2)
	C(1)	C(4)	133.3 (0.3)	C(2)	Cl(3)
	C(4)	C(2)'	135.6 (0.3)	C(2)	Cl(4)
	C(4)	C(2)'	135.6 (0.3)	C(3)	Cl(4)

<sup>a</sup> Estimated standard deviations calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses. <sup>b</sup> Primes designate atoms related by the crystallographic twofold axis:  $1 - x, y, 1/2 - z$ .

directions of anisotropic thermal motion are summarized in Table IV, and are also presented in the form of 50% probability thermal ellipsoids in the stereopair drawing, Figure 1.<sup>14</sup>

**Discussion of the Structure.** The perchloro[4]radialene molecule is found as expected to be nonplanar, and to conform very closely to D<sub>2d</sub> symmetry, although only a single twofold axis is required by the space

group. The molecular geometry is shown in a view perpendicular to the central ring in Figure 1 and as seen down the crystallographic twofold axis in Figure 2. Primes will be used in the subsequent discussion to designate atoms related to the eight unique atoms of the asymmetric unit by this C<sub>2</sub> axis.

The dichloromethylene groups are bent out of the plane of the central ring in order to increase the intramolecular Cl···Cl distances. If the molecule had been planar, and if we assume values of 1.724 Å for the C-Cl distances and 113° for the Cl-C-Cl angles as in tetrachloroethylene,<sup>15</sup> these intramolecular contacts would have been 2.69 Å. The actual Cl···Cl distances found are 3.338 ± 0.003 (Å) for Cl(1)···Cl(1)', 3.308 ± 0.002 for Cl(2)···Cl(3), and 3.313 ± 0.003 for Cl(4)···Cl(4)'. The sum of two chlorine van der Waals radii, a measure of normal intermolecular contacts in solids, is 3.60 Å,<sup>16</sup> but the value of 3.3 Å found here and in other chlorocarbons<sup>17</sup> more closely defines the lower limit for intramolecular approach. The amount of distortion present in perchloro[4]radialene can be measured by the separation of 2.454 Å between the plane of the four chlorines (1, 2, 3', 4') above and that of the four chlorines (1', 2', 3, 4) below the central ring. This deformation is achieved in part by puckering the four-membered ring to form a dihedral angle of 153.5 ± 0.6° between the planes C(1)'-C(1)-C(2) and C(2)-C(2)'-C(1)'. Although the origin of conformational differences among cyclobutanes is not very well understood, those cyclobutanes known to be nonplanar have dihedral angles ranging from 150 to 158°,<sup>18-24</sup> comparable to that in the present system. While the need for puckering in the highly hindered perchloro[4]radialene molecule is clear, we note that the dihedral angle is not alone sufficient to relieve the Cl···Cl contacts, and that the remainder of the distortion arises from bending at the sp<sup>2</sup> carbon atoms. Most of this bending occurs at the ring atoms: the angle formed by the C(1)=C(3) bond and the plane C(1)'-C(1)-C(2) is 15.3°, while that formed by C(2)=C(4) with C(1)-C(2)-C(2)' is 13.1°. Bending also occurs at the exocyclic carbons, but to a lesser extent. The angle between the C(1)=C(3)

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(19) I. L. Karle, J. Karle, and K. Britts, *J. Am. Chem. Soc.*, **88**, 2918 (1966).

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(12) Material supplementary to this article has been deposited as Document No. NAPS-00807 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting \$1.00 for microfilm or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to ASIS-NAPS.

(13) J. Gvildys' version (ANL Program Library B-115) of Busing, Martin, and Levy's Fortran function and error program, OR-FFE, was used.

(14) ORTEP is a Fortran thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory.

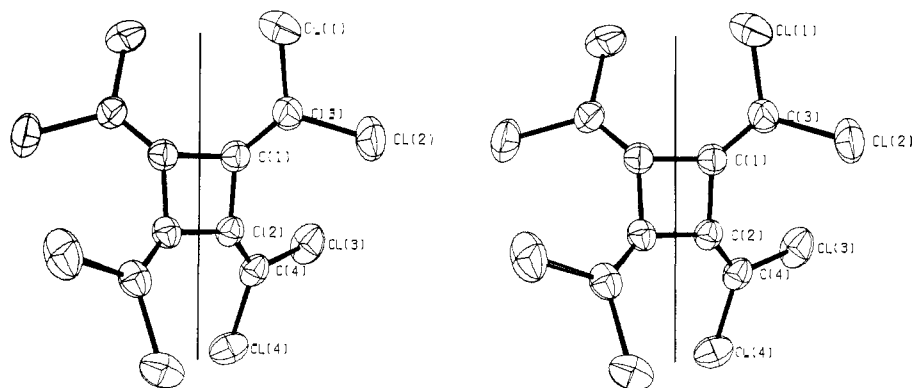


Figure 1. Three-dimensional view of perchloro[4]radialene showing ellipsoids of thermal motion at 50% probability. The crystallographic twofold axis, shown by the solid line, is vertical.

line and the Cl(1)–C(3)–Cl(2) plane is  $5.3^\circ$  and the corresponding angle between C(2)=C(4) and Cl(4)–C(2)–Cl(3) is  $1.5^\circ$ . All of these distortions are in such a direction as to increase the Cl $\cdots$ Cl intramolecular contacts. Table V further illustrates some

Plane 3 measures the absence of coplanarity in the cyclobutane ring. Relief of Cl $\cdots$ Cl interactions by twisting about the exocyclic double bonds is both an energetically unfavorable process and one inconsistent with  $D_{2d}$  symmetry; this process appears not to occur

Table IV. Root-Mean-Square Thermal Displacements along the Principal Axes of the Thermal Ellipsoids ( $\text{\AA}$ ) and Their Projections along the Axes of a Cartesian Coordinate System Referred to  $a$ ,  $b$ , and  $c$ .<sup>a,b</sup>

Atom	Axis 1			Axis 2			Axis 3			
Cl(1)	0.186 (2)	0.170 (2)	-0.021 (2)	-0.238 (3)	0.269 (2)	-0.106 (4)	-0.064 (5)	-0.090 (6)	0.003 (4)	0.327 (2)
Cl(2)	-0.071 (2)	0.178 (2)	-0.007 (2)	-0.048 (4)	0.266 (2)	-0.226 (4)	-0.132 (5)	-0.019 (3)	-0.157 (6)	0.276 (4)
Cl(3)	0.175 (2)	-0.033 (2)	-0.120 (2)	-0.124 (4)	0.250 (2)	-0.153 (4)	-0.153 (4)	-0.142 (4)	0.304 (2)	-0.124 (5)
Cl(4)	0.130 (2)	0.015 (2)	-0.079 (6)	-0.063 (6)	0.228 (2)	-0.077 (7)	-0.205 (3)	-0.254 (2)	0.276 (2)	-0.040 (7)
C(1)	0.054 (3)	0.167 (3)	0.183 (6)	-0.19 (2)	0.190 (5)	0.01 (9)	0.04 (7)	0.03 (4)	-0.101 (4)	-0.216 (6)
C(2)	0.03 (11)	0.14 (2)	0.168 (6)	-0.15 (3)	0.191 (5)	0.01 (6)	0.12 (4)	-0.05 (6)	-0.14 (2)	0.17 (2)
C(3)	0.10 (2)	0.08 (2)	0.185 (6)	-0.15 (5)	0.196 (6)	0.01 (6)	-0.07 (2)	-0.03 (2)	0.204 (5)	-0.08 (5)
C(4)	0.12 (6)	-0.13 (4)	0.177 (6)	-0.15 (2)	0.194 (6)	-0.10 (6)	0.11 (4)	-0.10 (2)	0.18 (1)	0.23 (1)
	0.07 (3)	0.10 (1)	0.13 (3)		-0.03 (3)				0.265 (6)	0.232 (5)
									0.19 (1)	-0.09 (2)

<sup>a</sup> Ordered on increasing magnitude. <sup>b</sup> Estimated standard deviations are given in parentheses as computed from the variance-covariance matrix obtained in the final least-squares cycle.

of these distortions in terms of deviations from selected least-squares planes in the molecule. For example, planes 1 and 2 measure the lack of coplanarity among the six atoms comprising the double bonds and their

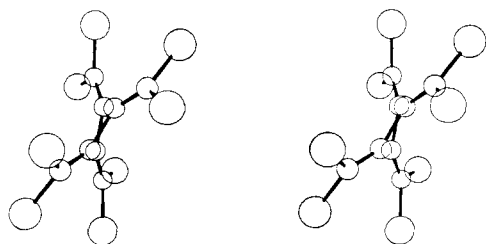
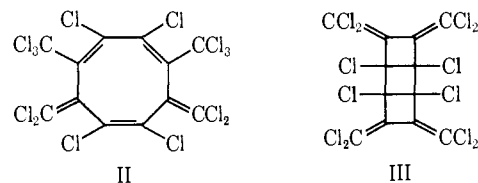


Figure 2. Three-dimensional view of perchloro[4]radialene as viewed down the crystallographic twofold axis.

four substituent atoms, while planes 4–7, determined by an  $sp^2$  carbon and the three atoms to which it is bonded, analyze this effect at each of the unique carbon atoms.

to any significant extent in perchloro[4]radialene (see Table V, planes 10 and 11). If bond twisting were the sole means for separating the chlorines (implying molecular  $D_4$  symmetry), the torsional angle at the double bonds would have to be  $31^\circ$  for 3.30  $\text{\AA}$  contacts. We note that twist angles of  $8^\circ$  have been reported for exocyclic dichloromethylene groups in the hindered perchloro(1,4-dimethyl-5,8-dimethylenecycloocta-1,3,6-triene) system (II) resulting from severe Cl $\cdots$ Cl contacts of 3.24  $\text{\AA}$ .<sup>25</sup> A third type of distortion has



also been observed in perchloro(3,4,7,8-tetramethylenetricyclo[4.2.0.0<sup>2,5</sup>]octane) (III),<sup>17</sup> where the adjacent

(25) A. Furusaki, *Bull. Chem. Soc. Jap.*, **41**, 2886 (1968).

Table V. Least-Squares Planes<sup>a-c</sup>

Atom	Plane												
	1	2	3	4	5	6	7	8	9	10	11	12	13
1	Cl(1)	Cl(3)	C(1)	Cl(1)	Cl(3)	C(1)	C(1)	Cl(3)	C(3)	Cl(1)	Cl(3)	Cl(1)	Cl(4)
2	Cl(2)	Cl(4)	C(2)	Cl(2)	Cl(4)	C(1)'	C(2)	Cl(4)	C(1)	Cl(2)	Cl(4)	Cl(1)'	Cl(4)'
3	C(1)	C(1)	C(1)'	C(1)	C(2)	C(2)	C(2)'	Cl(1)'	C(2)'	C(2)	C(1)	Cl(3)'	Cl(2)
4	C(1)'	C(2)	C(2)'	C(3)	C(4)	C(3)	C(4)	Cl(2)'	C(4)'	C(1)'	C(2)'	Cl(2)'	Cl(3)
5	C(2)	C(2)'											
6	C(3)	C(4)											
$m_1$	0.679	9.096	5.391	-0.364	9.782	1.443	8.385	5.366	9.813	0.718	9.070	-5.566	10.968
$m_2$	2.778	2.313	0	3.336	2.652	2.344	2.192	-0.229	6.483	2.761	2.299	-5.599	5.372
$m_3$	9.444	7.388	9.234	9.238	6.835	9.543	7.802	9.237	-2.309	9.449	7.408	6.934	3.144
$d$	0.240	6.554	5.004	3.035	6.584	3.582	6.308	6.186	5.235	3.218	6.597	-3.722	5.182
$\Delta d,1$	-0.057	0.068	-0.123	-0.011	0.008	0.116	0.027	0.027	-0.004	-0.002	0.025	-0.002	-0.096
$\Delta d,2$	-0.053	0.020	0.121	-0.011	0.008	-0.033	-0.100	-0.026	0.008	0.002	-0.024	0.004	0.045
$\Delta d,3$	-0.063	0.019	0.123	-0.016	0.011	-0.032	0.028	-0.027	-0.008	-0.002	-0.034	0.002	-0.043
$\Delta d,4$	0.157	-0.133	-0.121	0.038	-0.026	-0.052	0.044	0.026	0.004	0.002	0.034	-0.004	0.094
$\Delta d,5$	-0.067	0.089											
$\Delta d,6$	0.083	-0.064											

<sup>a</sup> Primes designate atoms related by the crystallographic twofold axis  $1 - x, y, 1/2 - z$ . <sup>b</sup> The planes are defined by the equation  $m_1x + m_2y + m_3z = d$ . <sup>c</sup>  $\Delta d,1$  refers to the deviation in ångströms of atom 1 from the least-squares plane, etc.

pairs of exocyclic double bonds remain coplanar and the chlorine repulsions are eased by opening the C=C=CCl<sub>2</sub> angles. Comparison of these results suggests that the most favorable means for accommodating these interactions is opening of the C=C=CCl<sub>2</sub> angles. Out-of-plane rotations about the single bonds may occur when, as in perchloro[4]radialene, the former type of distortion cannot reduce the overall strain. Torsional changes around the double bonds appear to be the least favored process. The available evidence thus suggests that the conformational systematics of compounds with exocyclic dichloromethylene groups can be complex, and may also be of general significance. In this context, we note that Furusaki, in some interesting recent work, has shown how conformational relationships among exocyclic dichloromethylene groups can control the course of isomerization in unsaturated chlorocarbons.<sup>25</sup>

The atomic coordinates in perchloro[4]radialene crystals deviate in small, but statistically significant, amounts from D<sub>2d</sub> molecular symmetry. The atoms of planes 8-13 of Table V should, for example, all be perfectly coplanar in an ideal D<sub>2d</sub> system. The deviations actually found in no case exceed 0.10 Å and are for the most part much less; we attribute them to crystal packing forces.

Our observation that D<sub>2d</sub> symmetry is basically respected in the solid state provides evidence in support of the theoretical interpretation of radialene electronic spectra advanced by Heilbronner,<sup>4</sup> who, by combining an independent systems approach with symmetry arguments, showed that when the point groups of the even radialenes are reduced from D<sub>nh</sub> to D<sub>(n/2)d</sub> the forbidden A<sub>1g</sub> → B<sub>1g</sub> (for n/2 even) or A<sub>1g</sub> → B<sub>1u</sub> (for n/2 odd) transitions become allowed. Comparison of the uv spectra of perchloro[4]radialene<sup>5</sup> and the parent hydrocarbon, tetramethylenecyclobutane<sup>2</sup> shows a close similarity; the principal differences are the usual red shift arising from chlorine substitution and an enhanced intensity, by a factor of 2.5, in the low-energy A<sub>1g</sub> → B<sub>1g</sub> transition in the more highly hindered perchloro compound. We have seen that there is a permanent D<sub>(n/2)d</sub> deformation in perchloro[4]radialene; whether the weaker A<sub>1g</sub> → B<sub>1g</sub> band in tetramethylenecyclobutane originates in a lesser degree of permanent deformation or in D<sub>(n/2)d</sub> vibrational modes is not known.

cyclobutane originates in a lesser degree of permanent deformation or in D<sub>(n/2)d</sub> vibrational modes is not known.

Bond distances and angles in perchloro[4]radialene are in very close agreement with literature values. The four C-Cl bonds agree with each other within experimental error and their average length, 1.711 Å, is identical with the standard value for a C-Cl distance to sp<sup>2</sup> hybridized carbon.<sup>26</sup> We find Cl-C-Cl angles of 113.7 and 114.0°, very similar to the value of 113.3° in tetrachloroethylene.<sup>15</sup> Our carbon-carbon double bond distances of 1.326 and 1.329 Å also compare closely with published values for 1,1-dichloroethylene (1.324 and 1.325 Å)<sup>27,28</sup> and for tetrachloroethylene (1.327 Å).<sup>15</sup> All of these distances are slightly shorter than the values (1.337, 1.339, and 1.332 Å) that have been reported for ethylene itself,<sup>29-31</sup> presumably because of the effect of more electronegative substituents (the bond length in C<sub>2</sub>F<sub>2</sub> is even shorter, 1.313 Å<sup>32</sup>). Differences among our three unique C-C single bonds, 1.466 ± 0.007, 1.486 ± 0.007, and 1.494 ± 0.005 Å, are probably not significant. Their average value, 1.485 Å, when weighted according to the calculated standard deviations, is slightly longer than the average value of 1.466 Å for C-C single bonds between sp<sup>2</sup> hybridized carbons in a set of 37 compounds.<sup>26</sup> This feature is consistent with elongation of single bonds in sp<sup>3</sup> hybridized cyclobutanes, where bond distances are commonly 0.02-0.03 Å longer<sup>20</sup> than for sp<sup>3</sup>-sp<sup>3</sup> single bonds in noncyclic alkanes. These results thus indicate that no unusual shortening of the single bonds or lengthening of the double bonds occurs in perchloro[4]radialene.

A simple Hückel calculation on planar tetramethylenecyclobutane predicts a delocalization energy of 1.66β and bond orders of 1.35 for the endocyclic

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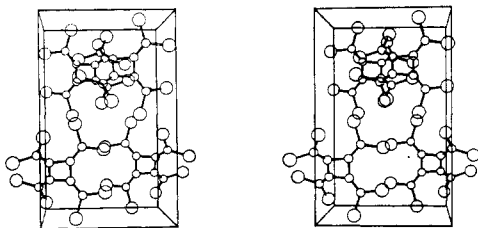


Figure 3. Three-dimensional view of molecular packing in perchloro[4]radialene as viewed down the  $z$  axis. The  $y$  axis is horizontal and the  $x$  axis is vertical. The cell outline is drawn from an origin at  $1/4, 0, 0$ .

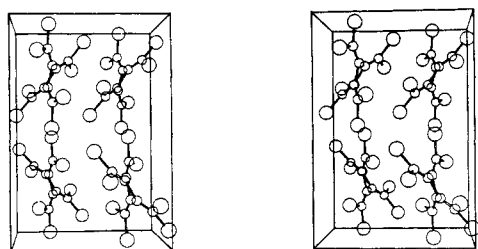


Figure 4. Three-dimensional view of molecular packing in perchloro[4]radialene as viewed down the  $y$  axis. The  $z$  axis is horizontal and the  $x$  axis is vertical. The cell origin is at  $1/4, 0, 0$ .

and 1.85 for the exocyclic C–C bonds.<sup>33</sup> These figures represent an appreciable amount of conjugation, and although perchloro[4]radialene is significantly nonplanar, the complete absence of metric evidence for conjugation in this molecule is noteworthy.

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The molecular packing can be seen in three-dimensional views down the  $y$  and  $z$  axes in Figures 3 and 4, respectively. The molecules lie on sheets perpendicular to the  $z$  axis and exhibit no unusually short intermolecular contacts (Table VI); the shortest Cl...Cl distances of 3.615 and 3.626 Å are just above the sum of two chlorine van der Waals radii (3.60 Å).<sup>16</sup> There are no C...Cl intermolecular contacts below 3.601 Å or C...C distances below 3.534 Å.

Table VI. Closest Intermolecular Approaches,<sup>a</sup> Å

I	$x$	$y$	$z$
II	$1/2 - x$	$1/2 + y$	$z$
III	$1/2 - x$	$1/2 - y$	$1/2 + z$
IV	$x$	$-y$	$1/2 + z$
V	$1 - x$	$-y$	$1 - z$
VI	$x$	$y - 1$	$z$
VII	$1 - x$	$y - 1$	$1/2 - z$
VIII	$1 - x$	$y$	$1/2 - z$
Cl(1) (I)...	Cl(2) (II)		3.670 (2)
Cl(2) (I)...	Cl(3) (II)		3.695 (2)
Cl(2) (I)...	Cl(4) (II)		3.626 (2)
Cl(3) (I)...	Cl(1) (III)		3.895 (2)
Cl(3) (I)...	Cl(2) (III)		3.615 (2)
Cl(3) (I)...	Cl(2) (IV)		3.790 (2)
Cl(3) (I)...	Cl(4) (V)		3.809 (2)
Cl(4) (I)...	Cl(1) (VI)		3.734 (2)
Cl(4) (I)...	Cl(1) (VII)		3.669 (2)
Cl(4) (I)...	Cl(1) (IV)		3.737 (2)

<sup>a</sup> Estimated standard deviations calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

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