Tetrahedron. Vol. 25, pp. 2693 to 2699. Pergamon Press 1969. Printed in Great Britain

CONFORMATION OF NON-AROMATIC RING COMPOUNDS—LI[1]

THE CRYSTAL STRUCTURE OF *TRANS*-1,4-DICHLORO-CYCLOOCTANE AT −180°

J. v. Egmond and C. Romers
Chemistry Department, University of Leiden, The Netherlands

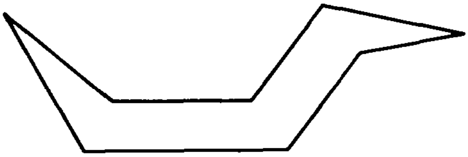
(*Received in the UK* 21 *December* 1968; *Accepted for publication* 27 *January* 1969)

Crystals of *trans*-1,4-dichloro-cyclooctane are monoclinic with space group $P2_1/c$ and Z = 4. The unit cell dimensions at −180° are a = 14·10, b = 5·53, c = 12.18Å and β = 113·1°.

The structure was solved by calculation of a minimum function M_4 and refined by the least-squares method. The ring has the boat-chair conformation, its symmetry being approximately C_s. The one chlorine atom at the top of the chair moiety points to the axial direction, the other one to a (pseudo-) equatorial direction. The mean ring valency angle is 116·4°. Due to steric interaction the carbon chlorine bonds are large, their mean value being 1·83Å.

INTRODUCTION

The conformation of cyclooctane has been studied by several workers. Hendrickson,[2–4] Wiberg[5] and Bixon[6] have carried out semi-empirical enthalpy calculations of a number of symmetrical cyclooctane conformations and concluded that the boat-chair form with symmetry C_s has the lowest energy content. Dunitz and his co-workers[7, 8] have determined the crystal structures of *trans*- and *cis*-1,2-cyclooctane dicarboxylic acids and found that these two molecules do have the boat-chair form. Recently, Groth[9] investigated the crystal structure of 3,6-spiro-dicyclooctylidene-1,2,4,5-tetraoxacyclohexane and concluded that the cyclooctane rings of this compound also have the boat-chair conformation.



Henniger *et al.*[10] investigated the transannular reaction mechanism of several cyclooctane derivatives and analysed their NMR, Raman and IR spectra. Henniger[11] synthesised a number of dichloro-cyclooctane derivatives and found that the title compound is the *trans*-1,4-isomer. In view of the difficult interpretation of the spectra mentioned it was deemed necessary to determine the crystal structure of trans-1,4-dichloro-cyclooctane (hereafter DCC).

EXPERIMENTAL

Crystals of DCC (m.p. 10°) were prepared from a solution (40% wt) in *n*-hexane at −20°. The crystals are monoclinic needles elongated along the unique axis [010]. The unit cell dimensions were determined from zero layer Weissenberg photographs about [010] and [001] taken with CuK$_\alpha$ radiation (λ = 1·5418Å) and superposed with aluminum powder lines (a = 4·0489 Å) for calibration purposes. The spacings d(100), d(010), d(001) and the angle β were refined with a least-squares procedure resulting in the unit cell constants listed in Table 1. From the observed density (flotation method) and the cell volume it is concluded that the cell contains four molecules.

TABLE 1. CRYSTALLOGRAPHIC DATA OF DCC

trans-1,4-Dichloro-cyclooctane, $C_8H_{14}Cl_2$,
Melting point 10°;
Monoclinic prismatic, $P2_1/c$;
a = 14·102 ± 0·005, b = 5·528 ± 0·004, c = 12·179 ± 0·007 Å,
β = 113·1 ± 0·1 at −180°, stated errors are three times standard deviations;
d^{20}_{exp} = 1·34 g cm^{-3}, d_x^{-180} = 1·38 g. cm^{-3}, $Z = 4$;
$F(000) = 384$; V = 873 Å^3; μ(CuK$_\alpha$) = 59·3 cm^{-1}.

A series of equi-inclination Weissenberg photographs (Ni-filtered Cu-radiation, multiple film technique) was taken at −180° about [010] with levels $k = 0\ldots4$ and about [001] with levels $1 = 0\ldots9$, the latter being of rather a poor quality. The intensities were estimated visually and corrected for Lorentz, polarization, spot shape and absorption (cylindrical approximation) effects. The data of both zones were correlated and put on a common relative scale. During the final least-squares cycles (next section) the c-axis data were discarded and separate scale factors were refined for the levels $k = 0\ldots4$. A total of 1559 reflexions, including 278 non-observed ones were used during the refinement.

Structure determination and refinement

The systematic absent reflexions (h01 for 1 is odd and 0k0 for k is odd) indicate the space group $P2_1/c$ in accordance with the interpretation of the Patterson function $P(uvw)$. The positions of the two independent chlorine atoms were derived directly from this vector map. A minimum function[12] M_4 was calculated with a program developed by Mrs. E. W. M. Rutten and outlined elsewhere.[13] Applying the required shifts to the equivalent positions of Cl (10) (cf. Fig. 1 for the numbering of atoms) the complete structure (the hydrogen atoms excepted) was revealed. Structure factor calculations based upon the obtained atomic positions resulted in a reliability index R = 22%.

The refinement was carried out in the usual way with the least-squares method in block-diagonal approximation to the matrix of normal equations. During the final stage of anisotropic refinement (3 cycles) of all heavy atoms the hydrogen atoms were included at calculated positions but not refined. The ultimate R index* is 11·5% if non-observed reflexions are included and 8·8% if those reflexions are omitted.

The average positional standard deviation $\sigma(r)$ (Table 2) is 0·006 Å for the carbon atoms and 0·0015 Å for the chlorine atoms. Multiplying these numerical values with a factor two according to Hamilton's stringent procedure[14] we arrived at the averaged standard errors of 0·017 Å for C—C bonds and 0·013 Å for C—Cl bonds. Assuming chemical equivalence of the eight C—C bonds we estimated a more optimistic value of 0·008 Å for the standard deviation of the C—C bonds. The estimated standard errors in valency and torsional angles are 1° and 1·5° respectively. The influence of errors of the lattice constants is in our case negligible. The positional and vibrational parameters are listed in Tables 2 and 3.

DISCUSSION OF THE STRUCTURE

A perspective drawing of DCC is shown in Fig. 1. It can be seen that the conformation is a boat-chair. The torsional angles which determine the shape of the molecule are indicated by numbers along the bonds of the carbon–carbon framework. (cf. also Table 4). A careful comparison with the theoretical dihedral angles indicates that the agreement is best with Hendrickson's values. The observed deviations between the

---

* A list of calculated and observed structure factors is available upon request.

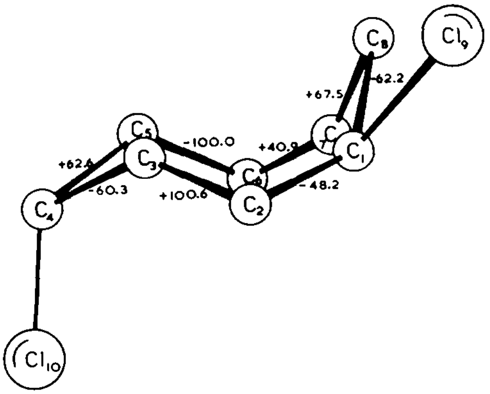


FIG. 1. A perspective drawing of the molecule *trans*-1,4-dichloro-cyclooctane, showing torsional angles.

three sets of experimental values (Table 4) are significant and are due to different chemical environment, different functional side groups and, perhaps, packing effects. Nonetheless, it is conspicuous that experimental values show better agreement than the theoretical values.

TABLE 2. POSITIONAL PARAMETERS (FRACTIONS OF CELL EDGES) AND THEIR CALCULATED STANDARD DEVIATIONS (10^{-4} Å UNITS)

Atom	X	$\sigma(X)$	$\sigma(Y)$	Y	Z	$\sigma(Z)$
C (1)	0·3851	52	0·6127	68	0·8243	56
C (2)	0·3053	53	0·5196	70	0·7052	50
C (3)	0·2005	53	0·6537	67	0·6617	50
C (4)	0·1129	52	0·5244	70	0·6838	57
C (5)	0·1269	55	0·4657	71	0·8117	56
C (6)	0·2150	61	0·2913	74	0·8806	57
C (7)	0·3140	59	0·4124	73	0·9678	53
C (8)	0·3496	54	0·6456	70	0·9264	51
Cl (9)	0·4330	13	0·9062	18	0·8001	13
Cl (10)	0·0803	13	0·2436	17	0·5962	13

TABLE 3. VIBRATIONAL PARAMETERS U_{ij}(IN 10^{-4}. Å^2 UNITS) IN THE TEMPERATURE FACTOR

$$\exp\left[-2\pi^2 \sum_{i}^{3} \sum_{j}^{3} h_i h_j a_i^* a_j^* U_{ij}\right]$$

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1)	134	166	222	53	11	134
C(2)	180	225	138	64	48	127
C(3)	172	134	135	24	45	54
C(4)	140	161	253	40	−10	128
C(5)	178	193	205	−8	9	123
C(6)	284	188	193	66	96	202
C(7)	283	206	130	75	99	124
C(8)	187	228	105	−9	−9	40
Cl(9)	158	179	219	−58	46	96
Cl(10)	168	184	188	−32	−32	34

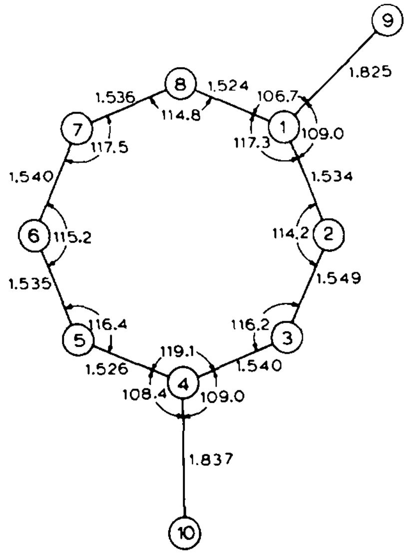


FIG. 2. A schematic drawing of *trans*-1,4-dichloro-cyclooctane showing bond distances and valency angles.

The bond lengths and valency angles are shown in a schematic drawing in Fig. 2 and listed in Table 5. They are not corrected for thermal motion. The mean value of the ring valency angles (116·4°) is unusually high and seems to be characteristic of cyclooctane derivatives. The carbon–carbon bond distances are quite regular. The largest deviation from the mean value (1·535 Å) is 0·014 Å.

The chlorine atoms Cl(9) and Cl(10) are connected to C(1) and C(4) in (pseudo-) equatorial and axial directions, respectively. Interestingly, Hendrickson[4] has predicted that this pair of positions and directions belongs to the four favourable combinations for disubstituted methyl derivatives of cyclooctane in boat-chair conformations.

The lengths of the bonds C(1)–Cl(9) and C(4)–Cl(10) are 1·825 and 1·837 Å, respectively. In view of the generally accepted interatomic distance of 1·79 Å for the

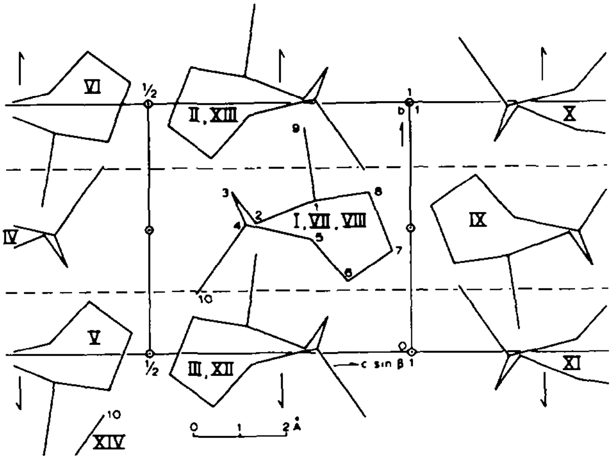


FIG. 3. Projection of the structure along [100]. The Roman numerals are explained in the text.

paraffinic C—Cl bond[15,16] the observed lengths seem to exceed the "normal" value on a 99·9% significance level. Other exceptions[17,18] to this rule are found in heterocyclic compounds with C—O—C—Cl fragments in gauche form and having C—Cl distances in the range of 1·81–1·85 Å. Electrostatic, dipole or electron lone pair interactions are invoked[19] to explain the irregularities. It is interesting to note that this effect is absent in the equatorial C—Cl bond (1·78 Å) of *cis*-2,3-dichloro-1,4-dioxane[20] and in the two C—Cl bonds of monochloroacetic acid anhydride[21] (1·76 and 1·75 Å).*

One might suppose that the lengthening effect is non-existent after all and that more careful measurements of paraffinic C—Cl distances are necessary. On the other hand, it is also possible to defend the view that the effects are real, but require a

Table 4. Calculated and observed dihedral angles of cycloochtane in boat-chair conformation

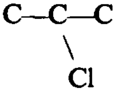
Bond	Hendrickson[3]	Wiberg[5]	Bixon[6]	Dunitz[7]	Groth[9]	This work	A v. Val.
1—2—3—4	+105·2	+95·2	+106	+100·9	+98·4	+100·6	101·1
2—3—4—5	−68·6	−49·4	−72	−70·3	−66·1	−60·3	64·4
3—4—5—6	+68·6	+49·4	+70	+70·8	+64·0	+62·6	64·2
4—5—6—7	−105·2	−95·2	−105	−105·9	−101·3	−100·0	102·1
5—6—7—8	+44·4	+44·8	+46	+46·8	+49·0	+40·9	45·2
6—7—8—1	+68·6	+73·3	+64	+62·0	+61·1	+67·5	66·1
7—8—1—2	−68·6	−73·3	−64	−63·0	−69·7	−62·2	67·0
8—1—2—3	−44·4	−44·8	−44	−43·4	−36·5	−48·2	43·6

Table 5. Observed bond lengths and calculated and observed valency angles of cyclooctane in boat-chair conformation

Bond	Hendrickson[3]	Wiberg[5]	Bixon[6]	Dunitz[7]	Groth[9]	This work
1—2	—	—	—	1·547	1·517	1·534
2—3	—	—	—	1·535	1·545	1·549
3—4	—	—	—	1·551	1·539	1·540
4—5	—	—	—	1·531	1·528	1·526
5—6	—	—	—	1·554	1·535	1·535
6—7	—	—	—	1·527	1·521	1·540
7—8	—	—	—	1·498	1·536	1·536
8—1	—	—	—	1·502	1·529	1·524
Angle						
1—2—3	113·5	109·6	114	115·6	116·7	114·2
2—3—4	114·3	117·4	114	115·4	115·3	116·2
3—4—5	115·2	125·3	115	115·1	118·8	119·1
4—5—6	114·3	117·4	113	112·7	115·8	116·4
5—6—7	113·5	109·6	115	115·0	114·8	115·2
6—7—8	114·3	114·0	116	117·3	117·3	117·5
7—8—1	115·2	114·4	116	118·2	115·2	114·8
8—1—2	114·3	114·0	116	118·3	118·1	117·3
mean v.	114·3	115·2	115	116·0	116·5	116·4

---

* In the examples of the latter compound nor of the title compound corrections for thermal motion have been applied. These corrections are increments of the order of 0·02 Å.

different explanation in this particular case. As stated before the ring valency angles are unusually large and, moreover, the largest values are observed at C(1) (117·3°) and at C(4) (119·1°). The conjunction of the largest C—Cl bond (1·837 Å) with the largest valency angle (119·1°) is conspicuous. It is remarkable that this correlation between  $\underset{\text{Cl}}{\text{C—C—C}}$ valency angle and C—Cl distance also exists in *trans*-2α,3β- and *trans*-2β,3α-dichlorocholestane[22,23] (108°, 1·76 Å; 112°, 1·82 Å; 113°, 1·81 Å; 115°, 1·83 Å) and in α-chloro-δ-valero-lactam[13] (114°, 1·82 Å). A proper explanation is difficult but we suspect that steric repulsions may play a major role.

The angle between the vectors C(1)–Cl(9) and C(4)–Cl(10) is 138·3°. Assuming partial moments of 2·15 D one calculates a dipole moment of 1·53 D. Henniger[11] measured the value of 1·83 D for this compound in a soln of CCl_4 and benzene. The higher value is in agreement with the assumption that other conformations might play a role in the solution. However, the difference (0·3 D) is too small to arrive at a conclusion at this point.

Packing

A part of the structure projected along [100] is shown in Fig. 3. Taking as a limit 4·2 Å the molecule I at *x*, *y*, *z* is surrounded by 13 neighbours at

$-x,$	$\frac{1}{2} + y,$	$1\frac{1}{2} - z$	(II)
$-x,$	$-\frac{1}{2} + y,$	$1\frac{1}{2} - z$	(III)
$-x,$	$1 - y,$	$1 - z$	(IV)
$x,$	$\frac{1}{2} - y,$	$-\frac{1}{2} + z$	(V)
$x,$	$1\frac{1}{2} - y,$	$-\frac{1}{2} + z$	(VI)
$x,$	$1 + y,$	z	(VII)
$x,$	$-1 + y,$	z	(VIII)
$1 - x,$	$1 - y,$	$2 - z$	(IX)
$x,$	$1\frac{1}{2} - y,$	$\frac{1}{2} + z$	(X)
$x,$	$\frac{1}{2} - y,$	$\frac{1}{2} + z$	(XI)
$1 - x,$	$-\frac{1}{2} + y,$	$1\frac{1}{2} - z$	(XII)
$1 - x,$	$\frac{1}{2} + y,$	$1\frac{1}{2} - z$	(XIII)
$-x,$	$-y,$	$1 - z$	(XIV)

The lattice repetitions, glide planes and screw axes always induce an even number of intermolecular interactions and result in this case in 10 contacts. The action of a centre of symmetry gives, however, only one intermolecular contact. In the case of DCC there are three inversion operations giving three contacts with molecules IV, IX and XIV.

REFERENCES

[1] Part L, H. R. Buys and H. J. Geise, *Tetrahedron Letters* 5619 (1968).

[2] J. B. Hendrickson, *J. Am. Chem. Soc.* **83**, 4537 (1961).

[3] Ibid. **86**, 4854 (1964).

[4] Ibid. **89**, 7036 (1967).

[5] K. B. Wiberg, *Ibid.* **87**, 1070 (1965).

[6] M. Bixon and S. Lipson, *Tetrahedron* **23**, 769 (1967).

[7] M. Dobler, J. D. Dunitz and A. Mugnoli, *Helv. Chim. Acta* **49**, 2492 (1966).

[8] J. D. Dunitz and A. Mugnoli, *Chem. Commun.* p. 166 (1966).

[9] P. Groth, *Acta Chim. Scand.* **21**, 2695 (1967).

[10] P. W. Henniger, E. Wapenaar and E. Havinga, *Rec. Trav. Chim.* **81**, 1053 (1962).

[11] P. W. Henniger, Thesis, University of Leiden (1967).

[12] M. J. Buerger, *Vector Space and its Application in Crystal Structure Investigations*, p. 230. John Wiley, New York (1959).

[13] C. Romers, E. W. M. Rutten, C. A. A. van Driel and W. W. Sanders, *Acta Cryst.* **22**, 893 (1967).

[14] W. C. Hamilton, *Trans Am. Cryst. Ass.* **1**, 17 (1965).

[15] *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 11 Chemical Society, London (1958).

[16] Ibid. Special Publication No. 18 (1965).

[17] N. de Wolf, C. Romers and C. Altona, *Acta Cryst.* **22**, 715 (1967).

[18] E. W. M. Rutten, N. Nibbering, C. H. MacGillavry and C. Romers, *Rec. Trav. Chim.* **87**, 888 (1968).

[19] C. Romers, C. Altona, H. R. Buys and E. Havinga, *Conformation of Heterocyclic Ring Compounds.* Topics in Stereochemistry, Volume 4 (Edited by E. L. Eliel and N. L. Allinger). Wiley and Interscience, New York.

[20] C. Altona, C. Knobler and C. Romers, *Acta Cryst.* **16**, 1217 (1963).

[21] A. J. de Kok and C. Romers, to be published.

[22] H. J. Geise and C. Romers, *Acta Cryst.* **20**, 257 (1966).

[23] H. J. Geise, Thesis, University of Leiden (1964).