Acta Cryst. (1981). B**37**, 1249–1252

Stereochemistry of Rings. II.* Cyclohexanone Derivatives. 1. The Structure of 2,6-Dichlorocyclohexanone in Correlation with the Geometry of Other Analogous Compounds Analyzed by X-ray Diffractometry Methods

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(*Received* 11 *February* 1980; *accepted* 18 *December* 1980)

Abstract

The title compound, $C_6H_8Cl_2O$ ($M_r = 167{\cdot}0$), crystallizes in the monoclinic system (space group $C2/c$) with cell parameters: $a = 12{\cdot}997\ (2)$, $b = 12{\cdot}169\ (2)$, $c = 9{\cdot}525\ (2)$ Å, $\beta = 102{\cdot}0\ (2)°$; $Z = 8$, $V = 1473{\cdot}6$ Å^3, $D_c = 1{\cdot}51$ Mg m^{-3}, μ(Cu $K\alpha$) = $0{\cdot}331$ mm^{-1}, λ(Cu $K\alpha$) = $1{\cdot}5418$ Å. The structure was solved by direct methods and refined by least squares, employing 1292 intensity data, to $R = 0{\cdot}067$. The conformational parameters of the compound under study are compared with those of all other cyclohexanone derivatives studied by X-ray diffractometry methods.

Introduction

The number of X-ray structure determinations of cyclohexanone derivatives is now large enough to stimulate us to seek correlations among their geometrical data, particularly concerning the stereochemistry of the ring and the conformational preference of halogen substituents.

Experimental

Preliminary unit-cell parameters were determined by rotation and Weissenberg photographs and refined by a least-squares fit on the $(\theta,\chi,\varphi)_{hkl}$ values of 12 independent reflections carefully measured on a diffractometer. The intensity data were collected using a Siemens AED single-crystal diffractometer with a crystal of dimensions $0{\cdot}65 \times 0{\cdot}36 \times 0{\cdot}21$ mm. To avoid decomposition by air the crystal was sealed in a Lindemann capillary under a nitrogen atmosphere. During the data collection a standard reflection was measured after every 20 reflections to check misalignment or decomposition of the specimen: no systematic variations were noted. With Cu $K\alpha$ radiation 1391 intensities were collected, but only 1292 of them with $I > 2\sigma(I)$ were considered observed and used in the structure analysis. No absorption correction was applied.

The approximate locations of the Cl and C atoms of the molecule were found by direct methods using *SHELX* (Sheldrick, 1975). The position of the O atom was determined by a subsequent difference Fourier map. Full-matrix least-squares refinement, first with isotropic and then anisotropic thermal parameters, resulted in $R = 0{\cdot}10$. The H atoms were located in a ΔF map computed at this stage and were refined isotropically. The weighting scheme used during the refinement is given by $w = 1/(\sigma^2F + 0{\cdot}005F^2)$. The final conventional R factor was $0{\cdot}067$.

The atomic coordinates with their standard deviations are given in Table 1.†

Table 1. *Atomic coordinates* (×10^4 *for* Cl, O *and* C, ×10^3 *for* H)

	x	y	z	B_{eq}* (Å^2)
Cl(1)	1138 (1)	5082 (1)	9235 (1)	4·87
Cl(2)	5116 (1)	3462 (1)	10145 (1)	5·42
O	3202 (2)	4370 (2)	10792 (2)	4·68
C(1)	3107 (2)	4219 (2)	9523 (2)	3·32
C(2)	3945 (2)	3715 (2)	8838 (2)	3·57
C(3)	3532 (2)	2652 (2)	8074 (3)	3·82
C(4)	2534 (3)	2872 (3)	6973 (3)	4·19
C(5)	1689 (2)	3398 (2)	7653 (3)	3·76
C(6)	2104 (2)	4461 (2)	8422 (3)	3·36
H(1)	407 (3)	422 (3)	797 (3)	
H(2)	348 (4)	209 (4)	889 (5)	
H(3)	402 (2)	238 (2)	759 (3)	
H(4)	228 (3)	216 (3)	659 (3)	
H(5)	257 (4)	339 (3)	613 (4)	
H(6)	109 (3)	363 (3)	698 (4)	
H(7)	155 (3)	295 (3)	839 (3)	
H(8)	228 (2)	498 (2)	770 (3)	

* Defined according to Hamilton (1959).

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* Part I: Bocelli & Grenier-Loustalot (1980).

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35810 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/061249-04$01.00

All the calculations have been carried out on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), with the financial support of the University of Parma.

All the bibliographic searches were carried out using the Cambridge Crystallographic Data Files through the Servizio Italiano di Diffusione dei Dati Cristallografici, Parma, Italy.

Molecular geometry

Fig. 1 shows a drawing of the molecule. Bond distances and angles are listed in Table 2; Table 3 reports the torsion angles.

The cyclohexanone ring is in the chair conformation. All the C–C distances in the ring are greater than 1·510 Å and the average value [1·522 (3) Å], far from the normal value for sp^3–sp^2 hybridization (1·505 Å; Lide, 1962), is similar to the value observed by Geise, Buys & Mijlhoff (1971) in cyclohexane (1·528 Å).

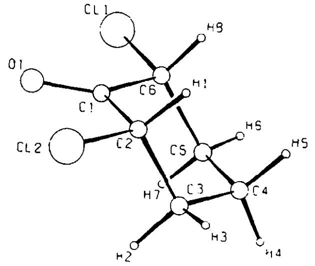


Fig. 1. Projection of the molecule.

Table 2. *Bond distances* (Å) *and angles* (°)

Cl(1)–C(6)	1·775 (3)	C(2)–H(1)	1·07 (3)
Cl(2)–C(2)	1·781 (3)	C(3)–H(2)	1·05 (5)
O–C(1)	1·203 (2)	C(3)–H(3)	0·92 (3)
C(1)–C(2)	1·511 (3)	C(4)–H(4)	0·97 (4)
C(1)–C(6)	1·522 (3)	C(4)–H(5)	1·03 (4)
C(2)–C(3)	1·526 (3)	C(5)–H(6)	0·94 (3)
C(3)–C(4)	1·513 (4)	C(5)–H(7)	0·94 (3)
C(4)–C(5)	1·527 (4)	C(6)–H(8)	1·00 (3)
C(5)–C(6)	1·529 (3)		
O–C(1)–C(2)	124·3 (4)	C(2)–C(3)–C(4)	110·3 (4)
O–C(1)–C(6)	123·8 (4)	C(3)–C(4)–C(5)	111·6 (4)
C(2)–C(1)–C(6)	111·8 (4)	C(4)–C(5)–C(6)	110·2 (4)
Cl(2)–C(2)–C(1)	110·9 (3)	Cl(1)–C(6)–C(1)	111·3 (3)
Cl(2)–C(2)–C(3)	*110·6 (3)*	*Cl(1)–C(6)–C(5)*	*111·0 (3)*
C(1)–C(2)–C(3)	109·7 (3)	C(1)–C(6)–C(5)	109·4 (4)
H(1)–C(2)–Cl(2)	113 (3)	H(5)–C(4)–C(3)	119 (4)
H(1)–C(2)–C(1)	110 (3)	H(5)–C(4)–C(5)	103 (4)
H(1)–C(2)–C(3)	102 (3)	H(6)–C(5)–C(4)	114 (4)
H(2)–C(3)–C(2)	106 (4)	H(6)–C(5)–C(6)	103 (3)
H(2)–C(3)–C(4)	117 (5)	H(6)–C(5)–H(7)	115 (6)
H(2)–C(3)–H(3)	107 (7)	H(7)–C(5)–C(4)	110 (4)
H(3)–C(3)–C(2)	109 (3)	H(7)–C(5)–C(6)	104 (3)
H(3)–C(3)–C(4)	107 (3)	H(8)–C(6)–Cl(1)	108 (3)
H(4)–C(4)–C(3)	106 (3)	H(8)–C(6)–C(1)	108 (3)
H(4)–C(4)–C(5)	108 (4)	H(8)–C(6)–C(5)	108 (3)
H(4)–C(4)–H(5)	109 (6)		

Table 3. *Torsion angles* (°)

O–C(1)–C(2)–Cl(2)	−3·9 (4)	C(6)–C(1)–C(2)–C(3)	−58·6 (3)
O–C(1)–C(6)–Cl(1)	4·2 (4)	C(1)–C(2)–C(3)–C(4)	57·1 (3)
C(2)–C(1)–C(6)–Cl(1)	−178·6 (2)	Cl(2)–C(2)–C(3)–C(4)	179·6 (2)
O–C(1)–C(6)–C(5)	−118·8 (3)	C(2)–C(3)–C(4)–C(5)	−57·2 (4)
O–C(1)–C(2)–C(3)	118·5 (3)	C(3)–C(4)–C(5)–C(6)	57·0 (4)
C(6)–C(1)–C(2)–Cl(2)	179·0 (2)	C(4)–C(5)–C(6)–C(1)	−56·2 (3)
C(2)–C(1)–C(6)–C(5)	58·3 (3)	C(4)–C(5)–C(6)–Cl(1)	−179·5 (2)

The exocyclic bond angles formed by the Cl atoms are always near to 111°, while the mean value of the endocyclic angles [110·4 (4)°] is very close to that reported by Geise *et al.* (1971) for cyclohexane (111°).

From the comparison of the present data with those observed for 2,4,6-trichlorocyclohexanone (Lectard,

Table 4. *Ring-puckering values* (Å *and* deg)

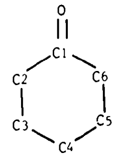
All calculations were performed using the sequence of atoms C(1), C(2), C(3), C(4), C(5), C(6).

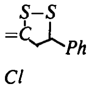
Reference	Q	q_2	$\|q_3\|$	θ	φ
1	0·62	0·16	0·60	14·7	174·1
2	0·61	0·04	0·61	3·6	358·8
3	0·29	0·26	0·13	64·3	333·0
4	0·52	0·04	0·52	4·4	242·3
5	0·54	0·15	0·52	16·4	338·6
6	0·59	0·02	0·59	1·6	180·0
7	0·51	0·39	0·33	50·3	336·9
8	0·52	0·02	0·52	2·3	91·5
9	0·54	0·03	0·54	3·1	268·9
10	0·56	0·05	0·56	5·6	154·9
11	0·56	0·14	0·54	14·3	192·6
	0·54	0·08	0·53	8·5	27·8
12	0·61	0·13	0·60	12·2	20·6
13	0·52	0·10	0·51	11·2	243·7
14	0·55	0·08	0·55	8·3	353·7
	0·55	0·09	0·55	8·9	160·6
15	0·64	0·64	0·00	90·0	97·0
16	0·51	0·11	0·50	12·9	0·0
17	0·58	0·01	0·58	1·3	294·9
18	0·54	0·07	0·53	7·1	339·9
19	0·73	0·73	0·01	90·5	257·6
20	0·51	0·07	0·51	8·2	347·3
21	0·63	0·01	0·63	0·8	219·1
22	0·59	0·01	0·59	0·9	7·9

References: (1), (2) Goaman & Grant (1964); (3) Stam & Evers (1965); (4) Calligaris, Giordano & Randaccio (1966); (5) Lambert, Carhart & Corfield (1969); (6) Lectard, Metras, Petrissans & Gaultier (1971); (7) Pinel *et al.* (1971); (8) Towns & Shapiro (1972); (9) Lectard *et al.* (1972); (10) De Graaff, Giesen, Rutten & Romers (1972); (11) Lectard, Petrissans & Hauw (1973); (12) Bruckner & Pitacco (1974); (13) Lichanot, Petrissans, Hauw & Gaultier (1974); (14) Calligaris, Manzini, Pitacco & Valentin (1975); (15) Lectard *et al.* (1975); (16) Lichanot, Lectard, Metras. Gaultier & Hauw (1977); (17) Grenier-Loustalot *et al.* (1977*a*); (18) Grenier-Loustalot, Andreetti, Bocelli & Sgarabotto (1977*b*); (19) Viani *et al.* (1978); (20) Grenier-Loustalot, Andreetti, Belletti, Bocelli & Sgarabotto (1978); (21) Grenier-Loustalot, Andreetti, Bocelli & Sgarabotto (1978); (22) present work.

Table 5. *Substituents, if non-hydrogen, at ring carbon atoms with the angle (°) between the line perpendicular to the mean ring plane and the bond line*

Equatorial substituents are indicated in italic type, axial ones in bold type.



References*	C(1)	C(2)				C(3)				C(4)				C(5)				C(6)			
1	53·3	*Br*	77·4			*Me*	62·8	**Me**	12·7					*Me*	56·0	**Me**	12·0				
2	53·1	*Br*	83·5			*Me*	60·9	**Me**	12·2					*Me*	57·2	**Me**	15·0	*Br*	83·0		
3	65·6	NO_2	64·0	**Me**	33·6			**Me**	33·5	NO_2	68·9	**Me**	32·7			**Me**	30·8	*Br*	60·8	**Br**	15·0
4	46·5	$CH{<}^{PhBr}_{CH_2NO_2}$	72·6																		
5	68·2									*Ph*	67·7	**Ph**	3·4								
6	66·9	*Cl*	72·1							*Bu*^{t}	76·1							*Cl*	72·1		
7	90·2		83·0																		
8	58·6					*Me*	62·2	**Me**	9·8					*Me*	58·8	**Ph**	13·1				
9	59·5	*Cl*	67·4									**Cl**	7·1					*Cl*	72·9		
10	61·1	*Cl*	72·0							*Bu*^{t}	77·8										
11	67·9 63·0	*Cl*	64·1 65·1	**Cl**	8·0 8·2					*Bu*^{t}	78·1 75·3										
12	52·8	$CH{<}^{PhBr}_{CH_2NO_2}$	69·7													**Me**	12·8				
13	64·3	*Cl*	61·1	**Cl**	12·9					*Me*	59·8	**Me**	12·0								
14	63·8 60·8	$CH{<}^{Ph}_{CH_2NO_2}$	73·5 30·0							*Bu*^{t}	78·7 75·3										
15	64·9									*Bu*^{t}	78·6										
16	72·7									*Me*	68·7	**Me**	3·9								
17	50·7	*Cl*	70·2			*Cl*	70·7											*Cl*	70·7		
18	60·2	*Cl*	65·5	**Cl**	6·8					*Cl*	70·4										
19	99·9					*Bu*^{t}	73·1					**CN**	30·3								
20	60·5	*Cl*	60·6	**Cl**	12·8	*Cl*	73·6			*Me*	60·0	**Me**	11·4								
21	48·2	*Cl*	69·3			*Cl*	71·4					**Me**	2·7					*Cl*	70·5		
22	52·2	*Cl*	71·3															*Cl*	71·9		

* References as in Table 4.

Metras & Gaultier, 1972) and for 2,3,6-trichlorocyclohexanone (Grenier-Loustalot, Andreetti, Bocelli & Sgarabotto, 1977*a*) it can be seen that the internal angles of the ring are affected not so much by the presence of α,α substituents but by a substituent which disrupts the pseudo *m* symmetry of the first two molecules.

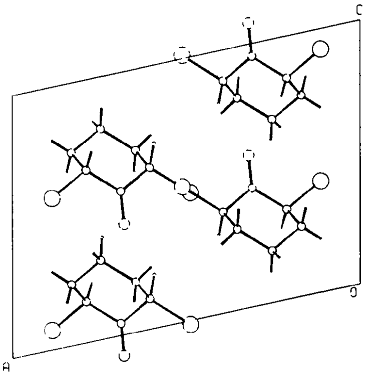


Fig. 2. Packing of the compound projected on to (010).

The packing, illustrated in Fig. 2, is consistent with van der Waals interactions; a non-bonding contact shorter than 3·6 Å is C(6)—O^{i} = 3·44 (4) Å (i: x, $1 - y$, $-\frac{1}{2} + z$).

Discussion

Upon examination of the 22 crystal structures of cyclohexanone derivatives retrieved from the Cambridge Data Files, whose selected structural parameters are given in Tables 4 and 5, we observe, with only four exceptions, a common chair conformation of the ring. The exceptions are 4-*tert*-butylcyclohexanone (Lectard, Lichanot, Metras, Gaultier & Hauw, 1975) and 2-(5-phenyl-1,2-dithiol-3-ylidene)cyclohexanone (Pinel, Mollier, Llaguno & Paul, 1971), which show a twist-boat and a half-chair conformation respectively, *trans*-2-*tert*-butyl-4-oxocyclohexanecarbonitrile (Viani, Lapasset, Aycard, Lafrance & Bodot, 1978), which presents a conformation midway between boat and twist-boat, and, finally, 6,6-dibromo-2,3;4,5-dimethano-2,4-dinitrocyclohexanone (Stam & Evers,

1965) which has a conformation intermediate between half-chair and twist-boat.

By use of the ring-puckering coordinates (Cremer & Pople, 1975), which for a six-membered ring are the spherical polar set (Q,θ,φ), the polar positions ($\theta = 0$ or 180°, $Q \neq 0$ Å) correspond to a perfect chair conformation. The θ values of the 18 rings (see Table 4) with chair conformations range between 0·75 and 16·4°, but the values are greater than 7·1° when a γ substituent is present in the molecule, with only two exceptions. These two cases (Goaman & Grant, 1964; Bruckner & Pitacco, 1974) are explained by the presence of a bulky group α to the carbonyl group with a consequent distortion of the normal conformation which particularly affects the internal angles of the ring.

The orientation of the substituents with respect to the mean cyclohexanone ring plane is indicated by the angle between the line perpendicular to the mean ring plane and the bond between the substituent and the respective C atom. This angle quantitatively gives a measure of the axiality or equatoriality of the substituent. From the data of Table 5 it can be seen that in the cases with only one non-hydrogen substituent at a ring C atom, an equatorial halogen gives a value of this angle in the range 69·3–83·5°, while a *tert*-butyl group causes it to be in the range 75·3–78·5°. Moreover, the variations in the value seem to depend approximately on the nature of the vicinal substituents and to be independent of the position with respect to the carboxylic function.

The number of available data is not sufficient, at the moment, to deduce the precise influence of the γ-*tert*-butyl group on the orientation of the α substituents as observed by Allinger, Allinger, Freiberg, Czaja & LeBel (1960) in solution; however, the preference of the α-halogens for the axial conformation, as observed in solution (Petrissans, Gromb & Deschamps, 1967), is now confirmed in the solid.

Some anomalies are noted in the internal angles at the ring and in the bond distances, particularly in the presence of a γ-*tert*-butyl, γ-*gem*-methyl or γ-*gem*-phenyl group, but it is still impossible to give a rationalization of these data.

The C=O bond distances are in the range 1·139 (8)–1·23 (2) Å with a mean value (only for cases where e.s.d.'s are reported) of 1·205 (3) Å.

Finally, the difference between $C-Cl_{eq}$ and $C-Cl_{ax}$ bond distances observed by Gaultier, Hauw, Lectard, Metras & Petrissans (1973) (1·777, 1·803 Å) is greatly reduced upon examination of all data now available [1·779 (4), 1·786 (5) Å].

Thanks are due to Dr M. F. Grenier-Loustalot (Pau, France) for providing the sample of the compound. The criticisms and suggestions of my colleagues Professor G. D. Andreetti and Dr P. Sgarabotto are gratefully acknowledged.

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