

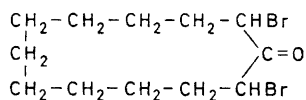
Crystal Structure of 2,12-Dibromo-cyclododecanone

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The crystal structure of 2,12-dibromo-cyclododecanone has been solved by the heavy-atom method at room temperature. The crystals are monoclinic with lattice parameters $a=5.00_2$ Å, $b=19.59_0$ Å, $c=14.59_2$ Å, and $\beta=106.4_2^\circ$. The space group is $P2_1/c$ and the cell contains four molecules. Full-matrix least squares refinement gave the R -value 9.6 % for 1484 observed reflections. The conformation of the 12-membered ring corresponds approximately to the idealized model with 422-symmetry, containing 8 synclinal and 4 anti-periplanar partial conformations. The carbonyl group is pointing inward making angles of 80.8° and 82.2° with the two ring planes.

2,12-Dibromo-cyclododecanone



has been synthesized by T. Ledaal at this university. The present structure analysis was carried out as part of a study of the orientations of the carbonyl group in 5-12 membered cycloalkanones,^{1,2} and also with the intention of obtaining information about the molecular geometry of the carbon skeleton of cyclododecanone.^{5,6}

CRYSTAL DATA

2,12-Dibromo-cyclododecanone belongs to the monoclinic system, the systematic absences leading to space group $P2_1/c$. The following cell parameters with their estimated standard deviations were obtained from a Guinier powder photograph:

$a = 5.002 \text{ \AA}$	$\sigma(\text{\AA}) = 0.003$
$b = 19.590 \text{ \AA}$	$\sigma(\text{\AA}) = 0.008$
$c = 14.592 \text{ \AA}$	$\sigma(\text{\AA}) = 0.009$
$\beta = 106.42^\circ$	$\sigma(^\circ) = 0.05$

The unit cell contains four molecules ($\rho_{\text{calc}}=1.61 \text{ g}\cdot\text{cm}^{-3}$, $\rho_{\text{obs}}=1.58 \text{ g}\cdot\text{cm}^{-3}$).

The intensity material was obtained from photometric measurements of integrated Weissenberg diagrams corresponding to $0kl\cdots 3kl$ (CuK α -radiation). The number of reflections accessible from these diagrams is 2048, 1484 of which were strong enough to be measured. The intensities were statistically, layer by layer, put on absolute scale. Since the maximum number of reflections handled by the available least squares program was 1500, accidentally absent reflections were excluded in the refinement.

No corrections have been made for absorption or secondary extinction effects.

DETERMINATION AND REFINEMENT

The $0kl$ -projection of the molecule was determined by the heavy atom method; the R -value arrived at after least squares refinement (with anisotropic temperature factors for Br-atoms) being $R_{0kl}=8.0\%$. The corresponding Fourier map, which is reproduced in Fig. 1, was used together with a model of the molecule in deriving approximate *relative* x -coordinates of all the atoms.

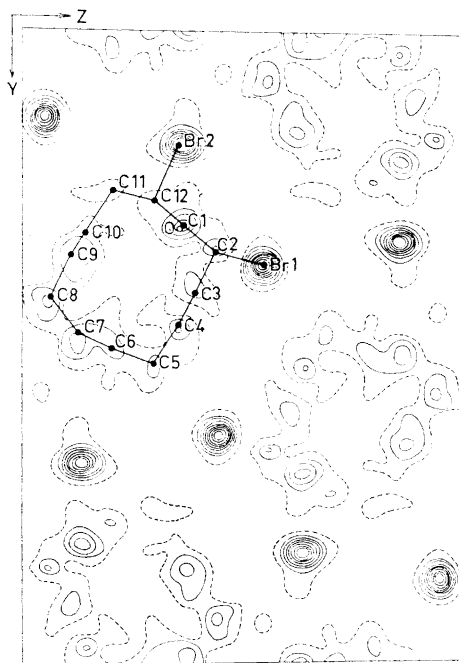


Fig. 1. Fourier projection along a -axis.

The absolute values, corresponding to the minimum R_{1kl} -value obtained by allowing the molecule to move in small steps parallel to the x -axis and calculate the R -factor for each step, were used as starting parameters in a three-dimensional full-matrix least squares refinement.³ The weighting scheme No. 1:

$$\begin{array}{ll} \text{for } F_{\text{obs}} \leq FB & W = A1(F_{\text{obs}})^{B1} \\ \text{for } F_{\text{obs}} > FB & W = A2(F_{\text{obs}})^{B2} \end{array}$$

was adapted by taking $A1=10.0$, $A2=20.0$, $B1=0.0$, $B2=-0.5$ and $FB=4.0$. The form factors calculated by Hanson, Herman, Lea and Skillman were used.⁴ Anisotropic temperature factors were introduced for the bromine atoms. The hydrogen atom positions were calculated assuming tetrahedral C—H bonds of lengths 1.03 Å. Hydrogen parameters (isotropic $B=5$ Å²) were not refined. The R -value arrived at for 1484 observed reflections was 9.6 %. The final fractional atomic coordinates and the thermal vibration parameters are given in Table 1 (a) and (b). The expressions for the anisotropic and isotropic vibrations, respectively, are:

$$\frac{\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]}{\exp[-B \cdot \sin^2\theta/\lambda^2]}$$

A comparison between calculated and observed structure factors is presented in Table 2. The principal axes of the thermal vibration ellipsoids given by the components in (Å) along the crystallographic axes, U_x , U_y , U_z ; the corresponding r.m.s. amplitudes, and the B -values, for the two bromine atoms are:

	U_x (Å)	U_y (Å)	U_z (Å)	$(\bar{u}^2)^{1/2}$ (Å)	B (Å ²)
Br ₁	0.127	0.107	-0.203	0.288	6.56
	0.102	-0.240	-0.029	0.265	5.56
	0.178	0.044	0.157	0.206	3.35
Br ₂	-0.357	0.093	-0.079	0.356	9.99
	0.030	0.030	0.321	0.316	7.86
	-0.055	-0.197	0.008	0.206	3.34

The pseudo equatorially bonded Br₂ has large thermal motion approximately parallel with the a -axis.

RESULTS

Interatomic distances and angles with their estimated standard deviations may be found in Figs. 2 and 3. The dihedral angles are listed in Table 3. The 2,12-dibromo-cyclododecanone ring has almost the same conformation as azacyclododecane hydrochloride and *trans* 1-13,13-dimethyl-13-azoniabicyclo-[10,1,0]-tridecane iodide,^{5,6} and may be described (Table 3) in terms of four roughly planar 4-atom chains, each sharing two "corner" atoms with adjacent

Table 1. (a) Final fractional coordinates and anisotropic temperature factors for bromine atoms. Estimated standard deviations in parentheses.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br ₁	0.44204 (0.00037)	0.365418 (0.000079)	0.55204 (0.00011)	0.0463 (0.0014)	0.003665 (0.000048)	0.006140 (0.000084)	-0.00151 (0.00033)	-0.00032 (0.00043)	-0.001058 (0.000093)
Br ₂	0.00457 (0.00053)	0.177226 (0.000077)	0.36485 (0.00015)	0.1035 (0.0019)	0.002527 (0.000043)	0.01006 (0.00014)	-0.00866 (0.00040)	0.01977 (0.00075)	0.00003 (0.00010)

(b) Final fractional coordinates and isotropic temperature factors for oxygen and carbon atoms. Estimated standard deviations in parentheses.

	x	y	z	B		x	y	z	B
O	0.4594 (0.0030)	0.30601 (0.00055)	0.36599 (0.00078)	5.71 (0.22)	C ₆	-0.2301 (0.0039)	0.49546 (0.00080)	0.2033 (0.0011)	5.71 (0.32)
C ₁	0.2208 (0.0037)	0.30499 (0.00062)	0.36770 (0.00090)	4.27 (0.24)	C ₇	-0.0921 (0.0040)	0.47221 (0.00085)	0.1297 (0.0012)	6.06 (0.34)
C ₂	0.1288 (0.0031)	0.34514 (0.00059)	0.44016 (0.00080)	3.81 (0.21)	C ₈	-0.2541 (0.0040)	0.41779 (0.00090)	0.0647 (0.0012)	6.23 (0.36)
C ₃	-0.0166 (0.0029)	0.41074 (0.00058)	0.39531 (0.00081)	3.79 (0.22)	C ₉	-0.2419 (0.0039)	0.34895 (0.00077)	0.1107 (0.0011)	5.53 (0.31)
C ₄	0.1511 (0.0034)	0.45998 (0.00066)	0.35743 (0.00094)	4.54 (0.25)	C ₁₀	0.0453 (0.0039)	0.31536 (0.00078)	0.1444 (0.0011)	5.73 (0.32)
C ₅	-0.0262 (0.0040)	0.52062 (0.00081)	0.2995 (0.0012)	6.00 (0.33)	C ₁₁	0.0627 (0.0034)	0.25051 (0.00072)	0.2053 (0.0010)	5.23 (0.28)
					C ₁₂	0.0069 (0.0032)	0.26397 (0.00059)	0.29861 (0.00088)	4.00 (0.23)

Table 3. Dihedral angles of the carbon skeleton of 2,12-dibromocyclododecanone.

	(°)
$C_1 - C_2 - C_3 - C_4$	61.6
$C_2 - C_3 - C_4 - C_5$	-171.6
$C_3 - C_4 - C_5 - C_6$	68.6
$C_4 - C_5 - C_6 - C_3$	68.9
$C_5 - C_6 - C_7 - C_8$	-150.2
$C_6 - C_7 - C_8 - C_9$	73.5
$C_7 - C_8 - C_9 - C_{10}$	63.0
$C_8 - C_9 - C_{10} - C_{11}$	-170.7
$C_9 - C_{10} - C_{11} - C_{12}$	64.9
$C_{10} - C_{11} - C_{12} - C_1$	68.1
$C_{11} - C_{12} - C_1 - C_2$	-153.8
$C_{12} - C_1 - C_2 - C_3$	79.0

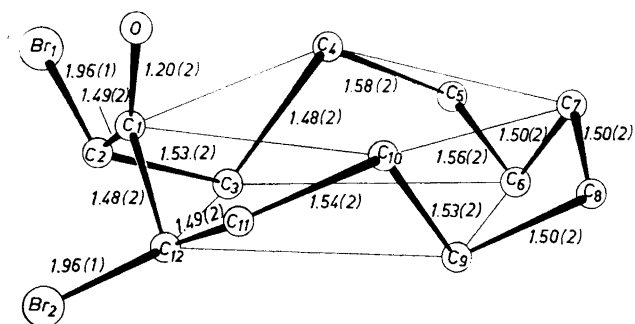


Fig. 2. Schematical drawing of the molecule showing interatomic distances.

chains. The mean value of the C—C—C angles in the cyclododecanone ring is 114.1° , somewhat larger than the corresponding values for the two compounds mentioned.

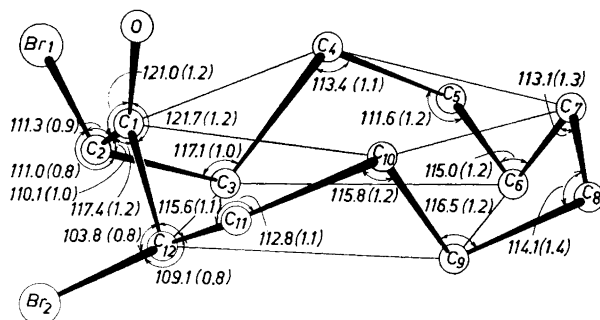


Fig. 3. Schematical drawing of the molecule showing interatomic angles.

In order to decide whether this compound corresponds to an "inside-carbonyl" conformation or not, the distance from the oxygen atom to the "plane" defined by $C_1-C_2-C_{11}-C_{12}$ was calculated, and found to be 0.41 Å inside.

The orientation of the carbonyl group is often expressed in terms of the angle between the $C=O$ direction and the "ring plane".² In 2,12-dibromocyclododecanone two least squares "ring planes" defined by $C_3-C_6-C_9-C_{12}$ and $C_1-C_4-C_7-C_{10}$ (indicated in Figs. 2 and 3) gave the following fit:

Atoms defining the plane	Dist. (Å)	Atoms defining the plane	Dist. (Å)
C_3	0.047	C_1	00.79
C_6	-0.048	C_4	-0.078
C_9	0.049	C_7	0.076
C_{12}	-0.048	C_{10}	-0.077

The angles between the $C=O$ direction (pointing inward) and these two planes were found to be 80.8° and 82.2° , values which agree with recent results obtained by NMR investigations.⁷

The shortest *intra* molecular distance between hydrogens not bonded to the same carbon atom is about 2.0 Å. Fig. 4 shows the packing of the mole-

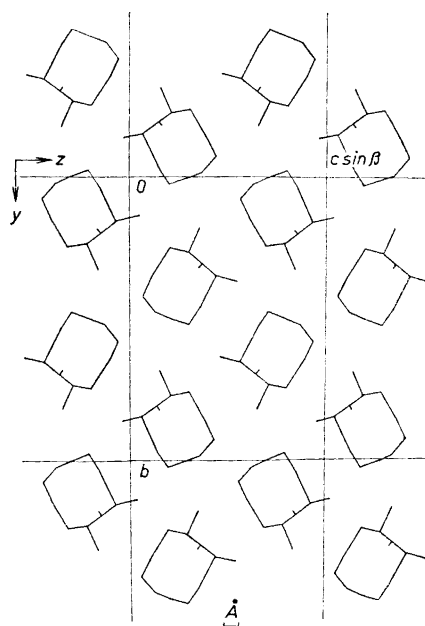


Fig. 4. The packing of the molecule viewed along [100].

cules viewed along [100]. The shortest *inter* molecular distances compared with the corresponding van der Waals values are:

	Distance (Å)	v.d. Waals contact (Å)
Br—Br	4.71	3.90
Br—O	3.72	3.35
Br—H	2.96	3.15
O—H	2.44	2.60
H—H	2.5	2.4

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