Crystal Structure of 2,12-Dichlorocyclododecanone

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The present crystal structure of 2,12-dichlorocyclododecanone was determined by X-ray analysis. The 12-membered ring has 422-symmetry, containing eight torsion angles having synclinal conformations of approximately 65° (average 68.05°); the other four torsion angles conforming antiperiplanar conformations are the average of 160.7°, respectively. The effects of the carbonyl group and the Cl atoms on the conformation of the ring are also discussed.

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C12 is a family of products that has at its core the chemistry of 12-membered ring hydrocarbons. The products of the cyclic structures have some excellent properties, such as lubricants, powder coatings, adhesives, corrosion inhibitors, fragrances and flame retardants. Cyclododecanone is also a starting material for macrocyclic musk lactones. These lactones have high substantivity and highly desirable musk odor properties, as well as good biodegradability and excellent fixative properties.¹

In the synthesis of 2-chlorocyclododecanone, by direct chlorination in methanol, we observed the stereoselective formation of a large amount of dichloro derivative of the starting compound, as a side product.² It has been shown that the α -chlorocyclododecanone is an intermediate for the formation of the dichloro derivative. Prolonged chlorination resulted in the formation of dichlorocyclododecanone as major product with 85% yield. Cyclododecanone was added to methanol suspension with potassium chlorate. When the mixture was being stirred, chlorine gas was passed into the solution at room temperature. The conversion rate was followed by a GC analysis of the aliquots. The reaction mixture was cooled in an ice bath and the precipitate was filtered out. The solid product was recrystallized from petroleum ether, yielding white needles (solid, m.p., 118°C with 85% yield). Its purity was checked by a GC analysis.

The X-ray analysis results are given in Tables 1–3. The positions of the H atoms bounded to C atoms were calculated [C–H distance 0.93 Å], and included in the structure factor calculation using a riding model. The cyclododecanone ring of the title compound has almost the same conformation as 2,12-dibromocyclododecanone,³ azacyclododecanone hydrochlorid,⁴

trans-13,13-dimethyl-13-azoniabicyclo[10.1.0]tridecane iodide.⁵ The observed bond lengths for C–C, except for the C1 bonds, have normal values for the Csp³–Csp³ bonds. The C1–O1 bond length [1.199(10) Å] suggests some double-bond character.

The C1–C4–C7–C10 and C3–C6–C9–C12 planes are parallel to each other with a dihedral angle of 0.77(20)°. The carbonyl group is almost perpendicular to the C1–C4–C7–C10 plane. The angles with the carbonyl group and these two planes are 89.90(45) and 81.36(42)°, respectively. The 12-membered ring has approximately 422-symmetry. Eight of the twelve torsion angles are approximately 65° (average 68.05°) and have synclinal conformations. The other four torsion angles have an average of 160.7° and conform antiperiplanar conformations.

Table 1 Crystal and experimental data

CCDC deposition number: CCDC-259268	
Formula: C ₁₂ H ₂₀ Cl ₂ O	
Formula weight: 251.18	
Crystal system: monoclinic	
Space group: <i>P</i> 2 ₁ / <i>n</i>	<i>Z</i> = 4
<i>a</i> = 5.062(2) Å	<i>β</i> = 92.28(2)
<i>b</i> = 19.120(5) Å	
<i>c</i> = 13.78(3) Å	
<i>V</i> = 1333(3) Å ³	
<i>D</i> _x = 1.257 g/cm ³	
<i>μ</i> = 0.462 mm ^{−1}	
<i>T</i> = 293 K	
Crystal color: colorless	
Crystal size: 0.48 × 0.24 × 0.21 mm	
<i>λ</i> (Mo <i>K</i> _α) = 0.71073 Å	
<i>R</i> = 0.053 <i>wR</i> = 0.150	
No. of reflections measured = 1761	
No. of reflections used = 1555	
No. of parameters = 136	
Goodness-of-fit = 0.979	
(Δ/ <i>σ</i>) _{max} = 0.000	
(Δ <i>ρ</i>) _{max} = 0.193 eÅ ^{−3}	
(Δ <i>ρ</i>) _{min} = −0.234 eÅ ^{−3}	
2 <i>θ</i> _{max} = 43.76°	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: SHELXS-97	
Refinement: full matrix

Fig. 1 Chemical diagram.

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
Cl1	0.1160(4)	0.1340(9)	0.5516(2)	0.0709(7)
Cl2	0.3501(5)	0.3238(2)	0.3687(2)	0.1016(9)
O1	-0.102(1)	0.2001(2)	0.3753(3)	0.067(2)
C1	0.135(2)	0.1996(3)	0.3769(5)	0.046(2)
C2	0.304(2)	0.1560(3)	0.4477(4)	0.044(2)
C3	0.410(2)	0.0903(3)	0.4004(4)	0.047(2)
C4	0.206(2)	0.0386(3)	0.3597(5)	0.053(2)
C5	0.330(2)	-0.0197(3)	0.2998(5)	0.068(2)
C6	0.440(2)	0.0050(4)	0.2049(6)	0.068(2)
C7	0.233(3)	0.0277(4)	0.1285(6)	0.073(2)
C8	0.317(2)	0.0874(4)	0.0621(5)	0.083(3)
C9	0.355(2)	0.1582(3)	0.1130(5)	0.068(2)
C10	0.102(2)	0.1897(4)	0.1499(5)	0.062(2)
C11	0.143(2)	0.2562(3)	0.2088(5)	0.059(2)
C12	0.287(2)	0.2430(3)	0.3057(5)	0.043(2)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Table 3 Bond distances (Å) and angles with the selected torsion angles (°)

Cl1	C2	1.798(6)		
Cl2	C12	1.794(6)		
O1	C1	1.198(7)		
C1	C2	C3	112.1(5)	
C2	C1	C12	115.5(6)	
Cl1	C2	C12	109.8(5)	
Cl2	C12	C1	104.2(5)	
O1	C1	C12	121.0(7)	
C3	C2	C1	C12	-77.4(7)
C2	C1	C12	C11	159.1(4)

C12-C1-C2-C3 [$-77.4(7)^\circ$] shows a significant deviation from the average value. The molecular geometry (Fig. 2) has an almost orthogonal axis system. The distances between C5-C11 and C2-C8 are almost the same values of 5.48(2) and 5.47(2) Å, respectively. The C2, C5, C8 and C11 atoms lie at the corners of a rectangle, like a square. The side lengths and angles of the rectangular are, respectively: C5-C8 = 3.85(2), C8-C11 = 3.92(2), C2-C11 = 3.86(2), and C2-C5 = 3.92(2) Å and C2-C11-C8 = 89.3(3), C11-C8-C5 = 89.8(3), C8-C5-C2 =

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 40% probability level.

89.4(2), and C5-C2-C11 = 89.5(2)°.

It can be seen that the existence of the carbonyl group and the Cl atoms doesn't cause any considerably change in the conformation of the ring. In cyclododecane, one face of the ring has four intra-annular H atoms, the shortest non-bound H-H distance lying in the range of 2.0–2.1 Å.⁶ In the title compound there are also four intra-annular H atoms; the shortest non-bonded H-H distances are in the range of 2.1–2.2 Å. The H12-H3A distance is rather longer than the others with a value of 2.35 Å.

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