Instrumental Achievements

Crystal Structure of 2,6-Di-(trichloroacetyl)-1-(*N*-morpholinyl)cyclohexene

Süheyla Özbey,* Hülya Şenöz,** and Nazan Tunoğlu**

*Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey
**Department of Chemistry, Hacettepe University, Beytepe 06532, Ankara, Turkey

The reaction of acid chlorides with enamines of cyclic ketones has received considerable interest as a synthetic route to afford a number of acylated products.[1] The *C*-acylation of morpholine, pyrrolidine and piperidine enamines is a suitable method for the synthesis of α-acylated carbonyl compounds.[2] During the course of our investigations on acylation reactions of trichloroacetyl chloride with enamines of medium-sized cyclic ketones, we have remarked that the enamino ketones were diacylated at the α and α'-positions. Such diacylation instead of monoacylation was probably due the great reactivity of the trichloroacetyl chloride. Morpholine enamine gave a better result than pyrrolidine and piperidine enamines since the diacylated product of morpholino cyclohexene could be successfully isolated during the reaction course but diacylated pyrrolidine and piperidine enamines underwent a hydrolysis reaction readily. The reaction of 1-(*N*-morpholinyl)-cyclohexene, trichloroacetyl chloride and activated zinc afforded the title compound as a yellow solid, which was then recrystallized in hexene solution.

We report here the crystal structure of 2,6-di-(trichloroacetyl)-1-(*N*-morpholinyl)cyclohexene, (**I**), obtained by the reaction of 1-(*N*-morpholinyl)cyclohexene with trichloroacetyl chloride (Fig. 1). A colorless prismatic crystal of (**I**) with approximate dimensions $0.16 \times 0.24 \times 0.44$ mm was used for all x-ray experiments. During the data collections three intensity control reflections were monitored every 2 h, showing no loss of intensity. The data were corrected for absorption using the ψ-scan data. The structure was solved by direct methods and refined by the full-matrix least-squares method using anisotropic displacement parameters for all non-hydrogen atoms. H atoms were placed geometrically 0.95 Å from their parent atoms, while the H atom of C7 was located in a difference Fourier map. For all H atoms a riding model was used and displacement parameters were fixed at $1.3U_{eq}$ of the parent atoms.

Table 1 shows the crystal and experimental data, while the final atomic parameters are given in Table 2. Bond distances and bond angles are given in Table 3.

The structure predicted from chemical and spectral analysis is confirmed. Structural results show that the cyclohexene ring adopts the half-chair conformation having the spherical polar set values,[3] $Q = 0.48(1)$Å, $\varphi = 158(1)$ and $\theta = 54.1(8)°$. The morpholine substituent, H atoms attached to the C7 and C2 atoms are in the equatorial position while C13 atom is in the axial position with respect to the best-plane of cyclohexene.
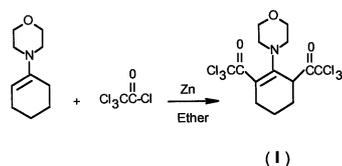
Fig. 1   Synthesis and chemical structures.
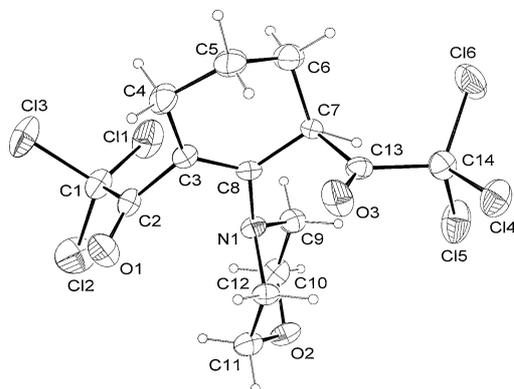
Fig. 2   ORTEP drawing of the title compound with atom labeling.

Table 1   Crystal and experimental data

Formula: $C_{14}H_{15}NO_3Cl_6$
Formula weight = 457.99
Crystal system: monoclinic
Space group: $P2_1/c$ $Z = 4$
$a = 16.843(2)$Å
$b = 6.441(1)$Å
$c = 18.670(1)$Å $\beta = 110.30(1)°$
$V = 1899.5(3)$Å^3
$D_x = 1.601$ g/cm^3
μ(Mo K$_\alpha$) = 0.92 mm^{-1}
$2\theta_{max} = 50.0°$ with Mo K$_\alpha$
No. of reflections used = 1556
No. of parameters = 220
$R = 0.054$
$(\Delta/\sigma)_{max} = 0.001$
$(\Delta/\rho)_{max} = 0.49$ eÅ^{-3}
$(\Delta/\rho)_{min} = -0.22$ eÅ^{-3}
Measurement: Enraf Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: SIR
Refinement: full matrix least-squares

Table 2   Atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	$B_{eq}/\text{Å}^2$
CL1	0.6316(2)	-0.0880(4)	0.3543(1)	6.79(6)
CL2	0.6768(2)	-0.4998(5)	0.3235(1)	7.70(7)
CL3	0.5151(1)	-0.4189(5)	0.3380(1)	7.34(7)
CL4	0.9070(1)	0.0291(4)	0.8239(1)	5.12(5)
CL5	0.9436(1)	0.1411(4)	0.6907(1)	6.37(6)
CL6	0.8176(2)	0.3633(3)	0.7297(1)	6.99(7)
O1	0.6729(3)	-0.5919(8)	0.4731(3)	5.1(1)
O2	0.9400(3)	-0.2501(8)	0.4784(3)	4.4(1)
O3	0.7927(3)	-0.2052(7)	0.7050(3)	5.0(1)
N1	0.7914(3)	-0.1831(9)	0.5118(3)	3.0(1)
C1	0.6242(4)	-0.349(1)	0.3716(4)	4.5(2)
C2	0.6569(4)	-0.413(1)	0.4579(3)	3.4(2)
C3	0.6578(4)	-0.251(1)	0.5157(3)	3.0(2)
C4	0.5838(4)	-0.247(1)	0.5434(4)	4.4(2)
C5	0.6017(4)	-0.110(1)	0.6130(4)	4.7(2)
C6	0.6501(4)	0.083(1)	0.6069(4)	4.3(2)
C7	0.7371(4)	0.034(1)	0.6002(3)	2.8(2)
C8	0.7267(4)	-0.135(1)	0.5423(3)	2.7(1)
C9	0.8340(4)	-0.013(1)	0.4888(3)	3.6(2)
C10	0.8813(4)	-0.094(1)	0.4400(4)	4.2(2)
C11	0.8991(4)	-0.415(1)	0.5022(4)	4.1(2)
C12	0.8538(4)	-0.340(1)	0.5537(3)	3.1(2)
C13	0.7961(4)	-0.043(1)	0.6802(3)	3.0(2)
C14	0.8617(4)	0.120(1)	0.7302(4)	3.8(2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*(\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

The ketone groups at α and α'-positions are twisted in the opposite direction with torsion angles C1-C2-C3-C8 and C8-C7-C13-C14 of –88.3(8) and 139.7(6)°, respectively.

The geometry observed for the morpholine ring shows no significant distortion from a perfect chair. The perpendicular distances of N1 and O2 atoms from the best plane defined by atoms C9, C10, C11 and C12 are 0.680(5) and –0.628(5)Å, respectively.   In terms of ring-puckering coordinates, amplitudes and phase magnitudes are $Q = 0.572(7)$Å, $\varphi = 27(9)$ and $\theta = 178.5(6)°$. The dihedral angle between the best planes of the cyclohexene and morpholine rings is 66.2(3)°.

Crystal packing is governed only by van der Waals interactions.

Table 3   Bond distances and bond angles of non-hydrogen atom (Å, °)

CL1 - C1	1.726(9)			C1 - C2	1.566(9)		
CL2 - C1	1.756(9)			C2 - C3	1.50(1)		
CL3 - C1	1.782(7)			C3 - C4	1.50(1)		
CL4 - C14	1.748(6)			C3 - C8	1.322(9)		
CL5 - C14	1.782(8)			C4 - C5	1.51(1)		
CL6 - C14	1.734(8)			C5 - C6	1.51(1)		
O1 - C2	1.192(9)			C6 - C7	1.55(1)		
O2 - C10	1.420(8)			C7 - C8	1.500(9)		
O2 - C11	1.419(9)			C7 - C13	1.559(7)		
O3 - C13	1.155(8)			C9 - C10	1.50(1)		
N1 - C8	1.428(9)			C11 - C12	1.50(1)		
N1 - C9	1.456(9)			C13 - C14	1.573(9)		
N1 - C12	1.472(8)						
C10 - O2 - C11		111.2(5)		C6 - C7 - C8			109.3(5)
C8 - N1 - C9		118.5(6)		C6 - C7 - C13			107.2(5)
C8 - N1 - C12		116.1(5)		C8 - C7 - C13			109.7(5)
C9 - N1 - C12		109.8(5)		N1 - C8 - C3			114.9(6)
CL1 - C1 - CL2		111.1(5)		N1 - C8 - C7			122.0(5)
CL1 - C1 - CL3		108.1(4)		C3 - C8 - C7			123.1(6)
CL1 - C1 - C2		115.3(5)		N1 - C9 - C10			109.7(6)
CL2 - C1 - CL3		108.8(4)		O2 - C10 - C9			111.3(5)
CL2 - C1 - C2		108.7(5)		O2 - C11 - C12			111.6(6)
CL3 - C1 - C2		104.3(5)		N1 - C12 - C11			108.0(5)
O1 - C2 - C1		118.0(6)		O3 - C13 - C7			124.6(5)
O1 - C2 - C3		123.8(6)		O3 - C13 - C14			119.1(5)
C1 - C2 - C3		117.9(6)		C7 - C13 - C14			116.2(5)
C2 - C3 - C4		117.1(6)		CL4 - C14 - CL5			108.0(4)
C2 - C3 - C8		116.8(6)		CL4 - C14 - CL6			110.2(4)
C4 - C3 - C8		125.9(6)		CL4 - C14 - CL3			110.2(5)
C3 - C4 - C5		111.2(6)		CL5 - C14 - CL6			108.7(4)
C4 - C5 - C6		111.6(7)		CL5 - C14 - CL3			106.9(5)
C5 - C6 - C7		112.7(6)		CL6 - C14 - CL3			112.8(4)

References

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