

5-Chloro-6-dichloromethylene-4-methoxy-1-methyl-4-trichloromethylhexahydro-2-pyrimidinone

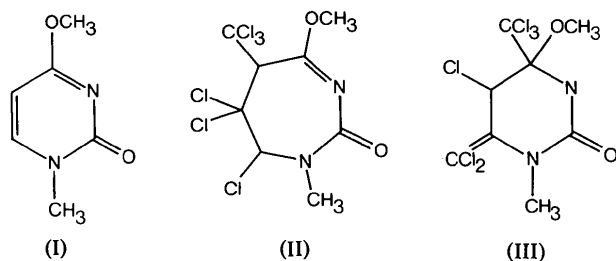
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Abstract. $C_8H_8Cl_6N_2O_2$, monoclinic, $C2/c$, $a = 22.765$ (5), $b = 7.846$ (3), $c = 17.525$ (4) Å, $\beta = 113.85$ (2)°, $Z = 8$. The final R for 1904 independent reflexions is 0.036. The six-membered ring has a sofa form. The C-Cl lengths are: C-Cl 1.791 (5), CCl_2 (average) 1.714, CCl_3 (average) 1.770 Å.

Introduction. In the reaction of 1-methyl-4-methoxy-2-oxo-1,2-dihydropyrimidine (I) with sodium trichloroacetate (as a source of $:CCl_2$) a compound of composition $C_8H_8Cl_6N_2O_2$ was obtained (Thiellier, 1977). Since in this type of reaction ring expansion often occurs, structure (II) containing a seven-membered ring is a possible reaction product. The usual spectroscopic techniques did not allow an unambiguous structural assignment; therefore an X-ray structure determination was undertaken. The compound turned out to be (III) in which the original ring skeleton is still present. The mechanism of this unusual reaction has not yet been elucidated.



1904 independent reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-4 automatic diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The structure was solved with *SIMPEL*, an interactive set of programs based on the symbolic addition method (Schenk, Overbeek & van der Putten, 1976). The best solution obtained with four symbols and the 250 strongest E values gave an E map in which six peaks stood out from the rest. These were assumed to represent the six Cl atoms. They were refined by isotropic least squares, after which Fourier synthesis revealed the remaining non-hydrogen atoms. Aniso-

tropic least-squares refinement proceeded smoothly to an R of 0.072. A difference synthesis at this stage revealed the positions of the eight H atoms and also contained almost identical features around each Cl atom, probably due to absorption. After application of an absorption correction and introduction of isotropic H atoms, continued refinement reduced R to 0.045. Comparison of observed and calculated structure factors revealed a number of discrepancies with $F_c > F_o$ for the strongest reflections, attributable to extinction. After introduction of an extinction correction

$$F_c^{\text{corr}} = F_c \left(1 + g \frac{1 + \cos^4 2\theta}{1 + \cos^2 2\theta} \cdot \frac{1}{\sin 2\theta} F_c^2 \right)^{-1/4}$$

Table 1. Fractional coordinates with their e.s.d.'s ($\times 10^5$ for Cl; $\times 10^4$ for C, N, O; $\times 10^3$ for H)

	<i>x</i>	<i>y</i>	<i>z</i>
Cl(1)	31185 (4)	-24385 (13)	10759 (6)
Cl(2)	42517 (4)	-17489 (13)	25559 (5)
Cl(3)	31017 (5)	2163 (15)	21818 (5)
Cl(4)	46847 (4)	15927 (13)	6640 (6)
Cl(5)	48434 (4)	-36589 (12)	8736 (6)
Cl(6)	37107 (5)	-42074 (15)	-6185 (7)
C(1)	3101 (2)	828 (5)	-240 (2)
C(2)	3812 (2)	576 (4)	1271 (2)
C(3)	4300 (2)	-140 (4)	945 (2)
C(4)	3971 (2)	-1216 (4)	189 (2)
C(5)	3588 (2)	-802 (5)	1748 (2)
C(6)	4150 (2)	-2798 (5)	137 (2)
C(7)	3349 (3)	-486 (7)	-1319 (2)
C(8)	3935 (3)	3526 (6)	1791 (3)
N(1)	3446 (2)	-388 (4)	-439 (2)
N(2)	3267 (2)	1218 (4)	577 (2)
O(1)	2653 (2)	1565 (4)	-788 (2)
O(2)	4140 (2)	1799 (3)	1891 (2)
H(3)	460 (2)	-77 (4)	136 (2)
H(71)	378 (2)	-81 (5)	-137 (3)
H(72)	296 (3)	-134 (7)	-163 (4)
H(73)	322 (3)	51 (6)	-159 (3)
H(81)	393 (3)	398 (6)	120 (3)
H(82)	354 (2)	355 (5)	180 (3)
H(83)	420 (2)	403 (6)	220 (3)
H(N2)	298 (2)	192 (5)	68 (3)

(Larson, 1970), additional refinement reduced R to 0.036. The final g value was 2.25×10^{-6} . The final coordinates are listed in Table 1.*

Discussion. The structure and shape of the molecule are depicted in Fig. 1 with the numbering of the atoms. Bond distances and angles are listed in Table 2. The six-membered ring can be described as a sofa in which the part C(2), N(2), C(1), N(1), C(4) is approximately planar (largest deviation from the best plane 0.034 Å) and with C(3) 0.61 Å from this plane.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34890 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

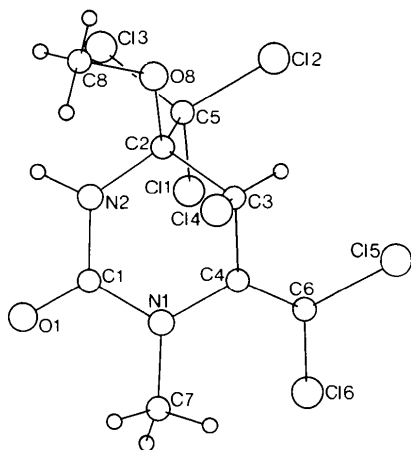


Fig. 1. Shape of the molecule and atomic numbering.

Table 2. Bond lengths (Å) and angles (°)

C(1)—N(2)	1.360 (5)	C(4)—N(1)	1.414 (5)
C(1)—O(1)	1.227 (5)	C(4)—C(6)	1.321 (5)
C(1)—N(1)	1.368 (6)	N(1)—C(7)	1.469 (6)
N(2)—C(2)	1.433 (5)	C(5)—Cl(1)	1.778 (4)
C(2)—C(3)	1.546 (7)	C(5)—Cl(2)	1.763 (4)
C(2)—O(2)	1.415 (4)	C(5)—Cl(3)	1.767 (5)
C(2)—C(5)	1.572 (6)	O(2)—C(8)	1.421 (6)
C(3)—C(4)	1.492 (5)	C(6)—Cl(5)	1.722 (4)
C(3)—Cl(4)	1.791 (5)	C(6)—Cl(6)	1.705 (4)
N(1)C(1)N(2)	118.8 (3)	N(1)C(4)C(6)	124.4 (3)
N(2)C(1)O(1)	120.5 (4)	C(1)N(1)C(4)	120.9 (4)
N(1)C(1)O(1)	120.7 (4)	C(1)N(1)C(7)	116.5 (3)
C(1)N(2)C(2)	126.3 (4)	C(4)N(1)C(7)	120.9 (5)
N(2)C(2)C(3)	108.6 (3)	C(2)C(5)Cl(1)	112.4 (3)
N(2)C(2)C(5)	109.7 (4)	C(2)C(5)Cl(2)	111.1 (3)
N(2)C(2)O(2)	114.9 (3)	C(2)C(5)Cl(3)	108.2 (3)
C(3)C(2)C(5)	112.5 (3)	Cl(1)C(5)Cl(2)	108.5 (3)
C(3)C(2)O(2)	107.2 (4)	Cl(1)C(5)Cl(3)	107.4 (3)
C(5)C(2)O(2)	104.0 (3)	Cl(2)C(5)Cl(3)	109.1 (2)
C(2)C(3)C(4)	110.9 (4)	C(2)O(2)C(8)	120.5 (3)
C(2)C(3)Cl(4)	109.3 (2)	C(4)C(6)Cl(5)	122.1 (3)
C(4)C(3)Cl(4)	108.1 (3)	C(4)C(6)Cl(6)	124.2 (3)
C(3)C(4)N(1)	113.2 (3)	Cl(5)C(6)Cl(6)	113.6 (3)
C(3)C(4)C(6)	122.3 (3)		

The urea part [N(1), C(1), N(2), O(1)] of the ring is strictly planar (largest deviation 0.003 Å). The pattern of bond lengths and angles within the ring is rather varied. Those of the urea part resemble those in urea itself, *i.e.* two relatively short C—N bonds at an angle of less than 120°. The other two C—N bonds in the ring are longer but still shorter than C—N single bonds. C(2)—C(3) has the length of a normal sp^3 — sp^2 bond but C(3)—C(4), adjacent to the double bond C(4)—C(6), is again rather short for an sp^3 — sp^2 bond. The endocyclic angles are normal except for the large angle of 126° at N(2). This is probably a consequence of the tendency of C(2), N(2), C(1), N(1), C(4) to assume a planar conformation. This planarity is impossible if all the endocyclic ring angles have normal values. N(2), as the only unsubstituted ring atom, apparently adapts itself to this requirement. Of the exocyclic bonds C(2)—C(5) is rather long for an sp^3 — sp^3 bond. The six C—Cl bonds are of three types: the isolated bond C(3)—Cl(4) of length 1.791 Å, which is a normal value for this type of bond (Altona, Knobler & Romers, 1963), the three cumulated bonds of the trichloromethyl group of average length 1.770 Å, which is in good agreement with recent results for other trichloromethyl compounds (*e.g.* 1.763 Å, Sheldrick & Hewson, 1975; 1.756 Å, Andreassen, Hazell & Grønbaek Hazell, 1977; 1.782 Å, Smith & Bennett, 1977; 1.767 Å Brianso & Surcouf, 1978), and the two bonds of the dichloromethylene group of average length 1.714 Å, which agrees well with the results for perchloro-*p*-xylylene (Galí, Miravittles & Font-Altaba, 1976), where the average for four such groups is 1.701 Å.

The double-bond system of C(4)—C(6) is not planar but shows a twist of about 10° around its axis. This might be due to steric interaction of the Cl atoms of C(6) with the atoms at adjacent ring atoms [Cl(5)···H(31) 2.55 Å, Cl(6)···C(3) 3.15 Å]. The nonplanarity of N(1) [the angles around N(1) total 358.4°] is in accord with this. The packing of the molecules is effected by normal van der Waals interactions.

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