Acta Cryst. (1990). C**46**, 1239–1241

Structure of 2,4-Dichlorophenyl 8-Oxo-1-azabicyclo[3.3.0]oct-2-ylacetate (*endo* and *exo* Isomers 92:8)

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(*Received* 19 *June* 1989; *accepted* 12 *September* 1989)

Abstract. $C_{15}H_{15}Cl_2NO_3$, $M_r = 328{\cdot}2$, triclinic, $P\bar{1}$, $a = 7{\cdot}256\,(1)$, $b = 8{\cdot}456\,(1)$, $c = 12{\cdot}665\,(1)$ Å, $\alpha = 96{\cdot}78\,(1)$, $\beta = 100{\cdot}40\,(1)$, $\gamma = 98{\cdot}11\,(1)°$, $V = 748{\cdot}4\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}46$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 4{\cdot}4$ cm^{-1}, $F(000) = 340$, $T = 294$ K, $R = 0{\cdot}045$ for 2004 observed reflections. The crystal contains two isomers, the major one (92%) being the *endo* isomer with the hydrogens at C5 and C8 *cis*. The fused five-membered rings of the major isomer both have envelope conformations. The external C—N—C angle is 131·6°.

Introduction. In the course of an investigation of synthetic routes to derivatives of *cis*-10-azatricyclo-[5.2.1.0^{4,10}]decane (1), we have obtained the title compound (2) as a mixture of C8 epimers (2*a*, 2*b*), starting from the known (Flitsch & Muter, 1971) ethyl 8-oxo-1-azabicyclo[3.3.0]oct-2-ylideneacetate (3).

Experimental. Stereochemical considerations indicate that catalytic hydrogenation of (3) (H_2, 1 atm, 294 K, 10% Pd/C, ethanol) should preferentially give the *endo* isomer (hydrogens at C5 and C8 mutually *cis*) of product (4) as required for further elaboration to (1). Compound (4) was obtained as a clear oil and its ^{1}H NMR spectrum indicated that it contained the expected isomers in the ratio 5–6:1. Conversion of ethyl ester mixture (4) to the corresponding dichlorophenyl esters (base hydrolysis, followed by acidification and reaction with 2,4-dichlorophenol and dicyclohexylcarbodiimide in diethyl ether) yielded a mixture of (2*a*) and (2*b*) and recrystallization from diethyl ether gave a sample containing *ca* 92% of the major isomer. Our X-ray analysis of this mixture shows that there are indeed two isomers present in the sample and that the major isomer has the desired *endo* configuration.

Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 20°$. Crystal dimensions $0{\cdot}50 \times 0{\cdot}50 \times 0{\cdot}25$ mm; intensities of reflections with indices h −9 to 0, k −10 to 10, l −16 to 16, with $2 < 2\theta < 54°$ measured; ω–2θ scans, ω scan width $(0{\cdot}65 + 0{\cdot}35\tan\theta)°$; graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 3604 reflections measured, 3258 unique, 2004 with $I > 3\sigma(I)$ labelled observed and used in structure solution and refinement; $R_{\text{int}} = 0{\cdot}012$. Data were corrected for Lorentz and polarization effects. No absorption correction. Space group $P\bar{1}$ was assumed and confirmed by the successful analysis. The structure was solved with the aid of *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement was by full-matrix least-squares calculations on F, initially with isotropic and then with anisotropic thermal parameters. Our NMR data were consistent with the presence of a small amount (*ca* 8%) of the minor isomer (2*b*) cocrystallizing with the major isomer (2*a*), and difference maps calculated towards the conclusion of the refinement did show two small peaks in the anticipated positions of alternative sites for N1 and C5 [which would be the major atom sites affected by the cocrystallization of the minor isomer (2*b*)]. In the final cycles of refinement, these atoms (N1* and C5*) were included and refined with isotropic thermal parameters. No evidence was found from difference maps to suggest that any of the other non-H atoms was significantly displaced from the positions occupied by the major isomer. The difference maps also showed maxima in positions consistent with the expected locations of the H atoms of (2*a*). In the final rounds of calculations the H atoms were positioned on geometrical grounds (C—H 0·95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 5·0 Å^2. An extinction correction was also refined (final value $6{\cdot}1 \times 10^{-7}$). The final cycle of refinement included 199 variable parameters, $R = 0{\cdot}045$, $wR = 0{\cdot}061$, goodness of fit 2·08, $w = 1/[\sigma^2(F_o) + 0{\cdot}04(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle 0·002; density in final difference map ±0·39 e Å^{-3}; there were no chemically significant features. Scattering factors

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and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1983).

Atomic coordinates* and details of molecular geometry are given in Tables 1 and 2. Fig. 1 is a view of the molecule prepared using *ORTEP*II (Johnson 1976).

Discussion. Our analysis establishes that (2*a*) has the required *endo* configuration at C8, with the hydrogen at C5 *exo* (Fig. 1), and confirms that *ca* 8% of isomer (2*b*) has cocrystallized with the major isomer. Because the minor isomer was only present as a small percentage of the total, no meaningful discussion of its structure or conformation is possible. In the major isomer (2*a*) both five-membered rings in the 8-oxo-1-azabicyclo[3.3.0]oct-2-yl skeleton have envelope conformations; one ring has C4 0·466 (3) Å from the N1,C2,C3,C5 plane, the other has C6 0·563 (3) Å from the N1,C5,C7,C8 plane and the two planes form a dihedral angle of 8·0°. In the related 1-azabicyclo[3.3.0]octan-2-one derivatives (5), (6) (Flippen-Anderson, D'Antonio & Konnert, 1984) and (7) (Winkler, 1979), the pairs of five-membered rings have the same conformations as found here for (2*a*) with the same atoms forming the envelope flap in each case. In (2*a*), unlike the situation in (7) where

Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

N1/N1* and C5/C5* are disordered-atom sites with occupancies 0·92/0·08. N1* and C5* were refined isotropically.

	x	*y*	*z*	*B*(Å^2)
Cl1	−0·2199 (1)	0·1021 (1)	0·90586 (6)	6·50 (2)
Cl2	−0·7616 (1)	0·3694 (1)	1·06116 (6)	5·78 (2)
O1	0·1766 (3)	0·2055 (3)	0·5025 (2)	5·55 (5)
O2	−0·2623 (3)	0·4029 (3)	0·7049 (2)	7·66 (5)
O3	−0·4244 (3)	0·1570 (2)	0·6926 (1)	4·47 (4)
N1	−0·0900 (3)	0·2809 (3)	0·4111 (2)	3·02 (4)
C2	0·0714 (3)	0·2177 (3)	0·4186 (2)	3·67 (5)
C3	0·0992 (4)	0·1765 (3)	0·3045 (2)	4·28 (6)
C4	−0·0934 (4)	0·1742 (4)	0·2341 (2)	4·81 (7)
C5	−0·1796 (4)	0·2922 (4)	0·3006 (2)	3·72 (6)
C6	−0·3848 (4)	0·2728 (5)	0·3082 (2)	5·70 (8)
C7	−0·3794 (4)	0·3603 (4)	0·4211 (2)	5·11 (7)
C8	−0·1983 (3)	0·3267 (3)	0·4920 (2)	3·64 (5)
C9	−0·2325 (4)	0·1995 (3)	0·5637 (2)	4·57 (6)
C10	−0·3041 (4)	0·2686 (3)	0·6603 (2)	4·38 (6)
C11	−0·5026 (4)	0·2097 (3)	0·7812 (2)	3·86 (6)
C12	−0·4229 (4)	0·1877 (3)	0·8837 (2)	4·02 (6)
C13	−0·5046 (4)	0·2342 (4)	0·9702 (2)	4·28 (6)
C14	−0·6652 (4)	0·3026 (3)	0·9515 (2)	4·24 (6)
C15	−0·7474 (4)	0·3226 (4)	0·8490 (2)	4·69 (6)
C16	−0·6667 (4)	0·2744 (4)	0·7624 (2)	4·73 (7)
N1*	−0·127 (3)	0·194 (2)	0·407 (1)	1·6 (3)
C5*	−0·239 (4)	0·206 (3)	0·297 (2)	2·5 (5)

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

Cl1—C12	1·725 (3)	C7—C8	1·535 (4)
Cl2—C14	1·737 (3)	C8—C9	1·510 (4)
O1—C2	1·216 (3)	C9—C10	1·502 (4)
O2—C10	1·180 (3)	C11—C12	1·367 (3)
O3—C10	1·345 (3)	C11—C16	1·374 (4)
O3—C11	1·402 (3)	C12—C13	1·381 (4)
N1—C2	1·347 (3)	C13—C14	1.369 (4)
N1—C5	1·454 (3)	C14—C15	1·367 (4)
N1—C8	1·449 (3)	C15—C16	1·381 (4)
C2—C3	1·503 (4)	N1*—C5*	1·51 (3)
C3—C4	1·512 (4)	C2—N1*	1·40 (2)
C4—C5	1·505 (4)	C4—C5*	1·47 (3)
C5—C6	1·497 (4)	C6—C5*	1·29 (3)
C6—C7	1·522 (4)	C8—N1*	1·66 (2)

C10—O3—C11	116·3 (2)	C12—C11—C16	120·7 (3)
C2—N1—C5	113·9 (2)	Cl1—C12—C11	120·3 (2)
C2—N1—C8	131·6 (2)	Cl1—C12—C13	119·5 (2)
C5—N1—C8	114·3 (2)	C11—C12—C13	120·1 (3)
O1—C2—N1	125·7 (2)	C12—C13—C14	118·9 (2)
O1—C2—C3	127·8 (3)	Cl2—C14—C13	118·8 (2)
N1—C2—C3	106·5 (2)	Cl2—C14—C15	119·8 (2)
C2—C3—C4	104·6 (2)	C13—C14—C15	121·3 (3)
C3—C4—C5	103·2 (2)	C14—C15—C16	119·7 (3)
N1—C5—C4	102·7 (2)	C11—C16—C15	119·2 (2)
N1—C5—C6	101·3 (2)	C3—C2—N1*	103·5 (8)
C4—C5—C6	124·8 (2)	O1—C2—N1*	122·1 (8)
C5—C6—C7	103·2 (2)	C3—C4—C5*	113· (1)
C6—C7—C8	105·2 (3)	C7—C6—C5*	116· (1)
N1—C8—C7	101·6 (2)	C7—C8—N1*	101·8 (6)
N1—C8—C9	113·3 (2)	C9—C8—N1*	90·0 (7)
C7—C8—C9	114·3 (2)	C2—N1*—C8	113· (1)
C8—C9—C10	110·2 (2)	C2—N1*—C5*	116· (2)
O2—C10—O3	122·4 (3)	C5—N1*—C8	94· (1)
O2—C10—C9	125·9 (3)	C8—N1*—C5*	104· (2)
O3—C10—C9	111·6 (2)	C4—C5*—C6	149· (2)
O3—C11—C12	120·3 (3)	C4—C5*—N1*	98· (2)
O3—C11—C16	118·8 (2)	C6—C5*—N1*	109· (2)

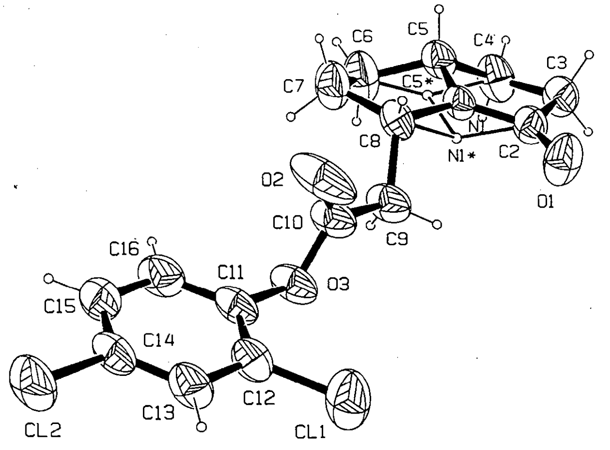

Fig. 1. A view of the $C_{15}H_{15}Cl_2NO_3$ structure. Ellipsoids are at the 50% level for the major isomer (2*a*); atoms N1* and C5* of the minor isomer (2*b*) are shown as spheres of arbitrary size.

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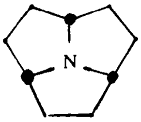
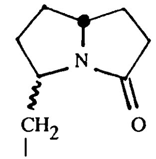
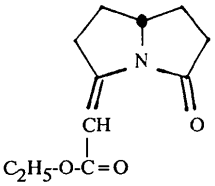
* Lists of structure factors, thermal parameters, calculated H-atom coordinates, mean planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52651 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the N atom is *ca* 0·20 Å from the plane of its substituents, there is no pyramidalization at N1 [angle sum 359·8 (2)°]; in (5) and (6) the corresponding angle sums at N are 355·7 (2) and 358·9 (2)° respectively.


(1)


(2*a endo*)
(2*b exo*)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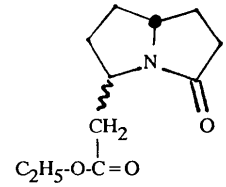
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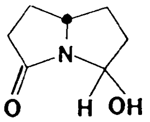
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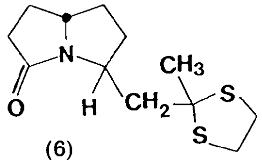
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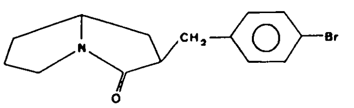
(7)

The molecular dimensions for (2*a*) are in accord with anticipated values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), and with the values found in (5) and in (6), with the same large external angle at C2—N1—C8 [131·6 (2)° in (2*a*), 128·0 (2)° in (5) and 130·7 (6)° in (6)]. The orientation of the —CH$_2$—C=O moiety at C8 is defined by the C8—C9—C10—O2 torsion angle (−33·0°) and is such that the carbonyl oxygen O2 is *cis* to the *exo* hydrogen at C8; such an orientation is well known for similar side chains (Mathieson, 1965). There are no unusual intermolecular contacts. Work is in progress on routes which may convert (2*a*) to (1).

We thank NSERC Canada for financial support through the award of an Operating Grant.

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Acta Cryst. (1990). C**46**, 1241–1244

Structure of *N*-(2,4-Dinitrophenyl)-4-(1-pyrrolyl)pyridinium Chloride Sesquihydrate

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(*Received* 26 *June* 1989; *accepted* 12 *September* 1989)

Abstract. $C_{15}H_{11}N_4O_4^+.Cl^-.1\cdot5H_2O$, $M_r = 373\cdot8$, monoclinic, $C2/c$, $a = 14\cdot970$ (3), $b = 13\cdot301$ (3), $c = 17\cdot544$ (4) Å, $\beta = 103\cdot30$ (2)°, $V = 3400$ (2) Å^3, $Z = 8$, $D_x = 1\cdot46$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2\cdot6$ cm^{-1}, $F(000) = 1544$, $T = 294$ K, $R = 0\cdot043$ for 2059 observed reflections. In the cation, the pyrrolyl and pyridinium rings are almost coplanar and the bond lengths are consistent with there being conjugation between them. The phenyl ring is inclined at 59·5° to the pyridinium plane. The chloride ion and water molecules are linked by a network of O—H···Cl hydrogen bonds 3·296 (3) to 3·428 (3) Å.

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