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Structure of Ethyl (3a*RS*,4a*SR*,5*RS*,6a*SR*,7a*SR*)-7-Benzyl-3-(*p*-chlorophenyl)-6-cyano-3a,4,4a,5,6,6a,7,7a-octahydrocyclobut[*b*]isoxazolo[4,5-*e*]pyridine-4a-carboxylate: a New Heterocyclic System

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Abstract. C₂₅H₂₄ClN₃O₃, $M_r = 449.84$, monoclinic, $P2_1/a$, $a = 17.021$ (4), $b = 11.100$ (3), $c = 12.177$ (3) Å, $\beta = 93.86$ (4)°, $V = 2295$ (1) Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.57$ cm⁻¹, $F(000) = 944$, $T = 293$ K, final conventional R is 0.055 for 1675 unique observed reflections. The *exo* configuration between the cyclobutane and the isoxazoline ring, as well as the *trans* configuration between the ethoxycarbonyl and the cyano group, supposed on the basis of NMR data, are confirmed. The piperidine ring adopts a twist-boat conformation.

Introduction. Our studies on the photocycloaddition of acrylonitrile on 1-benzyl-1,4-dihydronicotinamide (Adembri, Donati, Fusi & Ponticelli, 1985) and on ethyl 1-benzyl-1,4-dihydronicotinate (Adembri, Donati, Fusi & Ponticelli, 1987*a*) showed the site- and stereoselectivity of the reaction. Subsequent 1,3-dipolar addition of *p*-chlorobenzonitrile oxide on the two regioisomers obtained led, in high yield with stereo- and regioselectivity, to a new class of heterocyclic systems (Adembri *et al.*, 1987*a*). Some derivatives of these compounds show activity as non-competitive inhibitors of lactoperoxidase (Adembri *et al.*, 1987*b*). The X-ray crystallographic analysis of one of these compounds was undertaken in order to confirm the stereochemical assignments made in the preceding papers. The knowledge of the stereochemistry should be of interest both

from an organic and from a pharmacological point of view.

Experimental. Colourless prismatic crystals were obtained by slow hydration of an Me₂SO solution. Philips PW 1100 diffractometer, lattice parameters determined using 25 reflections with $5 \leq \theta \leq 9^\circ$, $2\theta < 50^\circ$, ω - 2θ scan technique, $-20 \leq h \leq 20$, $0 \leq k \leq 13$, $0 \leq l \leq 14$, 1675 unique reflections with $I \geq 3\sigma(I)$, three standard reflections (203, 113, 123), no significant variation of their intensity, L_p correction, no absorption correction, parallelepipedal crystal, $0.2 \times 0.3 \times 0.15$ mm. Structure solved by direct methods with *MULTAN80* system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); subsequent calculations by *SHELX76* system programs (Sheldrick, 1976) on the IBM 3081 at CNUCE (Pisa). The locations of all the H except those of the ethyl group were found by subsequent difference Fourier maps. The H atoms of the ethyl group were located geometrically before the refinement. Non-H atoms were refined with anisotropic thermal parameters, H atoms with a common isotropic temperature factor, $U = 0.073$ (4) Å²; the methyl group refined as a rigid body; refinement by full-matrix least squares minimizing $\sum w(F_o - F_c)^2$, 356 parameters, $R = 0.055$, $wR = 0.060$, $w^{-1} = \sigma^2(F) + 0.00394F^2$, $S = 1.06$, $(\Delta/\sigma)_{\max} = 0.17$ for non-H atoms. Max. and min. heights in the final

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Cl	696 (1)	-81 (2)	918 (1)	907 (8)
O(1)	3631 (2)	1446 (3)	6174 (3)	622 (14)
N(2)	3176 (3)	1521 (4)	5176 (3)	672 (14)
C(3)	2712 (3)	613 (4)	5068 (4)	887 (18)
C(3a)	2780 (3)	-248 (4)	6025 (4)	602 (17)
C(4)	2042 (3)	-338 (4)	6665 (4)	473 (14)
C(4a)	1929 (3)	812 (4)	7336 (4)	864 (24)
C(5)	1464 (3)	612 (6)	8374 (5)	588 (21)
C(6)	2245 (3)	593 (5)	9094 (5)	647 (26)
C(6a)	2667 (3)	1071 (5)	8093 (4)	554 (22)
N(7)	3366 (2)	410 (4)	7840 (3)	436 (16)
C(7a)	3486 (3)	268 (5)	6713 (4)	513 (20)
C(8)	4057 (3)	775 (5)	8548 (5)	581 (22)
C(9)	2487 (3)	-624 (6)	9472 (5)	441 (17)
N(10)	2659 (3)	-1559 (5)	9739 (5)	482 (18)
O(11)	1824 (2)	2860 (4)	6719 (4)	433 (17)
C(11)	1594 (3)	1854 (5)	6634 (5)	460 (18)
O(12)	990 (2)	1501 (3)	5966 (3)	485 (17)
C(13)	572 (4)	2436 (6)	5307 (6)	482 (18)
C(14)	39 (4)	1840 (8)	4492 (6)	629 (24)
C(31)	2201 (3)	470 (4)	4067 (4)	548 (18)
C(32)	1766 (3)	-575 (5)	3886 (4)	515 (20)
C(33)	1302 (3)	-735 (5)	2920 (5)	562 (20)
C(34)	1266 (3)	137 (6)	2127 (4)	781 (28)
C(35)	1690 (4)	1191 (6)	2285 (5)	779 (27)
C(36)	2140 (3)	1349 (5)	3249 (5)	844 (32)
C(81)	4764 (3)	-38 (5)	8453 (4)	717 (26)
C(82)	4732 (4)	-1228 (6)	8772 (5)	551 (21)
C(83)	5385 (5)	-1959 (6)	8703 (6)	603 (22)
C(84)	6055 (4)	-1533 (7)	8338 (6)	666 (25)
C(85)	6097 (4)	-338 (7)	8041 (7)	904 (29)
C(86)	5457 (4)	382 (6)	8108 (6)	974 (34)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

N(2)—O(1)	1.400 (5)	C(7a)—O(1)	1.491 (6)
C(3)—N(2)	1.281 (6)	C(7a)—N(7)	1.409 (6)
C(3)—C(3a)	1.505 (7)	C(8)—C(81)	1.515 (7)
C(4)—C(4a)	1.533 (7)	C(8)—N(7)	1.467 (6)
C(4)—C(3a)	1.527 (7)	C(9)—N(10)	1.120 (7)
C(4a)—C(6a)	1.535 (7)	C(9)—C(6)	1.477 (9)
C(4a)—C(5)	1.553 (7)	C(11)—O(11)	1.186 (6)
C(4a)—C(11)	1.526 (7)	C(11)—O(12)	1.325 (6)
C(6)—C(5)	1.543 (8)	C(13)—C(14)	1.458 (10)
C(6a)—C(6)	1.550 (7)	C(13)—O(12)	1.467 (6)
C(6a)—N(7)	1.449 (6)	C(31)—C(3)	1.458 (6)
C(7a)—C(3a)	1.528 (7)	C(34)—Cl	1.725 (5)
C(7a)—O(1)—N(2)	109.7 (3)	C(9)—C(6)—C(6a)	115.1 (5)
C(3)—N(2)—O(1)	110.0 (4)	C(6a)—C(6)—C(5)	88.6 (4)
C(31)—C(3)—N(2)	120.0 (4)	C(9)—C(6)—C(5)	113.6 (5)
C(3a)—C(3)—N(2)	113.9 (4)	N(7)—C(7a)—O(1)	111.7 (4)
C(31)—C(3)—C(3a)	126.1 (4)	C(3a)—C(7a)—O(1)	103.6 (4)
C(7a)—C(3a)—C(3)	101.7 (4)	N(7)—C(7a)—C(3a)	114.6 (4)
C(4)—C(3a)—C(3)	114.4 (4)	C(71)—N(7)—C(6a)	116.0 (4)
C(7a)—C(3a)—C(4)	112.8 (4)	C(8)—N(7)—C(7a)	116.1 (4)
C(4a)—C(4)—C(3a)	110.7 (4)	C(8)—N(7)—C(6a)	111.9 (4)
C(6a)—C(4a)—C(4)	110.5 (4)	C(81)—C(8)—N(7)	113.6 (4)
C(11)—C(4a)—C(4)	112.8 (4)	N(10)—C(9)—C(6)	178.4 (6)
C(11)—C(4a)—C(6a)	117.0 (4)	O(12)—C(11)—O(11)	124.7 (5)
C(5)—C(4a)—C(4)	113.8 (4)	O(12)—C(11)—C(4a)	111.4 (5)
C(6a)—C(4a)—C(5)	88.8 (4)	O(11)—C(11)—C(4a)	123.8 (5)
C(11)—C(4a)—C(5)	111.8 (4)	C(13)—O(12)—C(11)	117.0 (4)
C(6)—C(5)—C(4a)	89.9 (4)	C(14)—C(13)—O(12)	108.0 (6)
N(7)—C(6a)—C(4a)	115.3 (4)	C(35)—C(34)—Cl	119.7 (5)
N(7)—C(6a)—C(6)	115.1 (4)	C(33)—C(34)—Cl	120.0 (5)
C(6)—C(6a)—C(4a)	90.3 (4)		

Fourier synthesis 0.208 and $-0.127 e \text{\AA}^{-3}$. Atomic scattering factors from *SHELX76*.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Selected bonds and angles are given in Table 2. An *ORTEP* drawing (Johnson, 1965) with the atom-numbering scheme is shown in Fig. 1. The structure of the title compound consists of a Δ^2 -isoxazoline ring (*A*) and a cyclobutane ring (*C*) *cis*-fused to a piperidine ring (*B*). The *p*-chlorophenyl ring is coplanar with the O(1)—N(2)—C(3)—C(3a) plane of the isoxazoline ring: the torsion angle N(2)—C(3)—C(31)—C(36) is $-5.9 (5)^\circ$.

An *exo* configuration between rings *A* and *C* and a *trans* configuration between the ethoxycarbonyl and the cyano group are found. According to the puckering amplitudes (Cremer & Pople, 1975) reported in Table 3, the isoxazoline ring adopts an envelope conformation with C(7a) at the apex, and the cyclobutane ring deviates slightly from planarity. In addition, ring *B* assumes a conformation intermediate ($\varphi_2 = 12.6^\circ$) between a boat ($\varphi_2 = 0.0^\circ$) and a twist-boat (φ_2

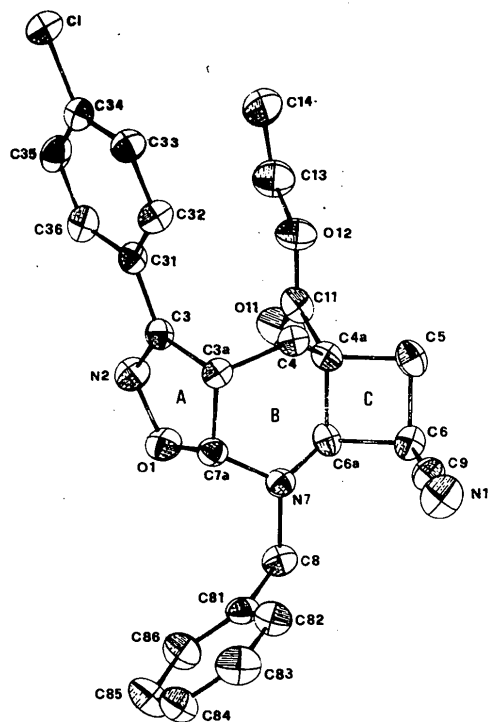


Fig. 1. Molecular structure of the title compound with numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

$= 30.0^\circ$). This conformation renders H(3a) synclinal with respect to H(4) and H(4'). The corresponding coupling constants in the $^1\text{H NMR}$ spectrum are consistent with this result. It is to be noted that the

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and non-essential bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51434 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Puckering parameters for the fused rings*

	A	B	C
q_1 (Å)	0.102 (6)	0.652 (5)	0.042 (2)
ϕ_1 (°)	140 (3)	12.6 (5)	
q_2 (Å)		-0.056 (5)	
Q_2 (Å)		0.654 (5)	
θ (°)		94.9 (5)	

methyl group of the ethoxycarbonyl moiety lies almost on the perpendicular axis of the *p*-chlorophenyl ring at 3.85 (1) Å from the least-squares plane. This feature may be correlated with the unusual chemical shift of the methyl protons ($\delta = 0.85$). This shielding effect is due to the diamagnetic anisotropy of the aromatic ring facing the methyl group. These observations assured us that the conformation of the system remains substantially unchanged in CDCl_3 solution.

Intermolecular distances shorter than the sum of the van der Waals radii are found for $\text{Cl}\cdots\text{Cl}(-x, -y, -z) = 3.154$ (4) Å and for $\text{C}(32)\cdots\text{O}(11)(0.5-x, y-0.5, 1-z) = 3.091$ (4) Å.

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Structure of 1-Adamantanylammonium Trinitromethide

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Abstract. $\text{C}_{11}\text{H}_{18}\text{N}_4\text{O}_6$, $M_r = 302.3$, orthorhombic, *Pnma*, $a = 23.802$ (9), $b = 8.431$ (3), $c = 7.166$ (2) Å, $V = 1438.0$ (8) Å³, $Z = 4$, D_m (floatation) = 1.37 (5), $D_x = 1.396$ g cm⁻³, m.p. 464 (1) K, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å (graphite monochromator), $\mu = 1.234$ cm⁻¹, $F(000) = 640$, $T = 293$ K, final $R = 0.048$ for 860 reflections with $I > 3\sigma(I)$. Both the adamantanylammonium cation and trinitromethide anion

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possess mirror symmetry. The cation is linked to three trinitromethide anions by six N–H \cdots O hydrogen bonds through the three ammonium hydrogens.

Introduction. There is considerable interest in the synthesis and chemistry of high density energetic materials (Alster, Iyer & Marchand, 1983/1984). The adamantane skeleton and nitro groups are attractive