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Structure of Linuron, 3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea

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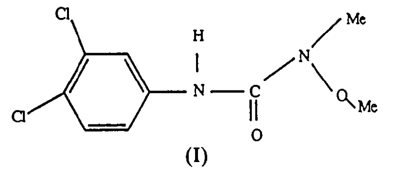
Abstract. $C_9H_{10}Cl_2N_2O_2$, $M_r = 249.1$, orthorhombic, $Pbc2_1$, $a = 6.133\,(1)$, $b = 8.834\,(2)$, $c = 20.653\,(3)$ Å, $Z = 4$, $V = 1119\,(1)$ Å^3, $D_m = 1.47$, $D_x = 1.48$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 52$ cm^{-1}, $F(000) = 512$, $T = 293$ K, $R = 0.030$ for 1123 reflections with $I > 3\sigma(I)$. The dihedral angle between the phenyl ring and the plane of the lateral chain is 21.9°.

Introduction. Linuron (I) is an active material used as a weedkiller. It is normally delivered to users under the form of a flowable concentrate which is a dense suspension of ground crystallites (2 to 5 μm) dispersed in a water and monopropylene glycol solution by using dispersing agents. Surfactants and other additives are added to stabilize the system and prevent the ripening of the solid particles. The particle size must remain unchanged for about two years despite the fact that temperature fluctuations induce dissolution of the smallest particles and growth of the largest ones. Prevention of ripening can be achieved only if some specific additives adsorb onto the crystal surfaces and block dissolution and growth. The number of ways of finding a good additive is limited and the most conventional involves speculation on the interactions between the crystal and additive molecules. A more suitable method is to explain and predict the efficiency of the additive on the basis of the interaction energies between the crystal surfaces and the additive molecules. However, in order to calculate these energies it is necessary to know the crystal morphology, the surface morphologies of the different crystal faces and consequently the crystal structure from which they can be deduced. This is why we undertook the structure determination of linuron.



(I)

Experimental. Linuron is industrially produced with a purity which is rarely better than 95%. The impurities present in the material disturb crystallization and prevent crystals suitable for X-ray diffraction measurements being obtained. Therefore, prior to any attempt at growing good crystals, several successive precipitations from ethanol were necessary to purify the material. After purification, linuron was dissolved at 313 K in an ethanol–water mixture (2:1 *v*/*v*). The concentrations were chosen so that, once the solutions were cooled to 293 K, the concentrations exceeded solubility (28.4 g l^{-1}) by 10 to 20%. Crystals obtained after a few hours or days, according to the supersaturation, were always elongated along the *b* axis. They could not be grown from pure water because the solubility (75 mg l^{-1} at 293 K) is too low.

The density, 1.47 g cm^{-3}, was measured by picnometry. The crystal used for the X-ray diffraction measurements was almost isometric with a mean dimension of 0.3 mm. The lattice parameters were determined by a least-squares procedure applied to the setting of 25 strong reflections in the range $0 < \theta < 45°$. Intensity data to maximum $\sin\theta/\lambda = 0.562$ Å^{-1} ($-5 \leq h \leq 5$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$) were measured with graphite-monochromated Cu $K\alpha$ radiation; intensities were measured by $\theta/2\theta$ scan with a scan speed of 10° min^{-1} and incremented by $\Delta\theta = 0.5 + 0.90\tan\theta$, on an Enraf–Nonius CAD-4 diffractometer. Three standard reflections (234, $\bar{1}46$, $\bar{2}36$) measured every hour showed a variation less than 3%. Systematic absences proved the space group to be $Pbc2_1$. After Lorentz and polarization corrections, the initial 9384 reflections (all equivalent reflections, $R_{\rm int} = 2.9\%$) were reduced to only 1123 nonequivalent observed data with $I > 3\sigma(I)$. No correction for absorption was made. The structure was solved by direct methods using *MULTAN*80 (Main,

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Table 1. *Atomic coordinates and equivalent isotropic thermal factors* (Å^2)

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

	x	y	z	B_{eq}
Cl(1)	0.0001 (4)	0.0348 (2)	0.5672	5.8
Cl(2)	−0.4515 (3)	−0.1191 (2)	0.5361 (1)	4.2
C(3)	−0.1396 (9)	0.0811 (5)	0.4995 (2)	2.9 (2)
C(4)	−0.3414 (8)	0.0141 (5)	0.4843 (2)	2.3 (1)
C(5)	−0.4598 (9)	0.0527 (5)	0.4315 (2)	2.7 (2)
C(6)	−0.3732 (9)	0.1625 (4)	0.3870 (3)	2.7 (2)
C(7)	−0.1694 (8)	0.2277 (5)	0.4013 (3)	2.6 (2)
C(8)	−0.0609 (8)	0.1848 (6)	0.4559 (3)	3.6 (2)
N(9)	−0.4893 (7)	0.2124 (4)	0.3348 (2)	3.0 (2)
C(10)	−0.6523 (8)	0.1373 (6)	0.3036 (2)	2.7 (2)
O(11)	−0.7187 (6)	0.0139 (3)	0.3170 (2)	3.3 (2)
N(12)	−0.7319 (8)	0.2113 (5)	0.2488 (3)	3.6 (2)
C(13)	−0.9465 (12)	0.1768 (8)	0.2256 (4)	5.7 (3)
O(14)	−0.6682 (7)	0.3669 (4)	0.2420 (2)	4.0 (2)
C(15)	−0.5480 (12)	0.3845 (8)	0.1839 (3)	5.0 (3)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°)

C(10)—N(9)	1.361 (6)	C(4)—Cl(2)	1.727 (5)
C(10)—O(11)	1.196 (6)	C(4)—C(5)	1.353 (6)
C(10)—N(12)	1.395 (7)	C(5)—C(6)	1.437 (7)
C(13)—N(12)	1.433 (9)	C(6)—C(7)	1.407 (7)
C(15)—O(14)	1.417 (8)	C(6)—N(9)	1.365 (6)
C(3)—Cl(1)	1.690 (5)	C(7)—C(8)	1.363 (8)
C(3)—C(4)	1.407 (6)	N(12)—O(14)	1.435 (7)
C(3)—C(8)	1.372 (7)		

N(12)—C(10)—O(11)	119.7 (5)	C(5)—C(6)—N(9)	122.0 (4)
N(9)—C(10)—O(11)	125.8 (5)	C(7)—C(6)—N(9)	119.8 (5)
C(4)—C(3)—Cl(1)	121.9 (4)	C(6)—C(7)—C(8)	119.6 (5)
C(4)—C(3)—C(8)	116.3 (4)	C(3)—C(8)—C(7)	123.8 (5)
C(8)—C(3)—Cl(1)	121.8 (4)	C(10)—N(12)—C(13)	119.5 (5)
C(3)—C(4)—Cl(2)	119.5 (4)	C(10)—N(12)—O(14)	115.6 (4)
C(3)—C(4)—C(5)	123.1 (4)	C(13)—N(12)—O(14)	114.9 (5)
C(5)—C(4)—Cl(2)	117.4 (4)	C(10)—N(9)—C(6)	126.8 (4)
C(4)—C(5)—C(6)	119.1 (4)	C(15)—O(14)—N(12)	109.2 (4)
C(5)—C(6)—C(7)	118.0 (5)		

C(5)—C(6)—N(9)—C(10)	−25.1 (8)	C(8)—C(3)—C(4)—C(5)	−3.0 (7)
C(7)—C(6)—N(9)—C(10)	160.0 (3)	C(5)—C(6)—C(7)—C(8)	0.4 (7)
C(10)—N(12)—O(14)—C(15)	119.1 (5)	Cl(2)—C(4)—C(5)—C(6)	−179.6 (2)
N(9)—C(10)—N(12)—C(13)	−157.5 (3)	C(6)—N(9)—C(10)—O(11)	−0.6 (8)
O(11)—C(10)—N(12)—C(13)	27.0 (8)	C(6)—N(9)—C(10)—N(12)	−175.7 (5)
C(13)—N(12)—O(14)—C(15)	−95.3 (5)	Cl(1)—C(3)—C(8)—C(7)	−178.8 (3)
C(3)—C(4)—C(5)—C(6)	2.7 (7)	C(8)—C(3)—C(4)—Cl(2)	179.4 (4)
C(6)—C(7)—C(8)—C(3)	−0.8 (8)	N(9)—C(6)—C(7)—C(8)	175.6 (3)
C(4)—C(3)—C(8)—C(7)	2.0 (8)	Cl(1)—C(3)—C(4)—Cl(2)	0.2 (6)
C(4)—C(5)—C(6)—C(7)	−1.3 (7)	N(9)—C(10)—N(12)—O(14)	−13.6 (6)
C(4)—C(5)—C(6)—N(9)	−176.4 (5)	O(11)—C(10)—N(12)—O(14)	170.9 (5)
Cl(1)—C(3)—C(4)—C(5)	177.8 (2)		

Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), with the theoretical geometry defined by *GenMol* (Pèpe & Siri, 1990) for calculating E values. The structure was refined by full-matrix least squares with anisotropic temperature factors for non-H atoms, and isotropic temperature factors blocked to $U = 0.05$ Å^2 for H atoms, and converged to $R = 0.030$, with $(\Delta/\sigma)_{max} = 0.21$ and $S = 0.72$. Maximum and minimum heights in the final difference Fourier synthesis were ± 0.18 e Å^{-3}. Anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The function minimized on 165 parameters was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1$. Calculations were performed with *SHELX76* (Sheldrick, 1976).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1* and the resulting bond lengths, bond angles and selected torsion angles are reported in Table 2. The numbering of the atoms is shown in Fig. 1. It is interesting to note the π-system deformation resulting from steric interactions between the lateral chain and the phenyl ring, which can be measured by the torsion angle at the junction bond level [atoms C(5), C(6), N(9), C(10), angle −25.1 (8)°] or by the dihedral angle between the phenyl ring and the mean plane of the chain [atoms N(9), C(10), O(11), N(12), C(13), O(14), angle 21.9 (7)°].

In Fig. 2, which displays the crystal along the a axis, it can be observed that π–π interactions are the dominant ones in the **b** direction (the elongation axis of the crystal), while in the other directions the contacts are of a van der Waals nature.

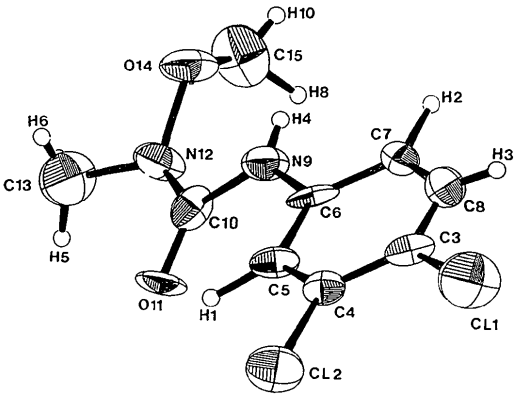

Fig. 1. Molecular view of 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea drawn using *ORTEP* (Johnson, 1965) with the thermal ellipsoids drawn at the 50% probability level. Spheres representing H atoms have arbitrary radii.

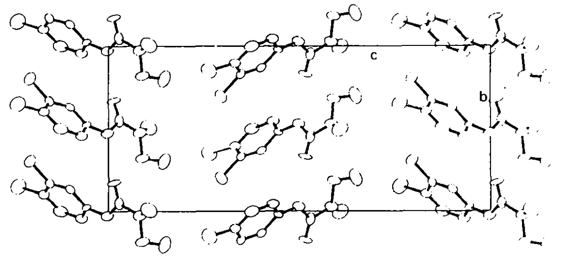

Fig. 2. Projection of the 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea crystal structure along the a axis.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55848 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1020]

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Structure of *cis*-1-{2-[(2-Butoxy)phenylcarbamoyloxy]cycloheptylmethyl}piperidinium Chloride

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Abstract. $C_{24}H_{39}N_2O_3^+.Cl^-$, $M_r = 439.0$, monoclinic, $P2_1/n$, $a = 11.749$ (7), $b = 7.083$ (4), $c = 28.763$ (21) Å, $\beta = 97.15$ (6)°, $V = 2375$ (3) Å^3, $Z = 4$, $D_m = 1.23$ (1), $D_x = 1.227$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.184$ mm^{-1}, $F(000) = 952$, $T = 293$ K, final $R = 0.060$ for 1624 unique observed reflections. The title compound, which is a potent local anaesthetic of the phenylcarbamate type, was designed to explore the stereostructural requirements of the anaesthetic receptor by locking the phenylcarbamate–amine link into a semirigid system. The mean planes of the piperidine (chair conformation) and the cycloheptane (twist-chair form) rings make a dihedral angle of 110.3 (4)° with each other. The lone pairs of electrons on the ether O atom and, to a lesser extent, on the amide N atom are delocalized through the adjacent aromatic system and there is an intramolecular hydrogen-bond interaction between the amidic N—H moiety and the ether O atom [N···O = 2.531 (3) Å]. The principal interaction between the cations and the chloride anions is an N^+—H···Cl^- hydrogen bond [N···Cl = 3.067 (3) Å].

Introduction. The title compound belongs to the phenylcarbamate class of local anaesthetics which are esters of 2-alkoxyphenylcarbamic acid with primary or secondary aminoalcohols. In order to explore the spatial relationship between primary anaesthesiophoric moieties (the phenylcarbamate and the ammonium groups), we report herein the crystal structure of the *cis* isomer of a semirigid derivative containing a central seven-membered ring system.

Experimental. Single crystals were grown from an ethanol solution. A colourless crystal of dimensions 0.20 × 0.25 × 0.50 mm was selected. D_m was determined by flotation. Systematic absences $k = 2n + 1$ for $0k0$ and $h + l = 2n + 1$ for $h0l$ were determined from Weissenberg photographs. A Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for the collection of the intensity data ($h = 0$ to 12, k = 0 to 7, $l = -30$ to 30). The unit-cell parameters and their e.s.d.'s were determined by a least-squares refinement of 15 reflections with $15 < 2\theta < 40$°. The θ–2θ scan mode was used with the scan rate ranging from 2.0 to 29.3° min^{-1}, depending on intensity. The background time to scan time used was 1.0, with a scan range from −1.0 to 1.0 (2θ) about the $K\alpha$ doublet. Two check reflections (11$\bar{3}$ and 3$\bar{1}\bar{3}$) were measured after every 100 reflections and only random fluctuation was observed. The intensities were corrected for Lorentz–polarization effects but not for absorption. Of the 3022 unique ($R_{\rm int} = 0.024$) reflections measured ($2\theta_{\max} = 45$°), 1624 with $I > 2\sigma(I)$ were considered observed. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by block-diagonal least-squares

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