Simonov, Gifeysman, Malinovsky, Andronati & Yavorsky, 1985). The second hydrogen atom of the NH_2 group is involved in intermolecular hydrogen bonding, which links the molecules in spirals around the 2_1 axis and whose parameters are: N(1)···O = 3·011, N(1)—H = 0·90, O(1)···H = 2·27 Å, N(1)—H—O(1) = 139° for the *exo* isomer and N(1)···O(1) = 3·056, N(1)—H = 0·91, O(1)···H = 2·26 Å, N(1)—H—O(1) = 146° for the *endo* isomer. The five-membered C(9)—C(12), N(3) ring is essentially planar (atomic deviations from the mean plane not exceeding 0·03 Å). The O atoms are displaced by 0·067 (*exo* isomer) and 0·112 Å (*endo* isomer) from this plane, both in the same direction. In the norbornene moiety the angles between planes C(10), C(11), C(13), C(16) and C(13), C(17), C(16), *i.e.* the flapping angles of the five-membered envelope rings, are 61·5 and 59·0° for the *exo* and *endo* isomers respectively, while the bending angles between planes C(10), C(11), C(13), C(16) and C(13)—C(16) in the six-membered rings are 70·4 and 112·7° for the *exo* and *endo* isomers respectively. The volumes occupied by the C(14)H, C(15)H and $C(17)H_2$ groups are rather close so that the molecular packing should change only insignificantly if the conformation of the norbornene fragment is changed, which is indicated by the great similarity in both crystal and molecular structures.

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Acta Cryst. (1987). C**43**, 2350–2353

Structure of *N*-(2-Chloroethyl)-2-furamide

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(*Received* 6 *February* 1987; *accepted* 10 *July* 1987)

Abstract. $C_7H_8ClNO_2$, $M_r = 173·60$, monoclinic, $P2_1/c$, $a = 9·348$ (3), $b = 9·887$ (3), $c = 9·693$ (5) Å, $\beta = 116·35$ (4)°, $V = 802·8$ (6) Å^3, $Z = 4$, $D_x = 1·436$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 4·21$ cm^{-1}, $F(000) = 360$, $T = 293$ K, final $R = 0·045$ for 914 observed reflections. The non-H atoms of the molecule, except the terminal C atom and the Cl atom attached to it, deviate within ±0·049 (5) Å from their mean plane. The exocyclic bond angles at the C(2) and C(5) atoms of the furan ring show marked differences: C—C(2)—C = 131·7 (4), C—C(2)—O = 119·0 (4) and H—C(5)—C = 130 (3), H—C(5)—O = 119 (3)°, respectively. These differences, common for furan compounds in the comparable range, may be due to possible rehybridization effects at the C(2) and C(5) atoms. The C=O and C(sp^2)—N bond lengths are 1·236 (4) and 1·337 (6) Å, respectively. The molecules are connected by N—H···O(=C) hydrogen bonds of 2·872 (5) Å in chains along the *c* axis.

Introduction. Compounds with one or more *N*-(2-chloroethyl) moieties show many pharmacological activities. They are cytotoxic (Bodenstein & Goldin, 1948), mutagenic (Auerbach & Moser, 1950), immunosuppressive (Skinner & Schartz, 1972) *etc.* For this reason they are called compounds with radiomimetic action (Dustin, 1947). Many of them are in use as drugs in chemotherapy of neoplastic diseases (Shephard & Harrp, 1982; Denny & Wilson, 1986).

Among others, *N*-(2-chloroethyl)-2-furamide has been synthetized (Vlahov, 1976) and tested on lymphohematopoietic cells (Vlahov, 1982; Vlahov & Volf, 1983).

In order to extend our knowledge about such furan derivatives the crystal structure of the title compound is presented.

Experimental. The compound was obtained by reaction of 2-chloroethylamine hydrochloride and furoyl chloride in water solution and characterized using elemental analysis and spectroscopic methods (Vlahov, 1976, 1982). Crystals suitable for X-ray examination were obtained by recrystallization from petroleum ether (b.p. 353–373 K). Intensity data collected from a crystal of dimensions 0·41 × 0·07 × 0·08 mm on a Philips PW 1100 four-circle diffractometer, θ–2θ scanning technique, scan width 1·20°, scan rate 0·04° s^{-1}. Unit-cell parameters obtained from least-squares analysis of 22 reflections with 2θ values ranging from 9 to 17°. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$, determined space group $P2_1/c$. Out of 1022 reflections scanned within a quadrant $\pm h,k,l$ (h 11–12; k 13; l 12), up to $(\sin\theta)/\lambda \leq 0{\cdot}70$ Å^{-1}, 967 unique reflections classified as observed. The intensities of three standard reflections ($30\bar{2}$, $3\bar{2}0$, $0\bar{1}3$) measured every 2 h showed a progressive decrease by an average of 25%. Corresponding scaling for reflection intensities was performed with the program *ZOAK*5 (Vicković & Sikirica, 1975) ordinarily used for processing diffractometer data. Corrections applied for Lorentz and polarization effects. No correction for absorption or extinction. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The E map calculated with 206 largest E values ($E \geq 1{\cdot}20$) revealed the positions of all non-H atoms. Subsequent calculations performed mainly with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). All H atoms located from a difference map. In final calculations 7 strong low-order reflections (020, 121, $\bar{2}21$, $\bar{3}21$, $\bar{2}31$, $\bar{2}02$, 012) strongly affected by extinction were rejected. Full-matrix least-squares refinement on F for 914 remaining reflections with $I > 2{\cdot}5\sigma(I)$ and anisotropic thermal parameters for non-H and isotropic for H atoms (132 parameters refined) gave $R = 0{\cdot}045$ and $wR = 0{\cdot}053$; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1{\cdot}00/\sigma^2(F_o)$ giving $S = 1{\cdot}44$; $(\Delta/\sigma)_{\max} < 0{\cdot}1$. Final difference map revealed residuals between −0·29 and 0·21 e Å^{-3}. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). All calculations performed on a Univac 1110 computer at the University Computing Centre in Zagreb.

Table 1. *Fractional positional parameters* (×10^4) *and equivalent isotropic temperature factors* (×10^2) *for non*-H *atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Cl	3031 (2)	1543 (2)	5059 (1)	8·03 (6)
O(1)	8932 (3)	1027 (3)	8048 (3)	5·0 (1)
O(2)	6701 (3)	3306 (3)	5002 (3)	4·5 (1)
N	6404 (4)	2757 (3)	7130 (4)	4·0 (1)
C(1)	7122 (4)	2658 (4)	6210 (4)	3·6 (2)
C(2)	8518 (4)	1774 (4)	6733 (4)	3·7 (1)
C(3)	9554 (5)	1522 (4)	6152 (5)	4·6 (2)
C(4)	10685 (5)	593 (4)	7145 (5)	5·1 (2)
C(5)	10268 (5)	316 (5)	8257 (5)	5·3 (2)
C(6)	4990 (5)	3551 (5)	6746 (5)	4·9 (2)
C(7)	3585 (5)	2726 (5)	6587 (5)	5·7 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *of non*-H *atoms and selected torsion angles* (°)

Cl—C(7)	1·775 (5)	C(1)—C(2)	1·461 (5)
O(1)—C(2)	1·372 (4)	C(2)—C(3)	1·342 (7)
O(1)—C(5)	1·368 (5)	C(3)—C(4)	1·409 (5)
O(2)—C(1)	1·236 (4)	C(4)—C(5)	1·327 (8)
N—C(1)	1·337 (6)	C(6)—C(7)	1·496 (7)
N—C(6)	1·437 (6)		
C(2)—O(1)—C(5)	106·1 (4)	C(1)—C(2)—C(3)	131·7 (4)
C(1)—N—C(6)	122·9 (3)	C(2)—C(3)—C(4)	107·3 (4)
O(2)—C(1)—N	123·4 (3)	C(3)—C(4)—C(5)	106·7 (4)
O(2)—C(1)—C(2)	119·9 (4)	O(1)—C(5)—C(4)	110·5 (4)
N—C(1)—C(2)	116·6 (3)	N—C(6)—C(7)	113·2 (4)
O(1)—C(2)—C(1)	119·0 (4)	Cl—C(7)—C(6)	111·3 (4)
O(1)—C(2)—C(3)	109·3 (3)		
O(1)—C(2)—C(1)—O(2)	−177·7 (3)	O(2)—C(1)—N—C(6)	4·9 (5)
O(1)—C(2)—C(1)—N	5·0 (4)	C(2)—C(1)—N—C(6)	−177·9 (3)
C(3)--C(2)—C(1)—N	−175·0 (4)	C(1)—N—C(6)—C(7)	117·5 (5)
C(3)—C(2)—C(1)—O(2)	2·2 (6)	N—C(6)—C(7)—Cl	−62·7 (4)

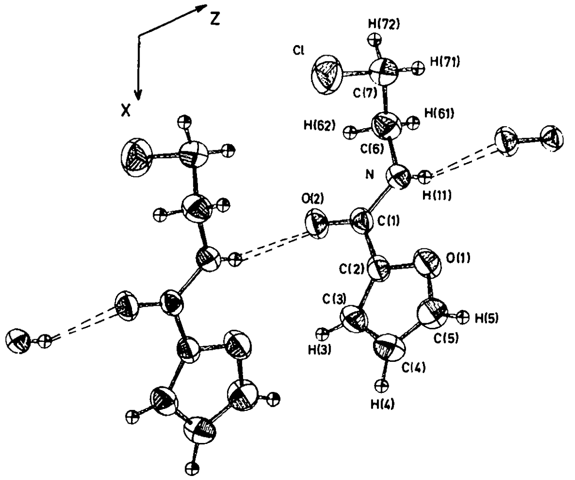

Fig. 1. An *ORTEP* diagram (Johnson, 1965) showing a chain of molecules connected by N—H···O hydrogen bonds viewed along **b** and the atom numbering. Ellipsoids are at the 50% probability level.

Discussion. The final atomic parameters are listed in Table 1* and bond lengths and angles with selected torsion angles in Table 2. Fig. 1 is a projection of the structure viewed along **b** showing a chain of the molecules connected by N—H···O hydrogen bonds and atom numbering.

The furan ring does not show any unusual features. It is planar within ±0·005 (5) Å. The two C=C bond lengths are 1·342 (7) and 1·327 (8) Å while C(3)—C(4) is a partial double bond length of 1·409 (5) Å. The exocyclic bond angles at the C atoms bonded to the O(1) atom show characteristic significant differences (Fig. 1, Table 2): the angle C(1)—C(2)—C(3) [131·7 (4)°] is larger than C(1)—C(2)—O(1) [119·0 (4)°] as well as H(5)—C(5)—C(4) [130 (3)°] which is larger than H(5)—C(5)—O(1) [119 (3)°]. Similar angle differences are characteristic of furan itself (Fourme, 1972; Mata, Martin & Sørensen, 1978) as well as its derivatives. Different substituents at the C(2) and C(5) atoms do not change essentially the difference between the exocyclic angles (Galešić, Vlahov & Galešić, 1987, Table 3). A possible explanation for this characteristic angle difference is given below in terms of the rehybridization effects at the C(2) and C(5) atoms.

In the furan molecule itself (Fourme, 1972), the symmetrically identical C atoms bonded to the O atom are generally sp^2 hybridized, but there are considerable differences between the hybrid orbitals describing their three different bonds. The population of the *p* orbital of an atom between its hybrid orbitals is increased in the region of the bond to the more electronegative atom (Domenicano, Vaciago & Coulson, 1975, and references therein). In this way, the hybrid orbital of the furan C(2) atom directed toward O(1) is very rich in *p* content and consequently poor in *s* content. The *s* character is mainly shared between the hybrid orbitals of the C(2)—C(3) and C(2)—H(2) bonds. This is the reason for the relatively large H(2)—C(2)—C(3) angle of 134 (2)° in furan. On the other hand, the corresponding endocyclic angle at the C(2) atom of 106·2 (6)° is primarily governed by the five-membered-ring geometry. We can illustrate our conclusions by very simple calculations. From the given angles, assuming that the hybrids on one centre are orthonormal (Maksić, 1986) and following the bond directions perfectly, the hybridization related to these bonds can be calculated. From the geometry of furan again (Fourme, 1972), the hybrid orbitals for the furan C(2)—C(3), C(2)—H(2) and C(2)—O(1) bonds were calculated to be $sp^{1\cdot8}$, $sp^{1\cdot2}$ and $sp^{4\cdot4}$, respectively, where the numbers are the ratios of the *p* and *s* populations of the corresponding hybrids. As can be seen the *s* character of the C(2)—C(3) hybrid is slightly increased when compared with ideal sp^2 hybridization, the greatest *s* character is in the C(2)—H(2) hybrid orbital and as expected the hybrid toward the O atom has the greatest amount of *p* character.

A substituted atom *R′* (belonging to a substituent *R*) attached to the C(2) or C(5) atom cannot change much the ratio between two corresponding exocyclic angles. For example, an electronegative *R′* substituted at the C(2) atom takes some of the *p* character from other hybrid orbitals, but more from the C(2)—C(3) hybrid orbital than from the hybrid orbital directed towards the O(1) atom. So the angle between the C(2)—C(3) hybrid orbital, rich in *s* content, and the C(2)—*R′* orbital remains large. The angle between the hybrid orbital directed towards the substituted atom *R′* and the orbital directed towards the O(1) atom remains small, as the angle between two orbitals rich in *p* content. Thus the ratio between the exocyclic angles does not change essentially.

Another approach to the explanation of the exocyclic-angle difference at the C(2) or C(5) atom is to consider possible asymmetric release of *R′*···O and *R′*···C(3) or *R′*···C(4) repulsions (Leiserowitz & Rabinovich, 1969). As we pointed out previously (Galešić, Vlahov & Galešić, 1987), we could not discern from available literature data any clear correlation between different substituted atoms *R′* and the exocyclic angles at the C(2) or C(5) atoms. In connection with this approach the relevant nonbonding contacts of the present structure are: C(1)···O(1) 2·441 (4), C(1)···C(3) 2·558 (6) and H(5)···O(1) 2·02, H(5)···C(4) 2·08 (4) Å. For evaluation of both approaches it would be of interest to know the structures of furan derivatives with *R′* = O or F, *i.e.* of the derivatives with the substituents at the C(2) or C(5) atoms of the furan ring having the same or stronger electronegativity with respect to the O(1) atom. Such a project is in progress.

Comparison of the above structure and the structure of *N*-(2-hydroxyethyl)-2-thiofuramide in the previous work reveals congruities of furan-ring bond lengths and endocyclic bond angles within limits of the e.s.d.'s.

The amide C(1) atom and the atoms bonded to it show a slight pyramidal arrangement with the C(1) atom in apical position. The atom displacements from the mean plane through the C(1), C(2), N, O(2) atoms are: C(1) −0·014 (4), C(2) 0·004 (4), N 0·005 (3), O(2) 0·005 (3) Å. The C(1)=O(2) and partial double bond C(1)—N lengths of 1·236 (4) and 1·337 (6) Å, respectively, are usual for amide groups (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980). Most of the molecule, including the non-H atoms of the furan ring, the amide group and the C(6) atom is, as in the

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* Lists of structure factors, anisotropic thermal parameters, mean planes, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44231 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure of *N*-(2-hydroxyethyl)-2-thiofuramide, approximately planar, deviating from planarity within ±0·049 (5) Å. Consequently, the torsion angles along the C(1)—C(2) and C(1)—N bonds are close to 0 or 180°. The intramolecular contact N···O(1) of 2·727 (4) Å with the H(11)···O(1) separation of 2·36 (4) Å might be considered as a hydrogen bond in spite of the relatively small N—H(11)···O(1) angle of 110 (4)°.

There are N—H···O intermolecular hydrogen bonds of 2·872 (5) Å with an H···O separation of 2·17 (4) Å and N—H···O angles of 150 (4)°. They connect the molecules in chains parallel to the *c* axis (Fig. 1).

The authors thank M. Bruvo MSc for collecting the diffractometer data. This investigation was supported by the Research Council of Croatia.

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Acta Cryst. (1987). C**43**, 2353–2355

Structure of 1,6-Cyclodecanedione Bis[(*o*-nitrophenyl)hydrazone]

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(*Received* 4 *November* 1985; *accepted* 13 *July* 1987)

Abstract. $C_{22}H_{26}N_6O_4$, $M_r = 438·49$, monoclinic, $P2_1/c$, $a = 7·889$ (2), $b = 14·335$ (4), $c = 10·117$ (2) Å, $\beta = 110·83$ (2)°, $V = 1069·3$ Å^3, $Z = 2$, $D_m = 1·356$, $D_x = 1·362$ Mg m^{-3}, m.p. = 451–455 K, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·1039$ mm^{-1}, $F(000) = 464$, $T = 298$ K, final $R = 0·080$ for 1107 independent reflections. The molecule has crystallographic $\bar{1}$ (C_i) symmetry and is made up of two planar (*o*-nitrophenyl)hydrazone ligands attached at the 1,6-positions of the ten-membered ring in *trans* form. The central ten-membered ring has approximate $2/m$ symmetry and boat–chair–boat conformation, which is energetically the most stable. As in other compounds with a ten-membered ring, the endocyclic bond angles [114·7 (10)–119·1 (8)°] are considerably larger than the usually accepted value of 112·7° in normal paraffins, indicating strain in the ring. The bond distances and angles are in good agreement with literature values.

Introduction. Molecules containing ten-membered rings are of great interest, because of physical and chemical

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