The Structure of 1,3-Dihydro-4-[(2S)-2,5-dihydro-2-furyl]-3-methyl-1-p-tolyl-2H-imidazole-2-thione, C₁₅H₁₆N₂OS

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Abstract. $M_r = 272$, monoclinic, $P2_1$, $a = 6.033$ (1), $b = 7.488$ (1), $c = 15.563$ (2) Å, $\beta = 99.55$ (5)°, $V = 693.3$ Å³, $Z = 2$, D_m(flotation in benzene/CCl₄) = 1.29, $D_x = 1.30$ Mg m⁻³, graphite-monochromated Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.21$ mm⁻¹, $F(000) = 288$, $T = 293$ K, final $R = 0.047$ for 1695 reflections. The furanose ring is approximately planar owing to the presence of the C(13)=C(14) double bond. The dihedral angles between the phenyl and dihydroimidazole and furanose and dihydroimidazole rings are 55.2 (2) and 99.1 (2)°. The packing of the molecules is governed by van der Waals contacts.

Introduction. The crystal structure of the title compound has been determined as part of an investigation of the conformational properties of imidazole-C-nucleosides.

The compound (II) has been obtained by reaction of 4-(2,3-di-O-tosyl-α-D-erythrofuranosyl)-1,3-dihydro-3-methyl-1-p-tolyl-2H-imidazole-2-thione (I) with sodium iodide and zinc powder in N,N-dimethylformamide.
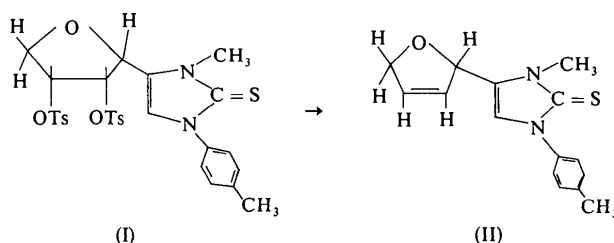
A previous NMR study showed an approximately planar conformation for the furanose ring (Fernandez-Bolaños, Fuentes-Mota & Fernandez-Bolaños Guzman, 1983).

Experimental. Yellowish crystal, 0.35 × 0.50 × 0.15 mm, $\omega/2\theta$ scan, Nonius CAD-4 diffractometer; lattice parameters from least-squares fit of 25 reflections in range $5.3 < \theta < 14.0°$; two standard reflections recorded every 100 min, only random deviations; 2156 reflections, $2\theta < 60°$, $\pm h$, $+k$, $+l$; 1695 with $I \geq 2\sigma(I)$; no absorption correction; systematic absences: 0k0, $k = 2n + 1$, space group $P2_1$; crystal

structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and subsequent difference Fourier syntheses; refinement by full-matrix least squares with anisotropic temperature factors for all non-H atoms, common isotropic temperature factors for H; refinement based on F and 220 parameters, $R = 0.047$, $w = 1/\sigma^2(F)$; max. Δ/σ for all parameters 0.08, av. 0.02; H atoms placed in geometrically calculated positions (C–H 1.08 Å, equal C–C–H) and allowed to ride on C atom to which they are attached; atomic scattering factors from *International Tables for X-ray Crystallography* (1962); all calculations carried out with the *XRAY* system (Stewart, Kundell & Baldwin, 1970); max. residual electron density in final difference map ± 0.3 e Å⁻³. y coordinate of S(1) held fixed to define the origin. Bond lengths and angles involving non-hydrogen atoms are given in Fig. 1. The absolute configuration is known from chemical source.

Discussion. Positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1.* The phenyl group is planar, maximum deviation from the best plane 0.009 (5) Å, with average C–C bond 1.384 (5) Å. The two substituent atoms, C(10) and N(1), are at −0.039 and 0.007 Å
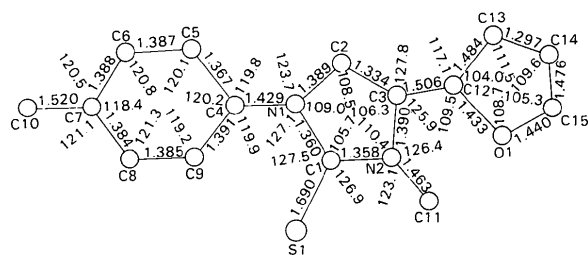

Fig. 1. Interatomic distances (Å) and bond angles (°). Mean standard deviations 0.005 Å and 0.4°.

Table 1. *Atomic parameters for* 1,3-*dihydro*-4-[(2S)-2,5-*dihydro*-2-*furyl*]-3-*methyl*-1-*p*-*tolyl*-2H-*imidazole*-2-*thione* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

For non-H atoms $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i a_j\cos(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	U_{eq}
S(1)	4258 (2)	6531	2408 (1)	59 (1)
O(1)	6560 (5)	12610 (6)	637 (1)	65 (2)
N(1)	4466 (5)	10012 (4)	2957 (2)	37 (1)
N(2)	6153 (5)	9540 (5)	1853 (2)	41 (1)
C(1)	4977 (6)	8713 (5)	2411 (2)	39 (1)
C(2)	5339 (6)	11626 (6)	2727 (2)	40 (1)
C(3)	6360 (6)	11353 (6)	2041 (2)	40 (1)
C(4)	3363 (6)	9791 (5)	3695 (2)	36 (1)
C(5)	4388 (6)	10363 (6)	4497 (2)	41 (1)
C(6)	3321 (6)	10165 (6)	5215 (2)	40 (1)
C(7)	1205 (6)	9392 (5)	5131 (2)	40 (1)
C(8)	169 (7)	8858 (6)	4311 (2)	43 (1)
C(9)	1228 (7)	9036 (6)	3591 (2)	42 (1)
C(10)	62 (8)	9146 (7)	5923 (3)	54 (1)
C(11)	7116 (8)	8588 (8)	1181 (3)	61 (2)
C(12)	7484 (7)	12715 (7)	1545 (2)	48 (1)
C(13)	9941 (7)	12525 (9)	1568 (3)	63 (1)
C(14)	10447 (8)	12535 (9)	790 (3)	71 (2)
C(15)	8372 (9)	12674 (10)	141 (3)	77 (2)
H(1C10)	91 (9)	974 (8)	643 (3)	50 (17)
H(2C10)	−6 (9)	812 (9)	610 (4)	63 (19)
H(3C10)	−129 (10)	971 (9)	587 (4)	73 (21)
H(1C11)	651 (10)	944 (9)	57 (4)	73 (20)
H(2C11)	623 (11)	737 (10)	105 (4)	103 (26)
H(3C11)	857 (11)	860 (10)	123 (4)	78 (21)
H(C2)	515 (6)	1246 (6)	305 (2)	6 (10)
H(C5)	569 (6)	1081 (6)	452 (2)	16 (11)
H(C6)	402 (5)	1052 (5)	573 (2)	0 (8)
H(C8)	−130 (7)	834 (6)	425 (3)	22 (12)
H(C9)	81 (8)	858 (7)	309 (3)	39 (15)
H(C12)	707 (6)	1372 (6)	176 (2)	10 (10)
H(C13)	1091 (8)	1260 (8)	209 (3)	46 (15)
H(C14)	1202 (8)	1267 (8)	63 (3)	41 (15)
H(1C15)	820 (9)	1342 (8)	−24 (4)	47 (17)
H(2C15)	792 (9)	1171 (9)	−40 (3)	49 (16)

from the phenyl plane. The C(10)—C(phenyl) 1·520 (6) Å and the inter-ring distance C(4)—N(1) of 1·429 (5) Å agree with those in analogous compounds (Pérez-Garrido, Conde & Márquez, 1974; Barragan, López-Castro & Márquez, 1977).

Dihydroimidazole ring. The value of 1·690 (5) Å observed for the bond length S(1)—C(1) is intermediate between the S—C single-bond distance of 1·81 Å and the double-bond value of 1·56 Å. This partial double-bond character is in agreement with the canonical resonance forms of the thiourea system and is a normal feature of these compounds. The average distances C(1)—N(1) and C(1)—N(2) of 1·359 (5), N(2)—C(3) and N(1)—C(2) of 1·389 (6) Å and the C(2)—C(3) distance of 1·334 (5) Å agree quite well with the mean values reported for analogous compounds (Conde, López-Castro & Márquez, 1978; Criado, Conde & Márquez, 1983). The dihydroimidazole ring is planar, maximum deviation from the least-squares plane 0·006 (5) Å. The four substituents S(1), C(11), C(12) and C(4) are 0·037 (2), −0·069 (5), 0·050 (5) and −0·079 (4) Å from the best plane. The C(11)—N(2) and C(12)—C(3) distances are 1·463 (6) and 1·506 (6) Å. The average angles C—N—C, N—C—C are 109·7 (5) and 107·4 (5)°. The N—C—N angle is 105·7 (3)°.

Furyl ring. This compound represents one of the first structural studies of an unsaturated pentafuranose ring and as expected the presence of the C(13)=C(14) double bond has a marked effect on the geometry. The $C(13)_{sp^2}=C(14)_{sp^2}$ double bond has a length of 1·297 (7) Å and is significantly shorter than the normal C=C bond of 1·337 (6) Å (*International Tables for X-ray Crystallography*, 1962). There is no apparent reason for this short bond but bonds of a similar length have been found [1·31 (2) Å, Galloy & Watson (1983) and 1·295 (6) Å, Mazhar-ul-Haque, Ahmed & Horne (1983)]. The C(14)—C(15) and C(12)—C(13) bonds of 1·476 (6) and 1·484 (6) Å are similar to those of 1·493 Å in L-ascorbic acid (Azarnia, Berman & Rosenstein, 1972). The C—O bonds are 1·433 (5) and 1·440 (6) Å and the average O—C—C angle is 104·7 (4)°. The five-membered ring is approximately planar, with maximum deviation from the mean-square plane −0·046 (6) Å. In terms of ring-puckinger coordinates (Cremer & Pople, 1975) the amplitude and phase magnitudes are $Q = 0·089$ (6) Å and $\varphi = 10$ (4)° for the sequence O(1)C(12)C(13)C(14)C(15), which corresponds to the $^3T_2$ conformation.

The dihedral angle between phenyl and dihydroimidazole rings is small (values found range from 60 to 80°) and could be indicative of a contribution of crystal forces to the phenyl–dihydroimidazole rotation. Table 2 shows the main torsion angles.

The crystal packing, as viewed along **b**, is depicted in Fig. 2; it is determined by van der Waals contacts.

Table 2. *Selected torsion angles* (°)

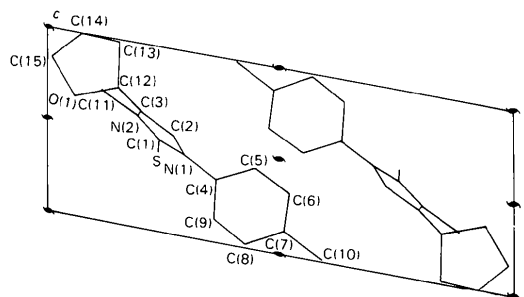|	
C(1)—N(2)—C(3)—C(12)	−177·8 (4)
C(11)—N(2)—C(3)—C(12)	4·6 (7)
C(13)—C(12)—C(3)—C(2)	116·0 (6)
C(1)—N(1)—C(4)—C(5)	123·2 (5)
O(1)—C(12)—C(3)—C(2)	−125·9 (5)

Fig. 2. A view along [010] of the unit-cell contents.

References

AZARNIA, N., BERMAN, H. M. & ROSENSTEIN, R. D. (1972). *Acta Cryst.* B28, 2157–2167.

BARRAGAN, I., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1977). *Acta Cryst.* B33, 2244–2248.

CONDE, A., LÓPEZ-CASTRO, A. & MÁRQUEZ, R. (1978). *Rev. Iberoam. Crystallogr. Mineral. Metalogen.* 1, 23–36.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* 97, 1354–1358.

CRIADO, A., CONDE, A. & MÁRQUEZ, R. (1983). *Acta Cryst.* C39, 122–125.

FERNANDEZ-BOLAÑOS, J., FUENTES-MOTA, J. & FERNANDEZ-BOLAÑOS GUZMAN, J. M. (1983). *An. Quím.* 79, 345–349.

GALLOY, J. & WATSON, W. H. (1983). *Acta Cryst.* C39, 348–350.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MAZHAR-UL-HAQUE, AHMED, J. & HORNE, W. (1983). *Acta Cryst.* C39, 383–385.

PÉREZ-GARRIDO, S., CONDE, A. & MÁRQUEZ, R. (1974). *Acta Cryst.* B30, 2348–2352.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* System. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Structure of (E)-3-(2-Methoxyphenyl)-1-phenyl-3-(1H-1,2,4-triazol-1-yl)-2-propen-1-one, C₁₈H₁₅N₃O₂

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Abstract. $M_r = 305.3$, $P2_12_12_1$, $a = 15.020$ (5), $b = 14.537$ (5), $c = 7.169$ (3) Å, $V = 1565.3$ Å³, $Z = 4$, $D_m = 1.32$ (2), $D_x = 1.30$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.51$ cm⁻¹, $F(000) = 640$, room temperature, final $R = 0.064$ for 1092 reflections classed as observed. The α,β-unsaturated carbonyl function is nearly planar and adopts a *cis* conformation. The methoxyphenyl ring is twisted by 59 (1)° out of the plane containing the carbon–carbon double bond while the triazolyl ring, which shows significant delocalization, lies almost in that plane. The unsubstituted phenyl ring is almost coplanar with the carbonyl group. The exocyclic angles of the triazolyl ring are very asymmetric with C–N–C [129.9 (6)°] significantly larger than C–N–N [122.4 (6)°].

Introduction. The title compound is one of a series of γ-ketotriazoles (Balasubramanyan & Lewis, 1976) that are good pre-emergence herbicides. We have determined its crystal structure to establish its conformation in the solid state as part of a programme to study the relationship between conformation and biological activity in this class of herbicides. We have previously reported the crystal structure of an analogue of the title compound, (E)-4,4-dimethyl-1-(1-naphthyl)-1-(1H-1,2,4-triazol-1-yl)pent-1-en-3-one (Branch & Nowell, 1985).

Experimental. Recrystallization from methanol:petrol 40–60 (1:2); D_m by flotation in carbon tetrachloride:petrol 60–80; crystal, yellow hexagonal prism, approximate dimensions $0.50 \times 0.40 \times 0.40$ mm, mounted about crystallographic c axis; Stoe Stadi-2 two-circle diffractometer; Lorentz, polarization but no absorption corrections applied; one standard reflection monitored for each layer collected, intensity variation < 3%; 2343 reflections up to $\sin\theta/\lambda = 0.70$ Å⁻¹, index ranges $h = 0$ to 20, $k = 0$ to 20, $l = 0$ to 9; 2331 independent reflections of which 1092 with $I > 3\sigma(I)$ considered observed; structure solved by multisolution direct methods; blocked-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 3.5939/[\sigma^2(F_o) + 0.0007(F_o)^2]$, of atomic coordinates and anisotropic temperature factors for all non-H atoms, isotropic temperature factors for all H atoms; H(5) located by difference synthesis but positional parameters not refined, remaining H atoms included in positions calculated from geometry of molecule (C–H = 1.08 Å); final $R = 0.0640$, $wR = 0.0880$; max. $(\Delta/\sigma) = 1.97$; min. $\Delta\rho = -0.24$, max. $\Delta\rho = 0.31$ e Å⁻³; no correction for secondary extinction; scattering factors calculated from analytical approximation (*International Tables for X-ray Crystallography*, 1974); computer programs *SHELX* (Sheldrick, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Final value of $U = 0.093$ (28) Å² refined for H(5) while common isotropic temperature factors applied to methyl, phenyl

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