

Structure of Ethyl [3-(4-chlorophenyl)-5-methyl-4H-1,2,4-triazol-4-yl]carbamate

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The title compound, C₁₂H₁₃ClN₄O₂, was prepared by the reaction of ethyl 2-(1-ethoxyethylidene)hydrazinecarboxylate with 4-chlorobenzohydrazide. The molecular structure and packing are stabilized by an N-H...N intermolecular hydrogen-bond and a partial π - π overlap of the aromatic rings.

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Triazoles are one important class of heterocyclic compounds with important biological and pharmacological properties. A wide range of substituted triazole derivatives exhibit biological activities, such as herbicides, bactericides, pesticides and fungicides.^{1,2} The title compound (I, Fig. 1) was synthesized to investigate its possible biological activities. The two-step synthesis of I involves, first, amide formation, and then cyclization reactions. In a 50 ml round-bottom flask fitted with a magnetic stir bar, 0.870 g (5 mmol) of ethyl 2-(1-ethoxyethylidene)hydrazinecarboxylate, which was prepared according to a literature procedure,³ was mixed with 0.853 g (5 mmol) of 4-chlorobenzohydrazide (Fluka). The mixture was heated to melt in an oil bath at around 110 - 115°C and refluxed for an additional 2 h at 130°C. Thereafter, the mixture was allowed to cool to the room temperature to give a colorless, viscous oil. A 5 ml portion of petroleum ether was added to the flask and left standing overnight at 0 - 2°C. The precipitate was filtered and washed with alcohol, dried *in vacuo* and recrystallized from dichloromethane/abs. ethanol (1:1 v/v) to give 0,754 g of I (54% yield); m.p., 192 - 193°C.

A colorless block crystal of I having approximate dimensions of 0.50 × 0.40 × 0.20 mm was selected for X-ray diffraction studies. The crystal and experimental data are given in Table 1.

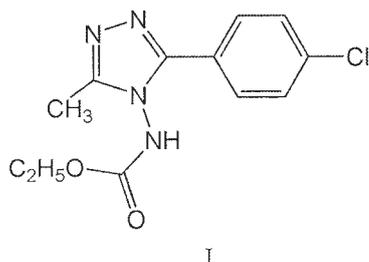


Fig. 1 Chemical structure of I.

The atomic coordinates and equivalent isotropic displacement parameters are presented in Table 2. All non-hydrogen atoms were refined anisotropically. All H atoms were fixed geometrically, except for H12, which was located from a difference Fourier map and refined isotropically. Geometrically fixed H atoms were allowed to ride on their corresponding parent atoms with C-H distances in the range of 0.93 - 0.97 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ of the parent atom for the methyl groups and $1.2U_{eq}(C)$ for the remainder. The methyl group attached to C10 exhibits a disorder of the H-atoms. It was

Table 1 Crystal and experimental data

| | |
|--|---|
| Empirical formula: | C ₁₂ H ₁₃ ClN ₄ O ₂ |
| Formula weight: | 280.71 |
| Wavelength: | 0.71073 Å |
| Temperature: | 295(2)K |
| Space group: | <i>P</i> 2 ₁ / <i>a</i> <i>Z</i> = 4 |
| <i>a</i> = | 12.2846(6)Å |
| <i>b</i> = | 10.6712(4)Å β = 117.903(2)° |
| <i>c</i> = | 12.4322(5)Å |
| <i>V</i> = | 1440.28(11)Å ³ |
| <i>D</i> _x = | 1.295 g/cm ³ |
| No. of reflections used = | 3983 |
| 2 θ _{max} = | 60.2° with Mo <i>K</i> α |
| <i>R</i> = | 0.082 |
| (Δ / σ) _{max} < | 0.003 |
| ($\Delta\rho$) _{max} = | 0.30 eÅ ⁻³ |
| ($\Delta\rho$) _{min} = | -0.26 eÅ ⁻³ |
| Measurement: | Rigaku RAXIS-RAPID S area-detector diffractometer |
| Data collection and cell refinement: | PROCESS |
| Structure determination: | direct method (SIR92) |
| Structure refinement: | full matrix least squares on <i>F</i> ² (SHELXL97) |
| Molecular graphics: | ORTEP-3 for Windows and PLUTON |
| Publication material: | WinGX |

CCDC 672056 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2 Atomic coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

| Atom | x | y | z | U_{eq} |
|------|-------------|--------------|-------------|------------|
| C11 | 0.35144(9) | 0.02449(10) | 0.84581(9) | 0.0914(3) |
| N8 | 0.66022(19) | 0.25150(17) | 0.56003(19) | 0.0529(5) |
| N9 | 0.73929(19) | 0.24632(17) | 0.50820(19) | 0.0535(5) |
| N11 | 0.74796(18) | 0.06767(16) | 0.59540(17) | 0.0470(4) |
| N12 | 0.7898(2) | -0.04890(16) | 0.64708(19) | 0.0533(5) |
| O14 | 0.9230(2) | -0.16744(16) | 0.79300(16) | 0.0719(6) |
| O18 | 0.9240(3) | 0.04126(18) | 0.82410(19) | 0.0913(8) |
| C1 | 0.4467(3) | 0.0564(3) | 0.7810(2) | 0.0607(6) |
| C2 | 0.4719(3) | -0.0366(2) | 0.7194(2) | 0.0611(6) |
| C3 | 0.5462(3) | -0.0102(2) | 0.6663(2) | 0.0568(6) |
| C4 | 0.5960(2) | 0.1093(2) | 0.6753(2) | 0.0482(5) |
| C5 | 0.5692(2) | 0.2010(2) | 0.7392(2) | 0.0567(6) |
| C6 | 0.4953(3) | 0.1752(3) | 0.7916(2) | 0.0629(6) |
| C7 | 0.6672(2) | 0.14344(18) | 0.6125(2) | 0.0463(5) |
| C10 | 0.7916(2) | 0.1362(2) | 0.5311(2) | 0.0500(5) |
| C13 | 0.8847(3) | -0.0494(2) | 0.7617(2) | 0.0595(6) |
| C15 | 1.0229(4) | -0.1849(3) | 0.9161(3) | 0.0979(12) |
| C16 | 1.1425(5) | -0.1667(7) | 0.9202(6) | 0.175(3) |
| C17 | 0.8804(3) | 0.0880(3) | 0.4921(3) | 0.0681(7) |

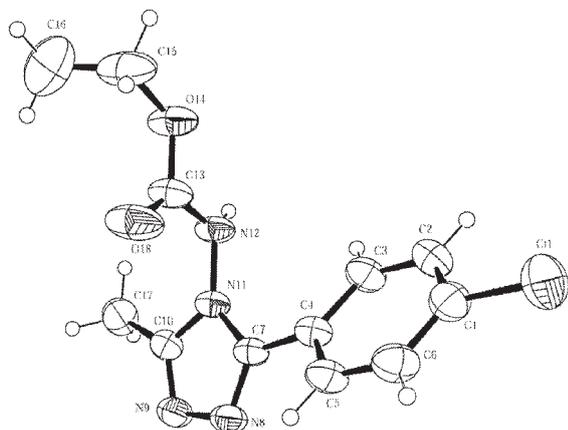


Fig. 2 Structure of (I) with the atom numbering scheme (displacement ellipsoids drawn at the 40% probability level; arbitrary spheres for the H atoms; only one orientation for the disordered methyl group is shown).

Table 3 Hydrogen-bond geometry (\AA , $^\circ$)

| D-H...A | D-H | H...A | D...A | D-H...A |
|---------------------------|---------|---------|----------|---------|
| N12—H12...N9 ⁱ | 0.80(3) | 2.03(3) | 2.827(3) | 175(4) |

Symmetry code: (i) $-x+3/2, y-1/2, -z+1$.

treated as an idealized disordered methyl group over two positions with H-atoms separating from each other by 60° and fixing the site occupancy factor at 0.5. The bond lengths and angles of the five-membered triazole and chlorine-substituted six-membered benzene rings in I (Fig. 2) are in agreement with those of related compounds.^{4,5} The triazole and benzene ring systems are planar within themselves, with r.m.s. deviations of 0.0039 \AA for the triazole and 0.0022 \AA for the benzene rings. The dihedral angle between them is $36.13(13)^\circ$. The plane of the carbamate substituent is almost perpendicular to that of the triazole ring, as indicated by the C10-N11-N12-C13 and C7-N11-N12-C13 torsion angles of $88.2(3)^\circ$ and $-82.3(3)^\circ$, respectively. Rings A (N8-N9-C10-N11-C7) and B (C1/C6) of the two neighboring molecules at (x, y, z) and $(1/2+x, 1/2-y, z)$, respectively, exhibit a partial π - π overlap, as indicated by the dihedral angle of $5.90(20)^\circ$ between their planes with a ring centroid separation of $4.212(2) \text{ \AA}$ and an interplanar spacing of *ca.* 3.538 \AA , corresponding to a ring-centroid offset of *ca.* 2.285 \AA . Additionally, intermolecular N12-H12...N9 hydrogen bonds contribute to the stacking by generating a chain along the *b* axis (Table 3).

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