Acta Cryst. (1994). C**50**, 1925–1928

Racemic 1-Methyl-1,2,4-triazolidine-3,5-dione (1-Methylurazole). Definitive Characterization of Pyramidal Hydrazide N Atoms and Racemate Intermolecular Hydrogen Bonding

Cal Y. Meyers and Hisham G. Lutfi

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901-4409, USA

Vera M. Kolb†

Department of Chemistry, University of California San Diego, La Jolla, CA 92093-0317, USA

Paul D. Robinson

Department of Geology, Southern Illinois University, Carbondale, IL 62901-4324, USA

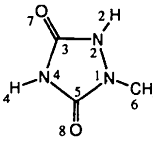
(*Received* 9 *December* 1993; *accepted* 25 *April* 1994)

Abstract

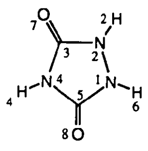
In contrast to the rapid formation of ribosides of urazole and 4-methylurazole through a hydrazide N atom, 1-methylurazole, $C_3H_5N_3O_2$ (I), fails to exhibit any reactivity with ribose; this has been evaluated crystallographically. The X-ray structure of (I) shows the imide N atom to be trigonal but both hydrazide N atoms to be pyramidal, with N1—C6 and N2—H *trans*, affording a torsion angle C6—N1—N2—H2 of −49 (2)°. These data suggest that attack on the N2 electron lobe of (I) must be *cis* to the N1 methyl, invoking a sterically hindered, relatively high-energy transition state and intermediate. The crystal structure shows both enantiomers, 1*R*,2*R* and 1*S*,2*S*, in a three-dimensional network of intermolecular N—H···O═C hydrogen bonds.

Comment

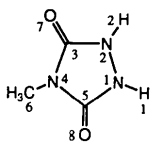
Recent studies of the prebiotic synthesis of urazole (II) and its ribosides (Kolb, Dworkin & Miller, 1994) showed that (II) reacts rapidly with ribose in aqueous solution at room temperature to provide a mixture of α- and β-furanosides and pyranosides. While 4-methylurazole (III) is very similar to (II) in reactivity and type of products formed, 1-methylurazole (I) failed to yield any products, even over longer periods of time at elevated temperatures (*e.g.* five months at 353 K). ^{13}C-NMR studies indicated that the site of reactivity in (II) and (III) was a hydrazide N atom (N1 or N2). The failure of (I) to undergo any observable reaction even though it has an unsubstituted hydrazide N atom (N2) led us to explore the possible effects steric hindrance may have on reactivity at N2. We therefore determined the crystal structure of (I).



(I)



(II)



(III)

The crystal structure and hydrogen-bonding pattern of racemic (I) are shown in Fig. 1. In the absence of X-ray data, Jackson, Bycroft & King (1988) calculated MNDO (modified neglect of diatomic overlap) optimized geometry values of (I), which suggested the pyramidal nature of its hydrazide N atoms. The ring planarity, trigonal imide N4 atom, pyramidal hydrazide N1 and N2 atoms, and *trans* juxtaposition of N1-methyl with N2—H are now apparent in the edge-on view of the structure of the *R*,*R* enantiomer in Fig. 2, and from the supporting data

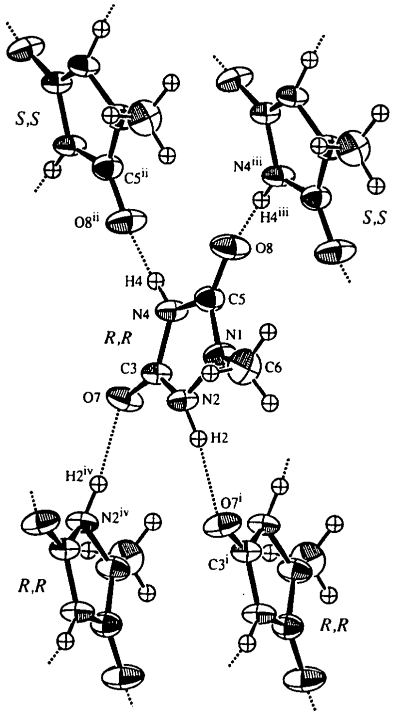


Fig. 1. Crystal structure of racemic 1-methylurazole (I) showing the atom numbering and hydrogen-bonding schemes. Displacement ellipsoids are at the 50% probability level. The origin molecule is at the center of the drawing and is hydrogen bonded to four crystallographically equivalent molecules in surrounding asymmetric units.

---

† On sabbatical leave from the Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000, USA.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

in Tables 3 and 4. The mean deviation of ring atoms from the least-squares ring plane is 0.032 Å. The distance of H4 from the ring plane is 0.082 Å, but H2 is −0.372 Å and C6 is 0.276 Å away from this plane, and the torsion angle C6—N1—N2—H2 is −49 (2)°. While the coplanarity of H4 with the ring is further illustrated by the torsion angle N1—C5—N4—H4 of 177 (3)°, the substantial non-coplanarity of H2 with the ring is further reflected in the torsion angle N4—C3—N2—H2 of −144 (2)°.

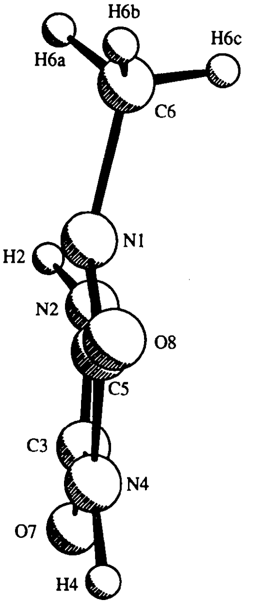


Fig. 2. Edge-on view of the crystal structure of (1*R*,2*R*)-1-methylurazole.

Baker, Timberlake, Alender, Majeste & Trefonas (1982) reported the crystal structure of related 4-phenyl-1-*t*-octylurazole, in which the pyramidal geometry of N1 and N2 became evident from the torsion angles calculated from the reported parameters, *viz.* C3—N2—N1—C6 147° [calculated by Jackson, Bycroft & King (1988)], and N4—C3—N2—H2 −140° (our calculations). Belaj (1992) studied the crystal structure of urazole (II) itself, for which he also reported that 'N4 has an almost planar geometry whereas N1 and N2 are pyramidal'. From Belaj's data we calculated the following torsion angles in (II): N1—C5—N4—H4 175, N4—C3—N2—H2 150 and N4—C5—N1—H1 148°; these are similar to the corresponding torsion angles in (I) and 4-phenyl-1-*t*-octylurazole. The *trans* disposition of the substituents on N1—N2 (C6 and H2) of (I) is evident from its crystal structure and the torsion angle C6—N1—N2—H2 of −49 (2)°. Likewise, C6 and H2 are *trans* in 4-phenyl-1-*t*-octylurazole, the corresponding torsion angle being −82° [our calculations based on the X-ray data of Baker, Timberlake, Alender, Majeste & Trefonas (1982)], and H1 and H2 are *trans* in (II), the torsion angle H1—N1—N2—H2 being 65° [our calculation from the crystal structure reported by Belaj (1992)].

As already noted, the formation of ribosides in the reaction of ribose with (II) as well as (III) has been shown to involve a hydrazide N site. Similar reaction with (I) would require attack on its N2 electron lobe which, because of the pyramidal nature of N2, would be *cis* to the N1-methyl (C6), invoking a sterically hindered high-energy transition state and intermediate relative to those for (II) and (III). The failure of (I) to provide results similar to those of (II) and (III) is, therefore, in accord with the structural parameters described here, although further evaluation is required.

Fig. 1 shows both enantiomers, 1*R*,2*R* and 1*S*,2*S*, of (I), in accord with the pyramidal nature of its hydrazide N atoms. It also shows a three-dimensional pattern of intermolecular hydrogen bonding in which each molecule is exclusively linked to two molecules of the *same* chirality as itself through their respective hydrazide H2 and O7 atoms, and to two molecules of *opposite* chirality exclusively through their respective imide H4 and O8 atoms. Each donor and acceptor atom participates in only one hydrogen bond, so that each molecule is linked to four other molecules, two of the same chirality and two enantiomers. These bonds are strong and almost linear; their geometrical parameters are given in Table 2.

All the urazole X-ray structures discussed here [(I), (II) and 4-phenyl-1-*t*-octylurazole] show hydrazide H atoms or substituents that are substantially out of the ring plane and *trans* configured. These observations do not support the recent statement by Bausch *et al.* (1991) that a methyl substituent bonded to a hydrazyl N atom in urazole '...may be constrained to be relatively coplanar with the imide–urazolyl moiety', in their accounting for the acidifying effect on urazole by the introduction of a 1-methyl substituent.

Experimental

For the comparative reactivity studies of urazoles (Kolb, Dworkin & Miller, 1994), (I) was prepared as reported by Bausch *et al.* (1991) by refluxing equimolar amounts of methylhydrazine and biuret in 1-pentanol for 9 h. The mass of crystals from the cooled mixture was isolated by filtration and recrystallized from ethanol; small, colorless crystals, m.p. 517–518 K (corr; colorless melt) [literature m.p. 518–519 K (Bausch *et al.*, 1991)]. An ethanolic solution of these crystals, evaporated very slowly, provided thick colorless crystals, m.p. 518–519 K, which were used for this X-ray study.

Crystal data

$C_3H_5N_3O_2$	Mo $K\alpha$ radiation
$M_r = 115.09$	$\lambda = 0.71069$ Å

Orthorhombic
Pna2_1
$a = 19.132$ (2) Å
$b = 6.717$ (1) Å
$c = 3.891$ (2) Å
$V = 500.1$ (3) $Å^3$
$Z = 4$
$D_x = 1.528$ Mg m^{-3}

Cell parameters from 24 reflections
$\theta = 19.0$–$21.8°$
$\mu = 0.121$ mm^{-1}
$T = 296$ K
Tabular
0.43 × 0.25 × 0.14 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
997 measured reflections
513 independent reflections
448 observed reflections [$I > 3.0\sigma(I)$]

$R_{\rm int} = 0.020$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 22$
$l = -4 \rightarrow 4$
3 standard reflections monitored every 100 reflections intensity variation: −2.7%

Refinement

Refinement on *F*
$R = 0.026$
$wR = 0.032$
$S = 1.47$
448 reflections
81 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} = 0.0002$
$\Delta\rho_{\rm max} = 0.11$ e $Å^{-3}$
$\Delta\rho_{\rm min} = -0.10$ e $Å^{-3}$

Extinction correction: Zachariasen (1963) type 2 Gaussian isotropic
Extinction coefficient: 0.8 (1) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* ($Å^2$)

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	*y*	*z*	$U_{\rm iso}/U_{\rm eq}$
O7	0.06337 (7)	0.3279 (2)	0.2987	0.046 (1)
O8	0.24426 (8)	0.6602 (3)	0.816 (1)	0.053 (1)
N1	0.12581 (8)	0.7240 (3)	0.761 (1)	0.038 (1)
N2	0.0721 (1)	0.6327 (3)	0.573 (1)	0.034 (1)
N4	0.16633 (9)	0.4531 (3)	0.530 (1)	0.037 (1)
C3	0.0966 (1)	0.4564 (3)	0.452 (1)	0.033 (1)
C5	0.1853 (1)	0.6195 (3)	0.713 (1)	0.036 (1)
C6	0.1199 (1)	0.9296 (4)	0.864 (1)	0.050 (1)
H2	0.030 (1)	0.652 (3)	0.663 (7)	0.052 (9)
H4	0.197 (2)	0.359 (3)	0.45 (1)	0.056 (8)

Table 2. *Selected geometric parameters* (Å, °)

O7—C3	1.227 (3)	N4—C5	1.375 (3)
O8—C5	1.227 (3)	N2—H2	0.88 (3)
N1—N2	1.403 (3)	H2···O7$^{\rm i}$	1.87 (3)
N1—C5	1.350 (3)	N2···O7$^{\rm i}$	2.751 (3)
N1—C6	1.442 (3)	N4—H4	0.91 (3)
N2—C3	1.357 (3)	H4···O8$^{\rm ii}$	1.83 (3)
N4—C3	1.369 (3)	N4···O8$^{\rm ii}$	2.737 (3)
N2—N1—C5	108.5 (2)	O7—C3—N2	127.2 (2)
N2—N1—C6	120.4 (2)	O7—C3—N4	126.9 (2)
C5—N1—C6	127.1 (2)	N2—C3—N4	105.8 (2)
N1—N2—C3	108.1 (2)	O8—C5—N1	127.9 (2)
N1—N2—H2	113 (2)	O8—C5—N4	126.4 (2)
C3—N2—H2	125 (2)	N1—C5—N4	105.8 (2)
C3—N4—C5	111.1 (2)	N2—H2···O7$^{\rm i}$	171 (2)
C3—N4—H4	124 (2)	N4—H4···O8$^{\rm ii}$	177 (3)
C5—N4—H4	125 (2)		

Symmetry codes: (i) $-x, 1-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $-x, 1-y, z-\frac{1}{2}$.

Table 3. *Deviations* (Å) *from the least-squares ring plane*

Atoms defining plane	Distance from plane
N1	−0.038(3)
N2	0.044(3)
C3	−0.034(3)
N4	0.008(3)
C5	0.037(3)

Mean deviation from plane: 0.032 Å.

Distances of other atoms from least-squares plane	
O7	−0.100
O8	0.094
H2	−0.372
H4	0.082
C6	0.276

Table 4. *Comparison of selected torsion angles* (°)

N2—C3—N4—H4	−172 (3)	*vs*	N4—C3—N2—H2	−144 (2)
N1—C5—N4—H4	177 (3)	*vs*	N4—C5—N1—C6	−163.8 (3)
O8—C5—N4—H4	−4 (3)	*vs*	O8—C5—N1—C6	17.4 (5)
O7—C3—N4—H4	7 (3)	*vs*	O7—C3—N2—H2	37 (2)
C3—N2—N1—C5	9.0 (3)	*vs*	C6—N1—N2—H2	−49 (2)

Redundant data were collected and averaged. The scan rate was 4° min^{-1} (in ω), weak reflections [$I < 10\sigma(I)$] were rescanned (maximum of 3 rescans) and the counts accumulated to improve accuracy. The positional and isotropic displacement parameters of the two H atoms involved in hydrogen bonding (H2 and H4) were refined. The methyl H atoms were placed at assumed positions (C—H = 0.95 Å, $U = 1.2U_{\rm eq}$ of the associated C atom) and fixed. The methyl group rotational orientation was determined from a difference Fourier synthesis.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

VMK thanks the NASA Specialized Center of Research and Training in Exobiology for an NSCORT Visiting Fellowship. CYM is grateful to Southern Illinois University, Carbondale, for supporting this research through Distinguished Professorship research funding.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baker, R. J., Timberlake, J. W., Alender, J. T., Majeste, R. & Trefonas, L. M. (1982). *Cryst. Struct. Commun.* **11**, 763–768.

Bausch, M. J., David, B., Dobrowolski, P., Guadalupe-Fasano, C., Gustowski, R., Selmarten, D., Prasad, V., Vaughn, A. & Wang, L.-H. (1991). *J. Org. Chem.* **56**, 5643–5651.
Belaj, F. (1992). *Acta Cryst.* C**48**, 1088–1090.
Jackson, D. E., Bycroft, B. W. & King, T. J. (1988). *J. Comput.-Aided Mol. Design*, **2**, 321–328.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Kolb, V. M., Dworkin, J. P. & Miller, S. L. (1994). *J. Mol. Evol.* **38**, 549–557.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1994). C**50**, 1928–1930

7-Dimethylamino-4-trifluoromethylcoumarin, a New Polymeric Form

JERRY P. JASINSKI AND ERNEST S. PAIGHT†

Chemistry Department, Keene State College,
229 Main Street, Keene, New Hampshire 03431, USA

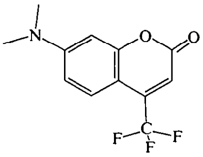
(*Received* 21 *October* 1992; *accepted* 5 *April* 1994)

Abstract

This molecule represents a new polymorph of the title laser-dye aminocoumarin compound, $C_{12}H_{10}F_3NO_2$. Torsion angles in the trifluoro moiety and intermolecular packing effects indicate significant structural differences when compared to its polymorphic analog. The crystal structure is stabilized by an intermolecular C—H···O contact of 3.324 (4) Å.

Comment

The title compound (I), also known as coumarin 152 (Eastman Kodak Co.) or coumarin 485 (Exiton Chemical Co.), is a fluorinated aminocoumarin and is used as a laser dye in the blue–green (Drexhage, 1973) as well as in the ultraviolet spectral regions (Eschrich & Morgan, 1985). Its structural features, including bond lengths and bond angles, closely resemble those of its polymorphic counterpart within experimental error (Chinnakali, Sivakumar & Natarajan, 1990), except for the torsion angles involving the F atoms [C3—C4—C12—F12*A* = 3.5 (4), C3—C4—C12—F12*B* = −11.64 (3), C3—C4—C12—F12*C* = 123.9 (3)°]. The C3—C4 bond of 1.340 (4) Å is clearly double in nature. The independent C—F bond lengths of 1.331 (3), 1.333 (4) and 1.328 (4) Å are normal (Krishnamurthy & Vijayan, 1979; Chinnakali, Sivakumar & Natarajan, 1992). Since this polymorph crystallizes in a different space group, $P2_1/a$, its packing characteristics are somewhat different. In addition, excited-state charge transfer from the amino (donor) to the carboxyl (acceptor) group (Masilamani, Chandrasekar, Sivaram, Sivasankar & Natarajan, 1986) is most likely influenced by the trifluoromethyl group in a somewhat different fashion (Guo & Feng, 1987).



(I)

There exists an intermolecular hydrogen bond of the type C—H···O [C3···O11^{i} 3.324 (4), C3—H3 0.91 (3), H3···O11^{i} 2.42 (4) Å, C3—H3···O11^{i} 168 (3)°; symmetry code: (i) 1 − *x*, −*y*, 1 − *z*] (Taylor & Kennard, 1982).

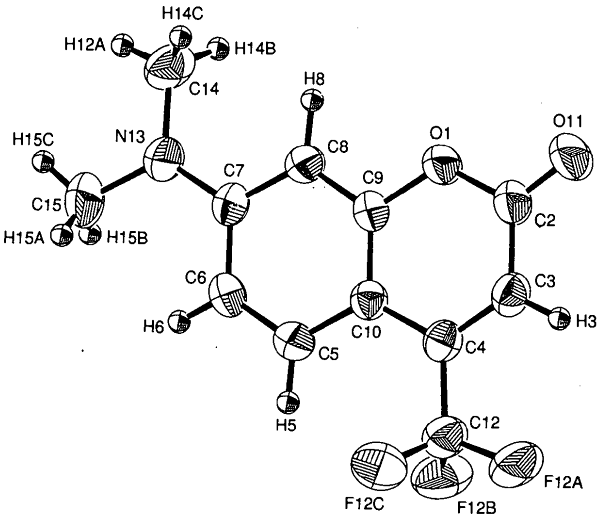


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule with 50% probability ellipsoids and atomic numbering scheme.

Experimental

Crystals of the title compound were grown from ethanol by slow evaporation and were supplied by Eastman Kodak Co., Rochester, NY 14650, USA.

---

† Present address: Pfizer Inc., Central Research Division, Eastern Point Road, Groton, CT 06340, USA.