F13*A*1	0.663 (2)	0.736 (2)	0.772 (1)	0.11 (1)
F13*B*1	0.746 (2)	0.8366 (7)	0.6982 (7)	0.076 (5)
F13*C*1	0.857 (2)	0.737 (1)	0.7588 (9)	0.085 (7)
F13*A*2	0.628 (1)	0.772 (2)	0.742 (2)	0.10 (1)
F13*B*2	0.793 (4)	0.829 (2)	0.702 (1)	0.14 (3)
F13*C*2	0.787 (4)	0.710 (2)	0.7766 (9)	0.08 (1)
O9	0.5766 (2)	0.4128 (2)	0.5345 (2)	0.048 (2)
N1	0.6565 (3)	0.5386 (2)	0.6048 (2)	0.033 (2)
N2	0.6423 (3)	0.6037 (2)	0.6632 (2)	0.036 (2)
C3	0.7363 (3)	0.6629 (3)	0.6654 (2)	0.035 (2)
C3A	0.8333 (3)	0.6462 (3)	0.6099 (2)	0.036 (2)
C4	0.9567 (4)	0.6016 (3)	0.6386 (2)	0.048 (3)
C4A	0.9637 (3)	0.4933 (3)	0.6079 (2)	0.041 (2)
C5	1.0589 (4)	0.4208 (3)	0.6182 (2)	0.056 (3)
C6	1.0522 (4)	0.3266 (4)	0.5830 (3)	0.065 (3)
C7	0.9541 (5)	0.3042 (3)	0.5387 (3)	0.057 (3)
C8	0.8583 (4)	0.3753 (3)	0.5288 (2)	0.044 (2)
C8A	0.8643 (3)	0.4697 (3)	0.5654 (2)	0.034 (2)
C8B	0.7727 (3)	0.5593 (3)	0.5643 (2)	0.033 (2)
C9	0.5679 (3)	0.4702 (3)	0.5858 (2)	0.036 (2)
C10	0.4523 (4)	0.4657 (3)	0.6330 (2)	0.045 (3)
C13	0.7436 (5)	0.7433 (4)	0.7226 (3)	0.050 (3)

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

O9—C9	1.202 (4)	C4—C4A	1.480 (5)
N1—N2	1.369 (4)	C4A—C5	1.378 (5)
N1—C8B	1.472 (4)	C4A—C8A	1.354 (5)
N1—C9	1.325 (4)	C5—C6	1.356 (6)
N2—C3	1.248 (4)	C6—C7	1.361 (7)
C3—C3A	1.476 (5)	C7—C8	1.369 (5)
C3—C13	1.470 (5)	C8—C8A	1.372 (5)
C3A—C4	1.526 (5)	C8A—C8B	1.491 (5)
C3A—C8B	1.527 (5)	C9—C10	1.513 (5)
N2—N1—C8B	113.2 (3)	C4A—C5—C6	118.3 (4)
N1—N2—C3	107.1 (3)	C4A—C8A—C8	121.1 (4)
N2—C3—C3A	116.9 (3)	C4A—C8A—C8B	110.7 (3)
C3—C3A—C4	114.2 (3)	C8—C8A—C8B	128.1 (3)
C3—C3A—C8B	101.2 (3)	N1—C8B—C3A	101.4 (3)
C4—C3A—C8B	107.1 (3)	N1—C8B—C8A	114.2 (3)
C3A—C4—C4A	104.3 (3)	C3A—C8B—C8A	104.9 (3)
C4—C4A—C5	126.5 (4)	O9—C9—N1	123.2 (4)
C4—C4A—C8A	112.8 (3)	O9—C9—C10	120.0 (3)
C5—C4A—C8A	120.7 (4)	N1—C9—C10	116.7 (3)

Each of the fluorine atoms attached to C13 is disordered over two sites, with the population of F13*A*1, F13*B*1 and F13*C*1 refining to 0.67 (3) and the occupancy of the alternative sites F13*A*2, F13*B*2 and F13*C*2 being constrained to one minus this value.

Data collection: *P3/PC Diffractometer Control Software* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Control Software*. Data reduction: *PROCESS TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *LS TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *FINISH TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 772–775

2-(2,6-Difluorophenyl)-1,3-dithiane and 2-(2,6-Difluorophenyl)-1,3-dithiane 1,1,3,3-Tetraoxide. The Role of Oxidation in Locking a Molecular Conformation

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Abstract

In 2-(2,6-difluorophenyl)-1,3-dithiane, (1), $C_{10}H_{10}F_2S_2$, described here, and its unfluorinated counterpart [Kalff & Romers (1966). *Acta Cryst.* **20**, 490–496], the conformation about the C—C bond joining the two rings is similar, with S—C—C_{ar}—C_{ar} torsion angles of 59.5 (2) and −67.6 (2)° in the former, and 59.7 and −66.0° in the latter. In the oxidation product 2-(2,6-difluorophenyl)-1,3-dithiane 1,1,3,3-tetraoxide, (2), $C_{10}H_{10}F_2O_4S_2$, the torsion angles become 42.8 (4) and −87.6 (3)°. There is a slight flattening of the tetrahedral geometry at atom C2, as indicated by the sum of the three non-H bond angles [335.7 (2) and 340.8 (3)° for (1) and (2), respectively]. Compound (2) is not unduly sterically congested since the shortest O···F contact of 2.712 (3) Å is close to the expected van der Waals distance of 2.75 Å. However, further twisting about the central bond would lead to an unacceptably short O···F contact of 1.501 Å, effectively blocking free rotation of the phenyl ring about this bond.

Comment

The structure determination of the title compounds, 2-(2,6-difluorophenyl)-1,3-dithiane, (1), and 2-(2,6-difluorophenyl)-1,3-dithiane 1,1,3,3-tetraoxide, (2), was carried out as part of a general investigation into the synthesis and chemistry of 2-fluoroaryl-1,3-dithianes, including studies of their hydrolysis and their oxidation to the corresponding bis(sulfone) compounds (Adamson

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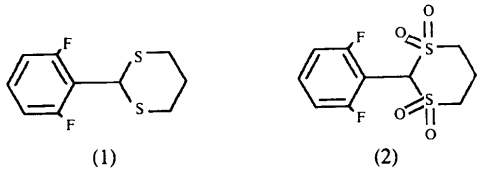
& Manley, 1989; Mothersdale, 1991). In particular, information was sought on the steric hindrance to rotation about the C2—aryl bond in the bis(sulfone) (2), relative to that in the 1,3-dithiane (1). Although comparison of the non-bonded intramolecular contacts in compounds (1) and (2) showed that steric congestion was not significantly increased in (2), it can be shown that oxygen blocks rotation about the inter-ring bond.



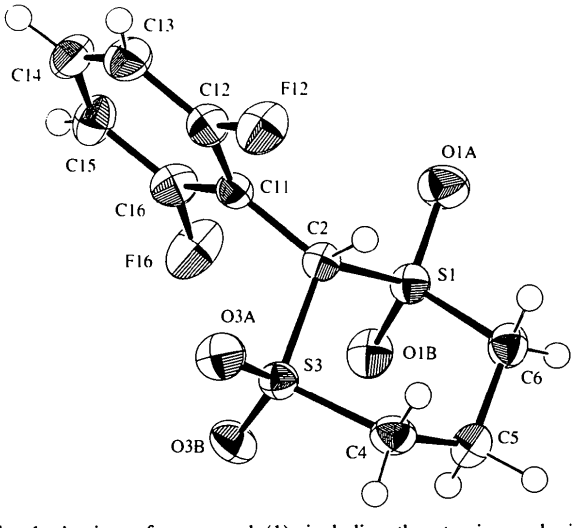


Fig. 1. A view of compound (1), including the atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids are at the 50% probability level.

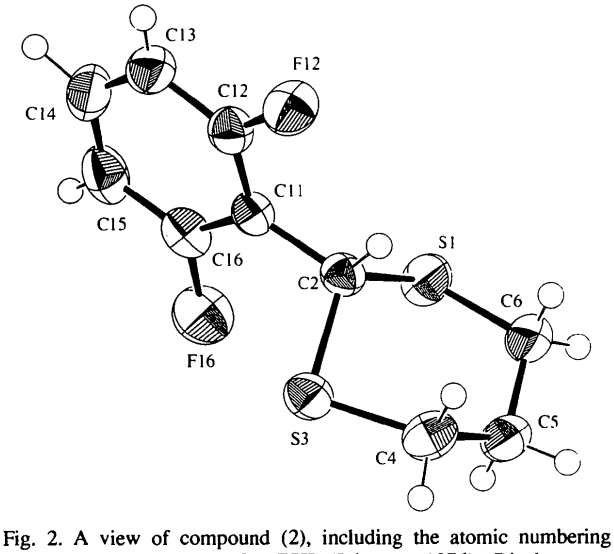


Fig. 2. A view of compound (2), including the atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976). Displacement ellipsoids are at the 50% probability level.

Experimental

A solution of propane-1,3-dithiol (1.70 g, 15.75 mmol) in anhydrous trichloromethane (10 ml) was added to a stirred solution of 2,6-difluorobenzaldehyde (2.25 g, 15.8 mmol) in trichloromethane (10 ml). Hydrogen chloride was bubbled rapidly through the solution (30 min) which was then stirred for a further 20 h. The resulting solution was washed with water (20 ml), aqueous potassium hydroxide (10% *w/v*, 2 × 20 ml) and water (2 × 20 ml) again, then dried ($MgSO_4$). The solvent was removed by rotary evaporation to afford a yellow oil which crystallized on cooling in an ice bath. The crystals obtained were recrystallized from glacial acetic acid to give 2-(2,6-difluorophenyl)-1,3-dithiane, (1) (3.14 g, 13.5 mmol, 86% yield), m.p. 329–329.5 K (found: C 51.4, H 4.5, F 16.2%, M^+ = 232; $C_{10}H_{10}F_2S_2$ requires C 51.7, H 4.3, F 16.4%, M^+ = 232). A mixture of aqueous hydrogen peroxide (30% *v/v*, 30 ml) and glacial acetic acid (10 ml) was added to a warm (323 K) solution of compound (1) (1.33 g, 5.7 mmol) in glacial acetic acid (*ca* 10 ml) and the resulting material was heated under reflux for 2 h and then cooled in an ice bath. The precipitate was removed by filtration, washed with water (3 × 10 ml) and dried (*ca* 393 K) to afford 2-(2,6-difluorophenyl)-1,3-dithiane 1,1,3,3-tetraoxide, (2) (1.65 g, 5.6 mmol, 97% yield), m.p. 493–494 K (found: C 40.3, H 3.4, F 12.6%; $C_{10}H_{10}F_2O_4S_2$ requires C 40.5, H 3.4, F 12.8%). The crystals for the X-ray study were obtained by recrystallization from glacial acetic acid.

Compound (1)

Crystal data

$C_{10}H_{10}F_2S_2$
M_r = 232.31
Triclinic
$P\bar{1}$
a = 5.294 (2) Å
b = 7.718 (2) Å
c = 13.274 (4) Å
α = 83.57 (2)°
β = 84.65 (2)°
γ = 74.94 (2)°
V = 519.3 (6) Å^3
Z = 2
D_x = 1.485 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 20.1–28.3°
μ = 0.48 mm^{-1}
T = 296 K
Plate
0.30 × 0.30 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3673 measured reflections
1834 independent reflections
1501 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.02

θ_{max} = 25.0°
$h = 0 \rightarrow 6$
$k = -7 \rightarrow 9$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 150 reflections
intensity decay: not significant

Refinement

Refinement on F
R = 0.0297

$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

wR = 0.0343
S = 2.159
1501 reflections
168 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.065
Extinction correction: Zachariasen (1967) Type 2, Gaussian isotropic
Extinction coefficient: 111 (1) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S1	0.55260 (10)	0.19834 (6)	0.78362 (4)	0.0514 (3)
C2	0.5278 (3)	0.4215 (2)	0.7191 (1)	0.038 (1)
S3	0.80223 (9)	0.43273 (6)	0.62734 (4)	0.0458 (3)
C4	0.7498 (5)	0.2792 (3)	0.5426 (2)	0.051 (1)
C5	0.7573 (4)	0.0911 (3)	0.5918 (2)	0.049 (1)
C6	0.5404 (4)	0.0833 (3)	0.6740 (2)	0.054 (1)
C11	0.4890 (3)	0.5594 (2)	0.7944 (1)	0.036 (1)
C12	0.2657 (3)	0.7022 (2)	0.7959 (1)	0.041 (1)
C13	0.2130 (4)	0.8307 (3)	0.8640 (2)	0.051 (1)
C14	0.3905 (5)	0.8183 (3)	0.9355 (2)	0.057 (1)
C15	0.6155 (5)	0.6827 (3)	0.9375 (2)	0.056 (1)
C16	0.6605 (4)	0.5578 (3)	0.8672 (2)	0.046 (1)
F12	0.0919 (2)	0.7154 (2)	0.72535 (9)	0.055 (1)
F16	0.8846 (2)	0.4234 (2)	0.86959 (10)	0.066 (1)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

S1—C2	1.814 (2)	S3—C4	1.809 (2)
S1—C6	1.802 (2)	C4—C5	1.516 (3)
C2—S3	1.821 (2)	C5—C6	1.517 (3)
C2—C11	1.503 (2)		
C2—S1—C6	97.8 (1)	S3—C4—C5	114.6 (2)
S1—C2—S3	113.27 (9)	C4—C5—C6	114.1 (2)
C2—S3—C4	97.7 (1)	S1—C6—C5	114.7 (2)

Compound (2)

Crystal data

$C_{10}H_{10}F_2O_4S_2$
M_r = 296.30
Triclinic
$P\bar{1}$
a = 5.257 (2) Å
b = 7.332 (2) Å
c = 15.474 (5) Å
α = 87.61 (3)°
β = 85.91 (3)°
γ = 78.47 (3)°
V = 582.7 (7) Å^3
Z = 2
D_x = 1.689 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 16.0–24.0°
μ = 0.47 mm^{-1}
T = 296 K
Rod
0.30 × 0.10 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3306 measured reflections
1810 independent reflections
1368 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.041
θ_{max} = 24.0°
$h = 0 \rightarrow 5$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 150 reflections
intensity decay: not significant

Refinement

Refinement on F
R = 0.0301
wR = 0.0356
S = 1.492
1368 reflections
203 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.035
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
S1	0.6301 (1)	0.49685 (9)	0.12698 (4)	0.0275 (4)
C2	0.6571 (6)	0.4263 (4)	0.2410 (2)	0.025 (1)
S3	0.5489 (1)	0.20652 (9)	0.26325 (4)	0.0275 (4)
C4	0.7607 (7)	0.0585 (4)	0.1914 (2)	0.034 (2)
C5	0.7570 (7)	0.1246 (4)	0.0970 (2)	0.037 (2)
C6	0.8501 (7)	0.3078 (4)	0.0790 (2)	0.034 (2)
C11	0.5449 (5)	0.5662 (3)	0.3093 (2)	0.026 (1)
C12	0.6836 (6)	0.5729 (4)	0.3823 (2)	0.031 (2)
C13	0.5967 (7)	0.6898 (4)	0.4491 (2)	0.040 (2)
C14	0.3606 (7)	0.8101 (4)	0.4442 (2)	0.040 (2)
C15	0.2131 (7)	0.8109 (4)	0.3740 (2)	0.038 (2)
C16	0.3073 (6)	0.6893 (4)	0.3093 (2)	0.033 (2)
F12	0.9148 (3)	0.4545 (3)	0.3870 (1)	0.045 (1)
F16	0.1586 (4)	0.6860 (3)	0.2416 (1)	0.052 (1)
O1*A*	0.7292 (5)	0.6649 (3)	0.1145 (1)	0.042 (1)
O1*B*	0.3761 (4)	0.4938 (3)	0.0999 (1)	0.037 (1)
O3*A*	0.6084 (4)	0.1511 (3)	0.3501 (1)	0.040 (1)
O3*B*	0.2863 (4)	0.2229 (3)	0.2395 (1)	0.038 (1)

Table 4. *Selected geometric parameters* (Å, °) *for* (2)

S1—C2	1.824 (3)	S3—C4	1.759 (3)
S1—C6	1.770 (3)	S3—O3*A*	1.426 (2)
S1—O1*A*	1.432 (2)	S3—O3*B*	1.434 (2)
S1—O1*B*	1.432 (2)	C4—C5	1.520 (4)
C2—S3	1.825 (3)	C5—C6	1.528 (4)
C2—C11	1.509 (4)		
C2—S1—C6	99.5 (1)	S3—C4—C5	114.7 (2)
S1—C2—S3	110.8 (2)	C4—C5—C6	114.2 (3)
C2—S3—C4	101.3 (1)	S1—C6—C5	111.5 (2)

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN LS*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond distances and angles involving H atoms, have been deposited with the IUCr (Reference: HA1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 775-777

Dimeric Hydrogen-Bonded Structure of Bis(3-fluorophenylmethine)carbonohydrazide

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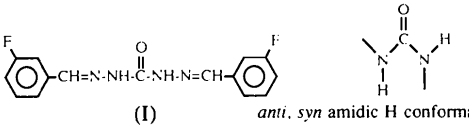
Abstract

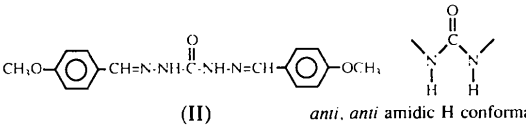
The title carbazone, $C_{15}H_{12}F_2N_4O$ (I), was found to be an intermolecularly hydrogen-bonded centrosymmetric dimer. [For a discussion of CAS/IUPAC nomenclature of carbazones see Grasselli & Weast (1989). In *Handbook of Data on Organic Compounds*, 2nd edition, Vol. I, Introduction, §§190, 252. Florida: CRC Press.] This is in contrast to the only other reported X-ray structure of a related carbazone, which was a non-centrosymmetric infinite hydrogen-bonded polymeric structure. The monomer unit of compound (I) is neither planar nor symmetrical. One amidic H atom is *anti* to the carbonyl O atom while the other is *syn*. The *syn* amidic H atom and the carbonyl O atom form strong hydrogen bonds with the respective atoms of a second molecule to produce an eight-membered ring which links the two monomeric units. The intermolecular N—H···O hydrogen-bond distances are 2.01 (2) Å for H···O and 2.873 (3) Å for N···O, and the N—H···O angle is 172 (2)°. The *anti* amidic H atom of compound (I) is not involved in hydrogen bonding.

Comment

Extending the study to deduce a relationship between Raman and IR carbonyl frequencies of a series of carbazones in the solid state with variations in the nature of their intermolecular hydrogen bonding (Kolb, Janota, Dantzman, Kozenski & Strommen, 1992), we initiated an investigation of their X-ray structures (Kolb, Meyers & Robinson, 1993). Our recent report on the crystal structure of bis(4-methoxyphenylmethine)carbonohydrazide, (II), describes its non-centrosymmetric infinite hydrogen-bonded polymeric nature (Kolb, Robinson & Meyers, 1994). We now report the X-ray crystal structure of the related compound bis(3-fluorophenylmethine)carbonohydrazide, (I).



(I) *anti, syn* amidic H conformation of (I)



(II) *anti, anti* amidic H conformation of (II)

Although molecules of compounds (I) and (II) are closely related, the first striking difference exhibited by their crystal structures is seen in the fact that in (I) one of the amidic H atoms is *anti* to the carbonyl O atom and the other is *syn*, while in (II) both amidic H atoms are *anti*. This difference in monomer conformation gives rise to the second striking difference, *i.e.* the availability of one *syn* amidic H atom per molecule of (I) permits reciprocal hydrogen bonding between two molecules *via* their respective *syn* amidic H atoms and carbonyl O atoms, the latter bridging with a single H atom, to provide the observed dimeric crystal structure in which the common linkage is an eight-membered ring. As shown in Fig. 1, the two molecules of a dimeric pair are related by a center of symmetry. The following characteristics of the eight-membered hydrogen-bonded-ring dimer bridge are noted: (*a*) the torsion angle O1—C8—N2—H6 is −9 (2)°; (*b*) the planes O1—C8—N2 and $O1^i$—$C8^i$—$N2^i$ are parallel and are offset (one above the other) by 0.65 Å; (*c*) Atoms H6 and $H6^i$ lie between the N2—C8—O1 and $N2^i$—$C8^i$—$O1^i$ planes, essentially on the N2···$O1^i$ and $N2^i$···O1 vectors, respectively; (*d*) the N—H···O intermolecular hydrogen bond has H···O and N···O distances of 2.01 (2) and 2.873 (3) Å, respectively, and an N—H···O bond angle of 172 (2)°. Only the *syn* amidic H atom of compound (I) is involved in hydrogen bonding, while in (II), which

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