

Monoclinic
*P*2₁/*a*
a = 10.1911 (11) Å
b = 11.3039 (13) Å
c = 11.0983 (11) Å
 β = 115.830 (2)°
V = 1150.8 (2) Å³
Z = 4
*D*_x = 1.302 Mg m⁻³
*D*_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 ψ scan empirical via ψ
 scans (Fair, 1990)
*T*_{min} = 0.928, *T*_{max} = 0.939
 2265 measured reflections
 2019 independent reflections

Refinement

Refinement on *F*²
R = 0.036
wR = 0.045
S = 0.96
 1557 reflections
 136 parameters
 H atoms constrained
w = 1/[$\sigma F^2 + (0.02F)^2$
 + 1.0], except *w* = 0
 if $F^2 < 3\sigma F^2$

Cell parameters from 25
 reflections
 θ = 11.47–20.92°
 μ = 0.309 mm⁻¹
T = 295 K
 Prismatic
 0.40 × 0.25 × 0.20 mm
 Light yellow

1557 reflections with
 $I > 3\sigma(I)$
*R*_{int} = 0.010
 θ_{\max} = 25.04°
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 13$
 $l = -13 \rightarrow 11$
 3 standard reflections
 frequency: 120 min
 intensity decay: -1.16%

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max}$ = 0.193 e Å⁻³
 $\Delta\rho_{\min}$ = -0.198 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

| | | | |
|----------|-----------|-----------|-----------|
| Cl—C4 | 1.743 (2) | N1—C7 | 1.339 (3) |
| O1—C1 | 1.353 (3) | C7—C10 | 1.496 (3) |
| O2—C9 | 1.256 (3) | C9—C11 | 1.499 (4) |
| N1—C6 | 1.418 (3) | | |
| C6—N1—C7 | 128.9 (2) | N1—C6—C5 | 122.7 (2) |
| O1—C1—C2 | 123.2 (2) | N1—C7—C8 | 121.0 (2) |
| O1—C1—C6 | 117.5 (2) | N1—C7—C10 | 119.9 (2) |
| Cl—C4—C3 | 119.6 (2) | O2—C9—C8 | 123.0 (2) |
| Cl—C4—C5 | 118.9 (2) | O2—C9—C11 | 118.8 (2) |
| N1—C6—C1 | 117.5 (2) | | |

Table 2. Hydrogen-bonding geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1...O2 ⁱ | 0.83 | 1.80 | 2.634 (2) | 178 |
| N1—H1 ⁱ ...O2 | 0.86 | 1.97 | 2.686 (3) | 139 |

Symmetry code: (i) $\frac{1}{2} + x, -\frac{1}{2} - y, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Giacovazzo, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON99* (Spek, 1999). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1291). Services for accessing these data are described at the back of the journal.

References

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Acta Cryst. (1999). **C55**, 1692–1698

'Push–pull' effects in nitroethenamines

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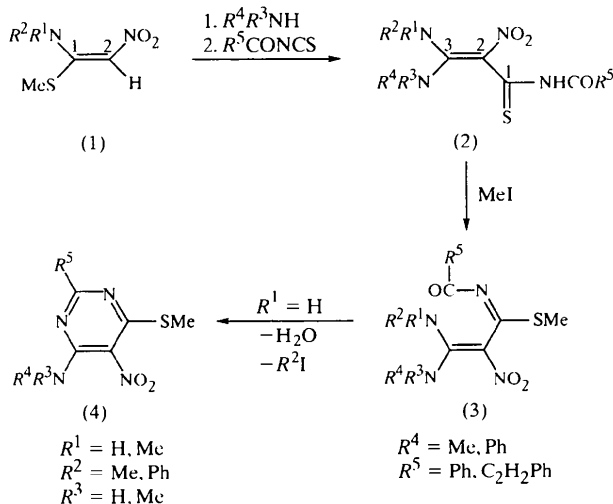
Abstract

(*E*)-*N*-methyl-1-(methylthio)-2-nitroethenamine, C₄H₈N₂O₂S, is a near-planar molecule with significant π -electron delocalization from the ethylene bond into the enamine C—N bond. In the two nitrothioacrylamide derivatives, *N*-benzoyl-3,3-bis(methylamino)-2-nitrothioacrylamide, C₁₂H₁₄N₄O₃S, and *N*-cinnamoyl-3,3-bis(dimethylamino)-2-nitrothioacrylamide, C₁₆H₂₀N₄O₃S, the formal ethylene bond has single-bond properties with a length of about 1.49 Å, while the magnitudes of the torsion angles about this bond approach 90°. The enamine N—C bonds have significant double-bond character and there is significant electron delocalization in the nitrothioacrylamide moiety of each molecule. These compounds can be described as 'push–pull' ethylenes rather than as enamines and are best represented by a zwitterionic formulation in which the charges are accumulated near the opposite ends of the ethylene bond. A strong intramolecular hydrogen bond involving the amide and nitro groups in each compound maintains a rigid confor-

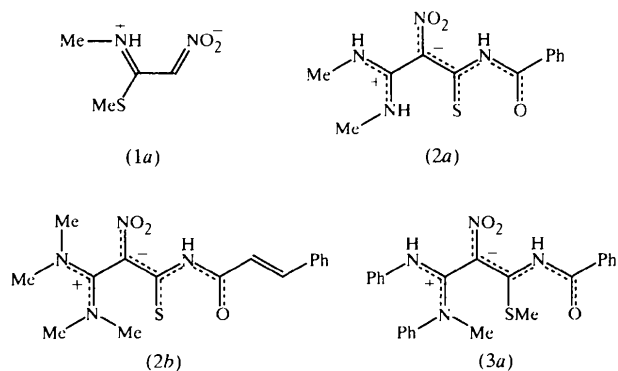
mation, which may explain why these compounds will not undergo cyclization reactions to the corresponding thioxypyrimidines. *S*-methyl *N*-benzoyl-3-(*N*-methyl-*N*-phenylamino)-2-nitro-3-(phenylamino)thioacrylimidate, C₂₄H₂₂N₄O₃S, exhibits similar 'push-pull' characteristics, but the absence of an intramolecular hydrogen bond gives the molecule flexibility and enables it to adopt a conformation in which it undergoes a cyclization reaction to the corresponding nitropyrimidine.

Comment

For the last few years, we have been interested in the use of 3,3-diamino-2-nitrothioacrylamides, (2), as intermediates in the synthesis of heterocyclic compounds (García Trimiño *et al.*, 1992; Moya Argilagos *et al.*, 1997). These nitrothioacrylamides can be synthesized from the precursor nitroenamines, (1) (Moya Argilagos *et al.*, 1997). NMR studies indicate that nitroenamines of type (1) possess considerable double-bond character around the enamine N—C bond and they are therefore more appropriately described as 'push-pull' ethylenes than as enamines (Rajappa, 1981). The introduction of a second amino group in conjugation with the nitroethene system, to form nitroketeneaminals, increases the enaminic activity, thereby allowing these compounds to be added easily to acyl isothiocyanates to yield the 3,3-diamino-2-nitrothioacrylamides, (2) (García Trimiño *et al.*, 1998). The X-ray crystal structures of two 3,3-diamino-2-nitrothioacrylamides of type (2) (Moya Argilagos *et al.*, 1997) indicate considerable double-bond character of the enamine C—N bonds (Scheme 1) and the ethylene C2—C3 bond, which one might formally depict as a double bond, is more like a pure single bond, because the bond length is about 1.49 Å and the magnitudes of the torsion angles about the C2—C3 bond approach 90° (range 74–103°). These features indicate that a more appropriate representation of (2) is as a zwitterionic structure.



Although *N*-acyl-3-aminothioacrylamides cyclize easily to thioxypyrimidines (Goerdeler & Gnad, 1965), all attempts to obtain thioxypyrimidines from *N*-acyl-3,3-diamino-2-nitrothioacrylamides, (2), under various conditions failed (Rajappa, 1981; Aggarwal *et al.*, 1982). Nevertheless, when compounds of type (2) were refluxed with MeI in ethanol, 6-amino-4-methylthio-5-nitropyrimidines, (4), were obtained (Linden *et al.*, 1994; Pomés Hernández *et al.*, 1995) instead of thioxypyrimidines (García Trimiño *et al.*, 1992). In order to gain a better understanding of this behaviour, the conformations of two of the synthesized nitrothioacrylamides, (2a) and (2b), and one of the nitrothioacrylimidates, (3a), have been established by X-ray crystallography. A preliminary account of this work was presented at a conference (García Trimiño *et al.*, 1994). In addition, the crystal structure of the nitrothioethenamine, (1a), has also been determined, proving that the initial substitution of an MeS group in 1,1-bis(methylthio)-2-nitroethene by methylamine yields the (*E*)-configured product.



The core of the molecule of (1a) (Fig. 1) is planar. The maximum deviation from the plane defined by N1, N2, C1, C2, C3 and S is 0.0291 (12) Å for C2, while the out-of-plane atoms C4, O1 and O2 deviate from this plane by -0.306 (2), -0.1844 (18) and 0.087 (2) Å, respectively, which results from small torsional twists about the S—C3 and N2—C2 bonds (Table 1). The bond lengths within the molecule indicate considerable conjugation of the N1—C3, C2—C3 and N2—C2 bonds. This is consistent with the molecule having significant zwitterionic character, with the positive charge located on the amine N atom and the negative charge on the nitro group. In particular, the C2—C3 bond length is similar to a normal aryl C—C bond and cannot formally be described as a double bond, while the N1—C3 and N2—C2 bonds are much shorter than formal single bonds and therefore must have substantial double-bond character. Nonetheless, a comparison with typical interatomic distances for organic compounds (Allen *et al.*, 1987) shows that all the bond lengths in the molecule are generally appropriate for their local environment. The amine H atom forms bifurcated hydrogen bonds (Table 2). One

is an intramolecular interaction with O1 of the nitro group and has a graph-set motif of $S(6)$ (Bernstein *et al.*, 1995), while the other is an intermolecular interaction, also with O1 of the nitro group. The latter interaction links the molecules into centrosymmetric dimers [graph set $R_2^2(12)$]. The C1—N1—C3, N1—C3—C2 and C3—C2—N2 angles are slightly larger than 120°, presumably because of steric influences. In addition to the delocalized bonding, the intramolecular hydrogen bond probably helps to retain the planar nature of the molecule and thereby prevents the molecule from twisting in order to relieve the steric strain between N1 and O1.

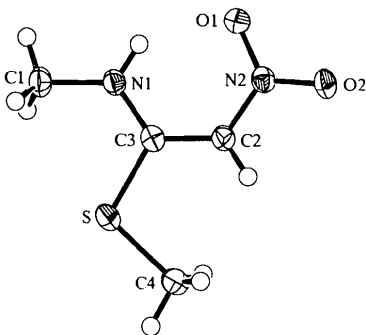


Fig. 1. View of the molecule of (1a) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The molecular structures of the two nitrothioacrylamide derivatives, (2a) and (2b), have very similar characteristics (Figs. 2 and 3). In each structure, the ethylene C2—C3 bond (Tables 3 and 5) is quite long and approaches the value for a normal single bond, while the magnitudes of the torsion angles about this bond approach 90°. The angles between the three-atom planes at each end of the C2—C3 bond, as defined by N3, C3 and N4, and C1, C2 and N2, are 85.23 (16) and 76.08 (18)° for compounds (2a) and (2b), respectively. Therefore, the C2—C3 bond, which is conveniently drawn as a double bond in chemical structure diagrams, has all the properties of a single bond and any significant π -orbital overlap between atoms C2 and C3 is precluded. The lengths of the short equivalent enamine N3—C3 and N4—C3 bonds are similar to the corresponding distance in compound (1a) and emphasize the considerable double-bond character of both of these N—C bonds. The N1—C4, N1—C1, C1—C2 and N2—C2 bonds have lengths characteristic of significant electron delocalization in this region of each molecule. This is supported by the planarity of the nitrothioacrylamide moiety in the molecule. The maximum deviations from the plane defined by N1, N2, C1, C2, C3 and S in (2a) and (2b) are 0.0451 (10) (atom N2) and 0.0281 (11) Å (atom C3), respectively. The O atoms of the nitro groups are

tilted slightly out of these planes, with O1 and O2 lying 0.147 (2) and -0.017 (2) Å, respectively, from the plane in (2a) and -0.123 (3) and 0.086 (3) Å, respectively, from the plane in (2b). These geometrical properties are typical of those consistently found in related compounds of this type and characterize the 'push-pull' behaviour across the ethylene bond generally demonstrated by nitroenamines (Rajappa, 1981; García Trimiño *et al.*, 1993, 1998; Moya Argilagos *et al.*, 1997, 1998). Once again, the best model that fits these observations is a zwitterionic structure, with the positive charge delocalized between the two amino groups and the negative charge distributed across the conjugated system stretching from the nitro group to the S atom and the amide group.

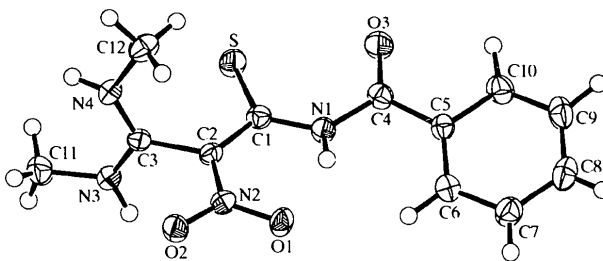


Fig. 2. View of the molecule of (2a) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

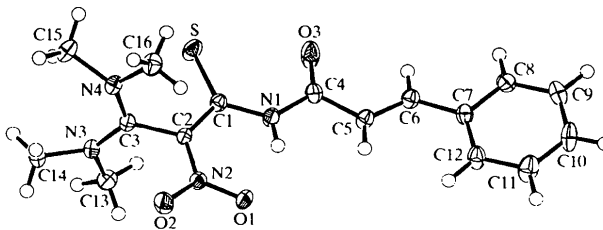


Fig. 3. View of the molecule of (2b) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

In (2a), atoms N3, N4, C2, C3, C11 and C13 are planar, with a maximum deviation from the plane of 0.0225 (16) Å for N4. The dimethylamino substituents in (2b) do not form a completely planar system. The angle between the three-atom planes defined by C13, N3 and C14, and C15, N4 and C16, is 42.73 (10)°. Presumably, steric interactions between the C14 and C15 methyl groups cause these twists. However, this does not appear to disturb the π -electron interactions along the enamine N—C bonds to any significant extent, as the bonds are barely significantly longer than the corresponding bonds in compound (2a). The benzoyl and cinnamoyl groups in (2a) and (2b), respectively, deviate slightly from the thioacrylamide plane. In (2a),

the chain progressively twists slightly, starting at the N1—C1 bond (Table 3), while in (2*b*) the plane of the entire chain is slightly bowed by torsional twists about the N1—C4, C4—C5 and C5—C6 bonds (Table 5). This bowing does not relieve the steric repulsion between the H atom at C5 and that at C12, which is compensated for by a significant enlargement of the C5—C6—C7 angle.

The amide H atom in both (2*a*) and (2*b*) forms a strong intramolecular hydrogen bond with O1 of the nitro group [graph set $S(6)$] (Tables 4 and 6). In (2*a*), the amine H atom at N3 forms bifurcated hydrogen bonds with each O atom of the nitro group of an adjacent molecule [binary graph set $R_1^2(4)$] and thereby links the molecules into infinite one-dimensional chains which run parallel to the *z* axis. The unitary graph-set motif for each of these bifurcated interactions is $C(6)$. The amine H atom at N4 has an intermolecular interaction with the amide O atom of a different neighbouring molecule. This links the molecules into infinite one-dimensional chains which run parallel to the *x* axis [graph set $C(8)$]. The combination of all these intermolecular interactions links the molecules into an infinite three-dimensional framework.

The zwitterionic character observed in the region around the ethylene C2—C3 bond in compounds (2*a*) and (2*b*) is also present in the structure of compound (3*a*) (Fig. 4), with the same pattern of bond lengths for the C1—C2, N2—C2, C2—C3, N3—C3 and N4—C3 bonds (Table 7). The angle between the three-atom planes at each end of the C2—C3 bond, as defined by N3, C3 and N4, and C1, C2 and N2, is 68.15(14)°. Atoms N1, N2, C1, C2, C3, C11 and S of the nitrothioacrylimidate moiety form a planar system, with a maximum deviation from the plane of 0.0288(18) Å for C1. The O atoms of the nitro group are tilted slightly out of this plane, with O1 and O2 lying 0.141(3) and -0.234(3) Å, respectively, from the plane. Atoms N3, C2, C3, N4, C12 and C13 of the two amine groups are also reasonably planar, with a maximum deviation from the plane of 0.0917(12) Å for C12, and C19 lies -0.191(3) Å from this plane. The imidate N1=C1 bond has lost some of its double-bond character, as it is slightly longer than a normal N=C bond, and there is a significant torsional twist about this bond: the C4—N1—C1—C2 torsion angle is -32.8(3)°. The bond lengths in this region suggest that the S atom is also involved in a 'push-pull' interaction with the imidate group. The amine H atom forms an intermolecular hydrogen bond with O2 of the nitro group of a neighbouring molecule and thereby links the molecules into infinite one-dimensional chains which run parallel to the *x* axis [graph set $C(6)$] (Table 8).

From the structure of compound (2*a*), it can be assumed that, in solution as well as in the solid state, the cyclization to a thioxopyrimidine is hindered due to the position of the amide carbonyl group relative to the amine groups at C3. The rigidity inflicted by the strong

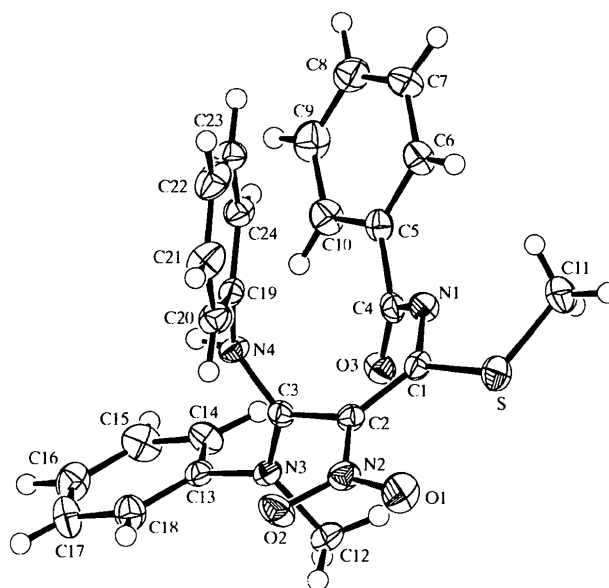


Fig. 4. View of the molecule of (3*a*) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

intramolecular hydrogen bond and the electron delocalization across the C1—C2 bond probably prevents the molecule from acquiring the necessary conformation for cyclization to occur. In compound (3*a*), however, the amide H atom and the associated intramolecular hydrogen bond are absent, and the molecule has twisted around so that one of the amino groups is situated in a more favourable position to react with the carbonyl group, thereby allowing the cyclization of (3) to the pyrimidines, (4). That the intramolecular hydrogen bond has a strong influence on the conformation and flexibility of the molecule can be seen in the enlarged bond angles for S—C1—N1, C1—N1—C4 and N1—C4—O3 in the structures of both (2*a*) and (2*b*) (Tables 3 and 5). These angles indicate strong steric repulsion between the S atom and O3, which are forced to be almost co-planar by the hydrogen bond. In (3*a*), the absence of the hydrogen bond allows the strain between the S atom and O3 to be relieved through the adoption of a different and presumably more flexible conformation, while still retaining the planarity about the C1—C2 bond caused by bond conjugation, albeit with the S atom now *cis* to the nitro group.

Experimental

Compound (1*a*) (m.p. 384–385 K) was synthesized by the method of Gompper & Schaefer (1967). The nitrothioacrylamides (2*a*) (m.p. 449.3–449.4 K) and (2*b*) (m.p. 447.5–448.0 K) were prepared according to the procedures of Moya Argilagos *et al.* (1997). The thioimide (3*a*) (m.p. 464 K) was prepared by the method of García Trimiño *et al.* (1992).

Suitable crystals were obtained by the slow evaporation of solutions of (1a), (2a), (2b) and (3a) in methanol, dimethylformamide (DMF), ethanol and DMF, respectively.

Compound (1a)

Crystal data

C₄H₈N₂O₂S $M_r = 148.18$

Triclinic

 $P\bar{1}$ $a = 7.105 (3) \text{ \AA}$ $b = 8.690 (3) \text{ \AA}$ $c = 5.777 (2) \text{ \AA}$ $\alpha = 90.65 (3)^\circ$ $\beta = 106.53 (3)^\circ$ $\gamma = 105.69 (3)^\circ$ $V = 327.7 (2) \text{ \AA}^3$ $Z = 2$ $D_x = 1.502 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 21 reflections

 $\theta = 19.5\text{--}20.0^\circ$ $\mu = 0.419 \text{ mm}^{-1}$ $T = 173 (1) \text{ K}$

Prism

 $0.42 \times 0.42 \times 0.20 \text{ mm}$

Pale yellow

Data collection

Rigaku AFC-5R diffractometer

 $\omega/2\theta$ scans

Absorption correction: none

2044 measured reflections

1902 independent reflections

1693 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.012$ $\theta_{\text{max}} = 30^\circ$ $h = 0 \rightarrow 9$ $k = -12 \rightarrow 11$ $l = -8 \rightarrow 7$

3 standard reflections

every 150 reflections

intensity decay: insignificant

Refinement

Refinement on F^2 $R(F) = 0.036$ $wR(F^2) = 0.108$ $S = 1.208$

1902 reflections

88 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.1545P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} < 0.001$ $\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$) for (1a)

| | | | |
|------------|-------------|-------------|-------------|
| S—C3 | 1.7505 (17) | N1—C3 | 1.325 (2) |
| S—C4 | 1.7973 (19) | N2—C2 | 1.369 (2) |
| N1—C1 | 1.457 (2) | C2—C3 | 1.401 (2) |
| C3—S—C4 | 104.11 (8) | N1—C3—C2 | 124.67 (14) |
| C3—N1—C1 | 125.24 (14) | N1—C3—S | 115.49 (12) |
| N2—C2—C3 | 123.83 (14) | C2—C3—S | 119.81 (12) |
| C4—S—C3—C2 | -11.48 (15) | O1—N2—C2—C3 | -4.8 (2) |

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (1a)

| D—H...A | D—H | H...A | D...A | D—H...A |
|-------------|----------|----------|-----------|---------|
| N1—H1...O1 | 0.82 (3) | 2.01 (2) | 2.652 (2) | 135 (2) |
| N1—H1...O1' | 0.82 (3) | 2.26 (2) | 2.948 (2) | 142 (2) |

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

Compound (2a)

Crystal data

C₁₂H₁₄N₄O₃S $M_r = 294.34$

Orthorhombic

 $P2_12_12_1$ $a = 11.7761 (16) \text{ \AA}$ $b = 17.172 (2) \text{ \AA}$ $c = 6.825 (4) \text{ \AA}$ $V = 1380.2 (8) \text{ \AA}^3$ $Z = 4$ $D_x = 1.416 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 18.5\text{--}20.0^\circ$ $\mu = 0.248 \text{ mm}^{-1}$ $T = 173 (1) \text{ K}$

Prism

 $0.43 \times 0.33 \times 0.28 \text{ mm}$

Red

Data collection

Rigaku AFC-5R diffractometer

 $\omega/2\theta$ scans

Absorption correction: none

4197 measured reflections

2302 independent reflections

(plus 1116 Friedel-related reflections)

2948 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$ $\theta_{\text{max}} = 30^\circ$ $h = -14 \rightarrow 16$ $k = -20 \rightarrow 24$ $l = -8 \rightarrow 9$

3 standard reflections

every 150 reflections

intensity decay: insignificant

Refinement

Refinement on F^2 $R(F) = 0.033$ $wR(F^2) = 0.090$ $S = 1.089$

3413 reflections

196 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.4796P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = 0.28 (8)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (2a)

| | | | |
|-------------|--------------|--------------|--------------|
| S—C1 | 1.6781 (19) | N3—C3 | 1.310 (3) |
| N1—C1 | 1.367 (3) | N4—C3 | 1.310 (3) |
| N1—C4 | 1.394 (3) | C1—C2 | 1.435 (3) |
| N2—C2 | 1.368 (2) | C2—C3 | 1.490 (3) |
| C1—N1—C4 | 129.28 (17) | N2—C2—C1 | 126.20 (17) |
| N1—C1—C2 | 115.96 (16) | N4—C3—N3 | 123.05 (18) |
| N1—C1—S | 125.95 (15) | O3—C4—N1 | 123.11 (19) |
| C4—N1—C1—C2 | -170.06 (19) | C1—C2—C3—N4 | -85.4 (2) |
| O1—N2—C2—C3 | 176.59 (18) | N2—C2—C3—N3 | -85.1 (2) |
| S—C1—C2—N2 | 175.82 (16) | C1—C2—C3—N3 | 94.5 (2) |
| N1—C1—C2—C3 | 176.89 (17) | C1—N1—C4—C5 | -176.19 (18) |
| N2—C2—C3—N4 | 95.0 (2) | N1—C4—C5—C10 | -171.06 (18) |

Table 4. Hydrogen-bonding geometry (\AA , $^\circ$) for (2a)

| D—H...A | D—H | H...A | D...A | D—H...A |
|--------------|----------|----------|-----------|---------|
| N1—H1...O1 | 0.88 (2) | 1.83 (2) | 2.599 (2) | 145 (2) |
| N3—H3...O1' | 0.87 (3) | 2.25 (3) | 2.937 (2) | 136 (2) |
| N3—H3...O2' | 0.87 (3) | 2.25 (3) | 3.060 (2) | 155 (2) |
| N4—H4...O3'' | 0.84 (3) | 2.14 (2) | 2.762 (2) | 130 (2) |

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

Compound (2b)*Crystal data*

C₁₆H₂₀N₄O₃S
M_r = 348.42
 Monoclinic
*P*2₁/*c*
a = 11.9391 (8) Å
b = 14.4523 (13) Å
c = 10.7398 (9) Å
 β = 108.930 (5)°
V = 1752.9 (2) Å³
Z = 4
D_x = 1.320 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 5354 measured reflections
 5107 independent reflections
 3051 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

Refinement on *F*²
R(*F*) = 0.051
 wR (*F*²) = 0.140
S = 1.010
 5107 reflections
 225 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.0973P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 5. Selected geometric parameters (Å, °) for (2b)

| | | | |
|--------------|-------------|-------------|-------------|
| S—C1 | 1.669 (2) | N4—C3 | 1.335 (3) |
| N1—C1 | 1.380 (2) | C1—C2 | 1.428 (3) |
| N1—C4 | 1.393 (3) | C2—C3 | 1.483 (2) |
| N2—C2 | 1.380 (2) | C4—C5 | 1.482 (3) |
| N3—C3 | 1.319 (3) | C5—C6 | 1.333 (3) |
| C1—N1—C4 | 130.02 (18) | N3—C3—N4 | 121.95 (17) |
| N1—C1—C2 | 115.95 (17) | O3—C4—N1 | 124.14 (19) |
| N1—C1—S | 125.54 (15) | C5—C6—C7 | 127.83 (19) |
| N2—C2—C1 | 126.67 (17) | C12—C7—C6 | 123.62 (18) |
| C4—N1—C1—C2 | 179.8 (2) | C1—C2—C3—N3 | 106.4 (2) |
| O2—N2—C2—C3 | -4.1 (3) | N2—C2—C3—N4 | 101.9 (2) |
| S—C1—C2—N2 | 179.06 (17) | C1—C2—C3—N4 | -76.5 (2) |
| N1—C1—C2—C3 | 176.93 (18) | C1—N1—C4—C5 | 174.3 (2) |
| C13—N3—C3—C2 | -18.1 (3) | N1—C4—C5—C6 | -174.8 (2) |
| C16—N4—C3—C2 | -12.1 (3) | C4—C5—C6—C7 | 171.3 (2) |
| N2—C2—C3—N3 | -75.3 (2) | C5—C6—C7—C8 | -171.1 (2) |

Table 6. Hydrogen-bonding geometry (Å, °) for (2b)

| | | | | |
|------------|----------|----------|-----------|---------|
| D—H...A | D—H | H...A | D...A | D—H...A |
| N1—H1...O1 | 0.85 (3) | 1.88 (3) | 2.616 (2) | 144 (3) |

Compound (3a)*Crystal data*

C₂₄H₂₂N₄O₃S
M_r = 446.52

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 15.5–19.0°
 μ = 0.206 mm⁻¹
T = 173 (1) K
 Prism
 0.27 × 0.25 × 0.13 mm
 Red

θ_{\max} = 30°
 h = -16 → 15
 k = -20 → 0
 l = 0 → 15
 3 standard reflections
 every 150 reflections
 intensity decay: insignificant

$(\Delta/\sigma)_{\max}$ = 0.001
 $\Delta\rho_{\max}$ = 0.47 e Å⁻³
 $\Delta\rho_{\min}$ = -0.25 e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Orthorhombic

*P*2₁2₁
 a = 11.922 (3) Å
 b = 17.628 (3) Å
 c = 10.442 (3) Å
 V = 2194.3 (9) Å³
Z = 4
D_x = 1.352 Mg m⁻³
D_m not measured

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 5488 measured reflections
 2852 independent reflections
 (plus 1475 Friedel-related reflections)
 3764 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on *F*²
R(*F*) = 0.035
 wR (*F*²) = 0.085
S = 1.023
 4327 reflections
 295 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 0.556P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 22 reflections

θ = 17.0–20.0°
 μ = 0.182 mm⁻¹
T = 173 (1) K
 Prism
 0.38 × 0.33 × 0.28 mm
 Yellow

R_{int} = 0.016
 θ_{\max} = 27.5°
 h = -11 → 15
 k = -20 → 22
 l = -12 → 13
 3 standard reflections
 every 150 reflections
 intensity decay: insignificant

$(\Delta/\sigma)_{\max}$ = 0.002
 $\Delta\rho_{\max}$ = 0.23 e Å⁻³
 $\Delta\rho_{\min}$ = -0.20 e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = -0.08 (7)

Table 7. Selected geometric parameters (Å, °) for (3a)

| | | | |
|--------------|-------------|-------------|-------------|
| S—C1 | 1.772 (2) | N3—C3 | 1.328 (2) |
| N1—C1 | 1.312 (3) | N4—C3 | 1.331 (3) |
| N1—C4 | 1.363 (3) | C1—C2 | 1.429 (3) |
| N2—C2 | 1.387 (3) | C2—C3 | 1.476 (3) |
| C1—N1—C4 | 125.52 (18) | N2—C2—C1 | 123.03 (19) |
| N1—C1—C2 | 124.71 (18) | N3—C3—N4 | 120.63 (18) |
| N1—C1—S | 116.32 (15) | O3—C4—N1 | 125.3 (2) |
| C4—N1—C1—C2 | -32.8 (3) | N2—C2—C3—N3 | -70.0 (2) |
| O1—N2—C2—C3 | 172.16 (19) | C1—C2—C3—N3 | 111.4 (2) |
| N1—C1—C2—C3 | 2.4 (3) | N2—C2—C3—N4 | 112.5 (2) |
| C13—N3—C3—C2 | 178.93 (17) | C1—C2—C3—N4 | -66.1 (3) |
| C12—N3—C3—C2 | -9.8 (3) | C1—N1—C4—C5 | 157.06 (19) |
| C19—N4—C3—C2 | -18.3 (3) | N1—C4—C5—C6 | 20.1 (3) |

Table 8. Hydrogen-bonding geometry (Å, °) for (3a)

| | | | | |
|-------------------------|----------|----------|-----------|---------|
| D—H...A | D—H | H...A | D...A | D—H...A |
| N4—H4...O2 ⁱ | 0.91 (3) | 1.99 (3) | 2.809 (2) | 150 (2) |

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.

Although none of the structures contain chiral molecules, compounds (2a) and (3a) crystallize in a polar space group. The reflection data for (2a) and (3a) included the intensities of the Friedel opposites of all unique reflections for which $\theta < 25^\circ$ and $\theta < 20^\circ$, respectively. The value of the absolute structure parameter (Flack, 1983) for (3a) confirms the absolute structure. For (2a), the result is ambiguous because of the magnitude of the standard uncertainty, but it suggests the presence of a degree of merohedral twinning.

For each structure, the positions of all H atoms were initially located in a difference electron-density map. The positions of the amine and amide H atoms were refined freely, as were their individual isotropic displacement parameters. The positions of all other H atoms were geometrically idealized and refined with a riding model (including free rotation about C—C bonds), with U_{iso} constrained to be $1.2U_{eq}$ ($1.5U_{eq}$ for methyl groups) of the parent C atom. For (2a), five reflections were considered to be severe outliers and were excluded from the final refinement.

For all compounds, data collection: *MSCI/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1991); cell refinement: *MSCI/AFSC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS86* (direct methods) (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1546). Services for accessing these data are described at the back of the journal.

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6,7,8,9-Tetrahydro-3-methyl-1H-pyrano-[4,3-b]quinolin-1-one

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Abstract

The condensation reaction of 4-amino-6-methyl-2-pyrone with 1-cyclohexenecarboxaldehyde and a catalytic amount of (*S*)-(+)-10-camphorsulfonic acid in toluene at 358 K gave a 1:2.5 ratio of the title compound, (1) (C₁₃H₁₃NO₂), and 7,8,9,10-tetrahydro-1H-pyrano[4,3-*c*]isoquinoline-1-one, (2). The formation of (2) presumably proceeds through an intermediate imine. Both (1) and (2) show inhibitory activities against acetylcholinesterase and human aldose reductase. Of the three linear-fused rings of (1), both ring *A* and ring *B* are planar and the angle between these planes is 0.46 (13)°. While the two C atoms of cyclohexane ring *C* attached to its common atoms with ring *B* are in the plane of the latter, as expected, the remaining two C atoms of ring *C* are out of this plane, by 0.342 (4) and –0.402 (3) Å, respectively.

Comment

In the search for new biologically active compounds, a class of tricyclic pyranopyrones was synthesized by Hua *et al.* (1997). In this reaction, 6-substituted 4-hydroxy-2-pyrones were condensed with 1-cyclo-