Crystal structure of (1*E*,3*E*)-4-methylthio-2-nitro-3-phenylsulfonyl-1-pyrrolidino-1,3-butadiene, C$_{15}$H$_{18}$N$_2$O$_4$S$_2$

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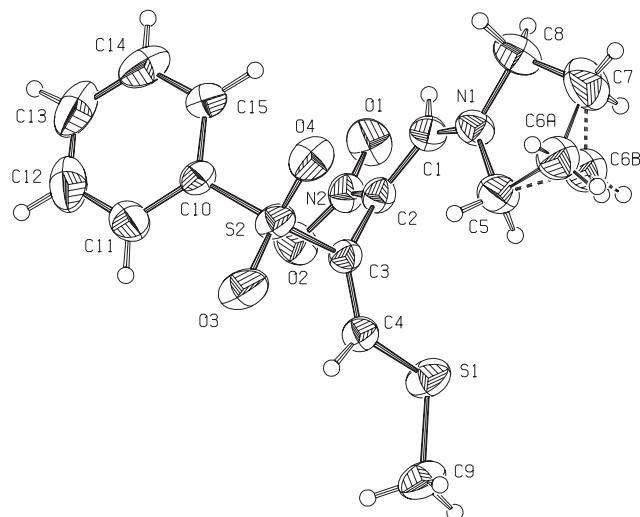
Abstract

C$_{15}$H$_{18}$N$_2$O$_4$S$_2$, monoclinic, *P*12$_1$/*c*1 (No. 14), *a* = 8.754(3) Å, *b* = 12.499(2) Å, *c* = 15.599(3) Å, *β* = 95.09(2)°, *V* = 1700.1 Å^3, *Z* = 4, *R*$_{gt}$(*F*) = 0.049, *wR*$_{ref}$(*F*^{2}) = 0.128, *T* = 294 K.

Source of material

The title compound was synthesized in 87% yield from 3-nitro-4-(phenylsulfonyl)thiophene [1] with a proper modification of our ring-opening procedure of thiophene derivatives [2] and crystallized from ethanol. Mp 463.7-464.3°.

Experimental details

In the refinement, the atoms C6A and C6B were considered as isotropic and the sum of their site occupancy factors was tied to unity [final values: 0.613(7) and 0.387(7) respectively, with *U*(C6A) = *U*(C6B) = 0.070(1) Å^2]. No further constraints were imposed on heavy atoms. The high displacement parameters of C7 indicated its trend to disordered behaviour, but the resolution of the data was not sufficient to consider the atom split over two distinct positions. Several H atoms were located by difference syntheses and refined without constraints; those bonded to C12 and C9 were subjected to a riding and to a rigid group refinement respectively. The positions of H atoms bonded to C6A and C6B were calculated but not allowed to be refined.

Discussion

The crystal structure of the title compound proves an (*E*,*E*)-configuration which is of relevance for the study of the reactivity of derivatives obtained therefrom in cyclization processes [3]. The structure is affected by disorder, one atom of the pyrrolidine ring

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being split over two different positions (C6A, C6B). For both of them the pyrrolidine moiety is in an envelope conformation, the ring asymmetry parameters [4,5] evidencing a pseudo-mirror plane through atom C7 in the "C6A-ring" [Δ*C*$_s$ = 0.002(2); atoms N1, C5, C6A, C8 coplanar within 0.002(6) Å], and another pseudo-mirror plane through atom C5 in the "C6B-ring" [Δ*C*$_s$ 0.017(3); atoms N1, C6B, C7, C8 coplanar within 0.022(9) Å]. The out-of-plane atoms (C7 and C5, respectively) lie at distances of 0.500(5) Å and 0.468(3) Å from the relevant mean planes above. The internal strain imposed by the bulky pyrrolidine moiety reflects on a short 1,5-intramolecular contact [C3···C5 3.093(4) Å] and, even more evidently, on a deviation of the C1=C2 *sp*^{2} system from planarity, the torsion angle N1–C1–C2–C3 being as large as 22.6(4)°. Correspondingly a rather long C1=C2 bond distance [1.370(3) Å] is found.

In order to ascertain the effect of packing forces on the molecular conformation, the geometry of the title compound was optimized with quantum mechanical calculations [6] at the HF/3-21G* level (263 basis functions). Starting data were the experimental coordinates, considering in separate calculations both the "C6A" and the "C6B" forms; they converged to the same molecular model. The resulting molecular conformation shows a remarkable increase of the C1–C2–C3–C4 torsion angle [from –114.6(3)° in the crystal to –93.0° in the isolated molecule], accompanied by a general relief of the steric hindrance, the N1–C1–C2–C3 torsion angle decreasing from 22.6(4)° to a mere 0.2° in the isolated molecule. Other changes in geometry are less dramatic: the C1=C2 bond distance decreases to 1.359°A and the short C3···C5 intramolecular contact increases to 3.152 Å. These values indicate however a residual strain due to the molecular overcrowding. On the other side, in the crystal the intermolecular distances are in the normal range, the shortest contact (with respect to the sum of the involved van der Waals radii) being *d*(C5···O3) = 3.162(3) Å (O3 in –*x*, 1–*y*, 1–*z*). Therefore, we consider that crystal forces are effective in amplifying the internal strain, as observed in the experimental conformation.

Table 1. Data collection and handling.

Crystal:	pale yellow prism, size 0.22 × 0.24 × 0.48 mm
Wavelength:	Mo *K$_α$* radiation (0.71070 Å)
μ:	3.33 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, *ω*
2*θ*$_{max}$:	54.94°
N(hkl)$_{measured}$, *N(hkl)*$_{unique}$:	3886, 3886
Criterion for *I*$_{obs}$, *N(hkl)*$_{gt}$:	*I*$_{obs}$ > 2 *σ*(*I*$_{obs}$), 2596
N(param)$_{refined}$:	244
Programs:	NRCVAX [7], SHELXL-97 [8], PLATON [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	4e		0.131(3)	0.806(2)	0.723(2)	0.056
H(4)	4e		0.246(3)	0.524(2)	0.496(2)	0.056
H(5A)	4e		0.010(3)	0.551(3)	0.688(2)	0.078
H(5B)	4e		−0.077(3)	0.592(2)	0.607(2)	0.078
C(6A)	4e	0.613(7)	−0.2263(6)	0.5786(4)	0.6980(4)	0.070(1)
C(6B)	4e	0.387	−0.176(1)	0.5593(7)	0.7374(6)	0.070
H(6A)	4e	0.613	−0.2357	0.5061	0.7192	0.084(1)
H(6B)	4e	0.613	−0.3058	0.5917	0.6519	0.084
H(6C)	4e	0.387	−0.1170	0.5208	0.7832	0.084
H(6D)	4e	0.387	−0.2576	0.5141	0.7122	0.084
H(7A)	4e		−0.168(5)	0.627(3)	0.816(2)	0.116

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(7B)	4e		−0.332(5)	0.666(3)	0.787(2)	0.116
H(8A)	4e		−0.218(3)	0.800(2)	0.701(2)	0.082
H(8B)	4e		−0.101(4)	0.794(2)	0.789(2)	0.082
H(9A)	4e		0.3047	0.3281	0.5604	0.086
H(9B)	4e		0.4639	0.3191	0.6145	0.086
H(9C)	4e		0.4506	0.3802	0.5264	0.086
H(11)	4e		0.311(3)	0.766(2)	0.356(2)	0.080
H(12)	4e		0.4322	0.9286	0.3255	0.108
H(13)	4e		0.393(4)	1.075(3)	0.400(2)	0.113
H(14)	4e		0.230(4)	1.073(3)	0.506(2)	0.101
H(15)	4e		0.095(3)	0.920(2)	0.542(2)	0.075

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4e	0.1072(3)	0.7505(2)	0.6908(2)	0.053(1)	0.043(1)	0.044(1)	−0.006(1)	0.000(1)	−0.0087(9)
C(2)	4e	0.2198(2)	0.7198(2)	0.6403(1)	0.046(1)	0.040(1)	0.044(1)	−0.0061(9)	0.0010(9)	0.0000(9)
C(3)	4e	0.2021(2)	0.6534(2)	0.5621(1)	0.047(1)	0.038(1)	0.043(1)	−0.0018(9)	0.0034(9)	−0.0004(9)
C(4)	4e	0.2603(3)	0.5566(2)	0.5514(2)	0.048(1)	0.045(1)	0.046(1)	−0.001(1)	0.001(1)	−0.002(1)
C(5)	4e	−0.0697(3)	0.5966(2)	0.6676(2)	0.068(2)	0.052(2)	0.079(2)	−0.016(1)	0.022(2)	−0.013(1)
C(7)	4e	−0.2365(5)	0.6582(3)	0.7694(3)	0.082(2)	0.108(3)	0.106(3)	−0.017(2)	0.044(2)	−0.003(2)
C(8)	4e	−0.1476(3)	0.7520(3)	0.7447(2)	0.054(2)	0.081(2)	0.070(2)	−0.004(1)	0.009(1)	−0.025(2)
C(9)	4e	0.3996(3)	0.3642(2)	0.5769(2)	0.062(2)	0.052(2)	0.100(2)	0.013(1)	0.002(2)	0.009(2)
C(10)	4e	0.1941(3)	0.8307(2)	0.4506(1)	0.053(1)	0.045(1)	0.050(1)	0.010(1)	0.002(1)	0.007(1)
C(11)	4e	0.2925(3)	0.8310(3)	0.3861(2)	0.063(2)	0.083(2)	0.055(2)	0.025(2)	0.007(1)	0.010(1)
C(12)	4e	0.3659(4)	0.9265(4)	0.3689(2)	0.064(2)	0.121(3)	0.086(2)	0.011(2)	0.021(2)	0.044(2)
C(13)	4e	0.3422(4)	1.0158(3)	0.4142(3)	0.070(2)	0.081(3)	0.129(3)	−0.007(2)	0.004(2)	0.051(2)
C(14)	4e	0.2453(4)	1.0147(2)	0.4782(3)	0.087(2)	0.046(2)	0.118(3)	−0.000(2)	0.002(2)	0.004(2)
C(15)	4e	0.1692(3)	0.9218(2)	0.4972(2)	0.071(2)	0.045(1)	0.071(2)	0.008(1)	0.013(1)	0.001(1)
N(1)	4e	−0.0255(2)	0.7047(2)	0.6980(1)	0.051(1)	0.051(1)	0.052(1)	−0.0044(9)	0.0071(8)	−0.0113(9)
N(2)	4e	0.3644(2)	0.7711(2)	0.6572(1)	0.051(1)	0.048(1)	0.051(1)	−0.0103(9)	0.0028(9)	−0.0008(9)
O(1)	4e	0.3874(2)	0.8309(2)	0.7200(1)	0.071(1)	0.074(1)	0.064(1)	−0.027(1)	0.0002(9)	−0.0203(9)
O(2)	4e	0.4641(2)	0.7536(2)	0.6080(1)	0.054(1)	0.073(1)	0.078(1)	−0.0142(9)	0.0168(9)	−0.011(1)
O(3)	4e	0.1021(3)	0.6414(2)	0.4002(1)	0.124(2)	0.054(1)	0.053(1)	0.013(1)	−0.026(1)	−0.0117(8)
O(4)	4e	−0.0507(2)	0.7433(2)	0.4977(1)	0.049(1)	0.066(1)	0.085(1)	−0.0009(9)	−0.0067(9)	0.010(1)
S(1)	4e	0.36130(9)	0.48596(6)	0.63147(4)	0.0748(5)	0.0546(4)	0.0631(4)	0.0107(3)	−0.0128(3)	0.0031(3)
S(2)	4e	0.09621(7)	0.71212(5)	0.47258(4)	0.0610(4)	0.0418(3)	0.0490(3)	0.0037(3)	−0.0094(3)	−0.0031(2)

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