ψ scan
Absorption correction:
multi-scan (*SADABS*; Sheldrick, 1997*a*)
$T_{\min} = 0.964$, $T_{\max} = 0.971$
25 360 measured reflections

$R_{\rm int} = 0.041$
$\theta_{\max} = 25.09°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.099$
$S = 1.116$
2280 reflections
274 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.6498P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.148$ e Å^{-3}
$\Delta\rho_{\min} = -0.175$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0086 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 4 (2)

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of five sets of exposures; each set had different χ and ω angles, and each exposure covered 0.5° in φ. The crystal-to-detector distance was 5 cm. Coverage of the unique set was over 99% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames between runs and analysing the duplicate reflections. The structure was solved by direct methods using *SHELXS*97 (Sheldrick, 1990). All non-H atoms were refined anisotropically using *SHELXL*97 (Sheldrick, 1997*b*). The H atoms were refined using a riding model. The isotropic displacement parameters were set to 1.2 (1.5 for CH_3 groups) times the equivalent displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Molecular graphics: *SHELXTL* (Siemens, 1995). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1249). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 373–376

2-(Isopropoxy)-4,12-diphenyl-4-(trifluoromethyl)-1,13-dithia-3,11-diazadispiro[4.0.4.3]trideca-2,11-diene

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Abstract

The title compound, $C_{25}H_{25}F_3N_2OS_2$, is one of two isomeric 1:1 cycloadducts of a thermally generated isopropoxy-substituted nitrile ylide and 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione. The structure shows the regiochemistry of the formation of the major isomer. The cyclopentane ring is disordered and shows both a half-chair and an envelope conformation. The heterocyclic rings have envelope conformations. The C—C bonds involving the heterocyclic spiro C atom are elongated due to electronic effects from the neighbouring S atoms. Delocalization effects result in asymmetric S—C bond lengths.

Comment

The regioselectivity of 1,3-dipolar cycloadditions of nitrile ylides is of theoretical (Houk, 1979) and preparative interest (Hansen & Heimgartner, 1984). It has been shown that substituents at C1 and C3 of the nitrile ylide, (I), have a distinct influence on the geometry of the ylide (propargyl-type *A versus* allenyl-type *B*; Caramella *et al.*, 1977).

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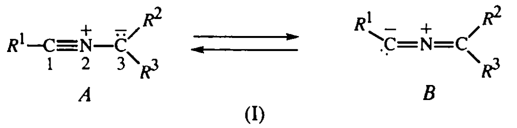
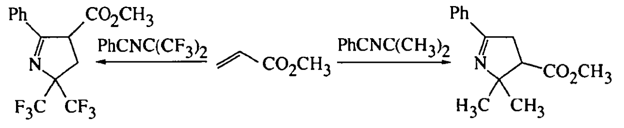
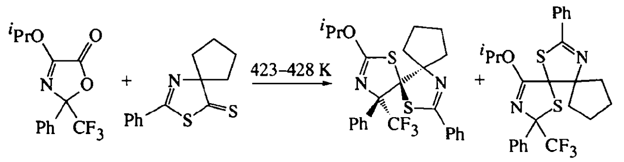


(I)

As the calculated coefficients at C1 and C3 of the HOMO (highest occupied molecular orbital) of the nitrile ylides are different in the linear (*A*) and in the bent structure (*B*), the regioselectivity of the cycloadditions with electron-deficient dipolarophiles also depends on the substituents at C1 and C3. For example, in the case of benzonitrile ylides (R^1 = Ph), the propargyl structure *A* is preferred when R^2,R^3 are electron-withdrawing substituents (*e.g.* CF_3) and the allenyl structure *B* is more stable when R^2,R^3 are electron-donating groups (*e.g.* CH_3). As a consequence, the HOMO of benzonitrilobis(trifluoromethyl)methanide (R^1 = Ph, R^2 = R^3 = CF_3) displays the largest coefficient on the ylide C3 atom, whereas in benzonitrilio-2-propanide (R^1 = Ph, R^2 = R^3 = CH_3), the nitrile C1 atom shows the largest coefficient. Therefore, the protonation of these nitrile ylides occurs at C3 (Burger *et al.*, 1976) and at C1 (Claus *et al.*, 1974; Padwa, Rasmussen & Tremper, 1976; Padwa, Smolanoff & Tremper, 1976), respectively. Furthermore, the cycloaddition with methyl acrylate yielded 3,4-dihydro-2*H*-pyrrole-4-carboxylate, (II) (Burger & Fehn, 1972; Burger *et al.*, 1974), and 3,4-dihydro-2*H*-pyrrole-3-carboxylate, (III) (Padwa *et al.*, 1973), as the major products formed *via* regioisomeric transition states.



(II) (III)



(IV) (V) (VI) (VII)

Much less is known about the influence of the substituent R^1 at C1 on the geometry and the regioselectivity of the cycloaddition of nitrile ylides (Houk, 1979). Therefore, we investigated reactions of nitrile ylides, (I), bearing a heteroatom substituent at C1, *i.e.* amino- (Dietliker & Heimgartner, 1983), arylthio- (Wipf *et al.*, 1988), and alkoxy-substituted nitrile ylides (Bozhkova & Heimgartner, 1989; Bojkova & Heimgartner, 1998). The cycloadditions of amino- and benzylthio-substituted nitrile ylides, (I) [R^1 = Ph(CH_3)N and $PhCH_2S$, respectively], with electron-deficient dipolarophiles all occurred in a regiospecific way, and even with R^1 = 2-naphthyl-*S*, R^2 = Ph and R^3 = CF_3, two stereoisomers of only one regioisomeric cycloadduct were formed (Wipf *et al.*, 1988). On the other hand, the thermolysis of 4-(isopropoxy)-2-phenyl-2-(trifluoromethyl)-1,3-oxazol-5(2*H*)-one, (IV), in the presence of 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione, (V), led to a *ca* 2:1 mixture of the two 1:1-adducts (VI) and (VII) (Bojkova & Heimgartner, 1998).

The only significant differences in the spectroscopic data are shown by ν(C=N) in the IR spectra [1615 cm^{-1} for (VI) and 1645/1635 cm^{-1} for (VII)] and by the ^{13}C NMR absorptions of the two spiro-C atoms [102.4 and 90.3 p.p.m. for (VI), and 90.8 and 85.9 p.p.m. for (VII)]. In spite of these differences, the unequivocal assignment of the isomeric structures (VI) and (VII) to the 1:1-adducts with melting points of 428–434 K and 371–374 K, respectively, was not possible. For this reason, the structure of (VI) was established by X-ray crystallography.

The cyclopropane ring in the structure of (VI) is disordered in that the ring adopts, alternately, a half-chair conformation twisted about the C2—C3 bond and an envelope conformation with C6 as the envelope flap. This resulted in the need to refine two positions for each of the atoms C4 and C5. The half-chair conformation predominates in the crystal with 66 (2)% of the molecules having this conformation (Fig. 1). The pseudo-rotation parameters, *P* and τ_m (Rao *et al.*, 1981), for the half-chair conformation are 2.7 (8) and 41.5 (4)°, respectively, with C2 and C3 being −0.29 (3) and 0.37 (3) Å, respectively, from the plane defined by the other three atoms. For the envelope conformation, *P* and τ_m are 299.0 (10) and 41.6 (8)°, with C6 0.612 (19) Å

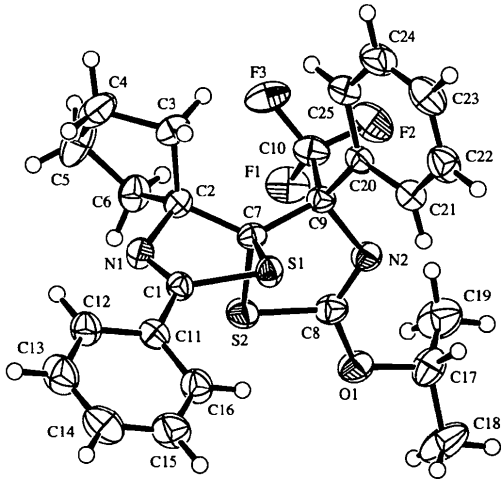


Fig. 1. View of the major conformation of compound (VI) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level. H atoms are represented by circles of arbitrary size.

from the plane of the remaining four atoms. The maximum deviation of these four atoms from their mean plane is 0.031 (12) Å for C4*A*.

Both heterocyclic rings adopt an envelope conformation with the spiro atom, C7, being the envelope flap in each case. For the ring containing S1, the values of P and τ_m are 116.1 (2) and 38.3 (1)°, with the deviation of C7 from the plane defined by the remaining four atoms being 0.659 (3) Å. The corresponding values for the ring containing S2 are 34.2 (3), 30.2 (1)° and 0.513 (3) Å, respectively. The maximum deviation of the in-plane atoms from the mean plane of each ring, defined by excluding C7, is 0.0238 (12) and 0.0357 (13) Å for N1 and N2, respectively.

Most of the bond lengths and angles have normal values, however, the elongated C2—C7 and C7—C9 bonds are noteworthy. It has frequently been observed in similar spirocyclic bisthiazole, thiazole–oxathiolane and thiazole–dithiolane compounds that C—C bonds involving the heterocyclic spiro-C atom are elongated with values in the range 1.56–1.61 Å (Büchel *et al.*, 1984; Wipf *et al.*, 1988; Mlostoń *et al.*, 1991, 1994; Kägi *et al.*, 1993; Shi *et al.*, 1994; Villalgordo *et al.*, 1995; Meier *et al.*, 1997). The bond elongation is presumably caused by the combined electron-withdrawing effects of the two S atoms adjacent to the spiro-C atom, but may be further enhanced by the unique electronic properties of these heterospirocyclic rings. This effect is much less pronounced in the structures of two thiazole–thiazolidines reported by Mlostoń *et al.* (1997).

The S—C bond lengths in (VI) are asymmetric about the S atoms and are about 0.08 Å shorter on the side closest to the C=N bonds. This indicates that the lone pairs of electrons on the S atoms are partially delocalized with the adjacent π electron system of the C=N bond. Similar asymmetry has also been observed in the related compounds referenced above. The relatively short C1—C11 bond indicates that the π system of the phenyl group at C1 is also interacting to some extent with the adjacent C=N π system, even though the S1—C1—C11—C16 torsion angle is −22.4 (3)°.

Experimental

The title compound, (VI), was obtained in 9% yield by heating a 1:2 mixture of 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione, (IV), and 4-(isopropoxy)-2-phenyl-2-(trifluoromethyl)-1,3-oxazol-5(2*H*)-one, (V), in a nitrogen atmosphere to 423–428 K (Bojkova & Heimgartner, 1998). Chromatography on silica gel and recrystallization from hexane–petroleum ether gave colourless prisms (m.p. 428–434 K).

Crystal data

$C_{25}H_{25}F_3N_2OS_2$
$M_r = 490.59$
Monoclinic
$P2_1/n$
$a = 11.097 (4)$ Å
$b = 18.745 (5)$ Å
$c = 12.237 (3)$ Å
$\beta = 108.95 (2)°$
$V = 2407.6 (10)$ Å^3
$Z = 4$
$D_x = 1.353$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 12.0–13.0°$
$\mu = 0.265$ mm^{-1}
$T = 295 (1)$ K
Irregular block
0.52 × 0.45 × 0.32 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
Wyckoff ω scans
Absorption correction: none
4772 measured reflections
4226 independent reflections
3302 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

$\theta_{max} = 25.0°$
$h = 0 \rightarrow 13$
$k = -1 \rightarrow 22$
$l = -14 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: insignificant

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.088$
$S = 1.038$
4226 reflections
337 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 1.3684P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.188$ e Å^{-3}
$\Delta\rho_{min} = -0.313$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0005 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C1	1.772 (2)	N2—C8	1.270 (3)
S1—C7	1.849 (2)	N2—C9	1.476 (3)
S2—C8	1.753 (2)	C1—C11	1.475 (3)
S2—C7	1.842 (2)	C2—C7	1.573 (3)
O1—C8	1.333 (3)	C7—C9	1.598 (3)
N1—C1	1.275 (3)	C9—C10	1.550 (3)
N1—C2	1.487 (3)	C9—C20	1.544 (3)
C1—S1—C7	87.81 (10)	C9—C7—S2	103.82 (13)
C8—S2—C7	88.11 (10)	C2—C7—S1	102.21 (13)
C1—N1—C2	112.89 (17)	C9—C7—S1	107.07 (14)
C8—N2—C9	111.43 (18)	S2—C7—S1	106.40 (10)
N1—C1—S1	117.01 (16)	N2—C8—O1	126.5 (2)
N1—C2—C7	105.13 (16)	N2—C8—S2	120.65 (17)
C2—C7—C9	128.94 (17)	O1—C8—S2	112.90 (17)
C2—C7—S2	106.77 (14)	N2—C9—C7	106.98 (16)
C2—N1—C1—S1	−4.6 (2)	S1—C1—C11—C16	−22.4 (3)
C2—C3—C4*A*—C5*A*	5 (2)	N1—C1—C11—C12	−20.0 (3)
C9—N2—C8—S2	−7.2 (3)	N2—C9—C20—C21	−25.6 (2)

The ψ scans of three reflections showed that absorption effects were negligible. Two methylene groups, C4 and C5, of the cyclopentane ring are disordered, which results in two distinct conformations for this ring. Two positions were defined for each of these atoms and their site-occupancy factors were refined. The major conformation has an occupancy of 0.66 (2). The conformation of the disordered region was restrained to maintain a reasonable geometry by applying *DELU* and *SAME* restraints (*SHELXL*97; Sheldrick, 1997) to the atoms C3, C4, C4*A*, C5, C5*A* and C6. All H atoms were placed in geometrically calculated positions and allowed to ride on their parent atoms. The orientations of the methyl H atoms were fitted to difference electron density maxima (*HFIX* 137). The isotropic displacement parameters of the H atoms of the disordered methylene groups were set equal to $1.2U_{\rm eq}$ of the parent C atom, while those of the remaining H atoms were refined freely. Two reflections whose intensities were considered to be severe outliers were excluded during the refinement.

Data collection: *P3/F* (Nicolet XRD Corporation, 1987). Cell refinement: *P3/F*. Data reduction: locally modified *XTAPE5* from *P3/F*. Program(s) used to solve structure: direct methods *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. 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: AB1528). Services for accessing these data are described at the back of the journal.

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meso-1-[3-(1-Hydroxy-3-butynyl)phenyl]-3-butyn-1-ol†

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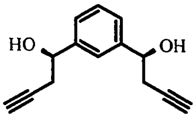
Abstract

The title compound, $C_{14}H_{14}O_2$, crystallizes with two independent molecules which are very similar and differ mainly by their involvement in the hydrogen-bonding system.

Comment

The title structure, (I), contains two independent molecules which are related by a pseudo-translation about vector $(\frac{1}{2},0,\frac{1}{2})$, leading to a pseudo-*B*-centered cell. This pseudo-translation is equivalent to a pseudo-inversion centre at $\frac{1}{4},0,\frac{1}{4}$ (Desiraju *et al.*, 1991). The independent molecules differ mainly in the relative orientation of the hydroxyl groups, which is a result of the different involvement of the molecules in the hydrogen-bonding system.



(I)

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† Alternative name: *meso*-1,1′-(*m*-phenylene)bis(but-3-ynol).