Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
O1	0.0659 (3)	0.6626 (2)	0.87665 (15)	0.0282 (5)
O2	−0.1716 (3)	0.9239 (2)	0.54636 (13)	0.0196 (4)
O3	0.0722 (3)	0.74704 (15)	0.71695 (13)	0.0173 (4)
O4	−0.3226 (3)	1.0525 (2)	0.86010 (14)	0.0202 (4)
C1	−0.0128 (3)	0.7445 (2)	1.0138 (2)	0.0161 (5)
C2	−0.0683 (4)	0.6564 (2)	1.0590 (2)	0.0193 (5)
C3	−0.0801 (4)	0.6553 (2)	1.1549 (2)	0.0242 (6)
C4	−0.0346 (4)	0.7409 (3)	1.2060 (2)	0.0267 (7)
C5	0.0239 (4)	0.8271 (2)	1.1610 (2)	0.0238 (6)
C6	0.0333 (4)	0.8292 (2)	1.0649 (2)	0.0194 (6)
C7	0.0036 (4)	0.7399 (2)	0.9112 (2)	0.0176 (5)
C8	−0.0550 (3)	0.8242 (2)	0.8520 (2)	0.0134 (5)
C9	−0.0177 (3)	0.8223 (2)	0.7561 (2)	0.0132 (5)
C10	−0.0819 (3)	0.8991 (2)	0.6987 (2)	0.0130 (5)
C11	−0.1858 (3)	0.9739 (2)	0.7360 (2)	0.0150 (5)
C12	−0.2218 (4)	0.9762 (2)	0.8297 (2)	0.0148 (5)
C13	−0.1568 (3)	0.9014 (2)	0.8877 (2)	0.0146 (5)
C14	−0.0535 (3)	0.9023 (2)	0.5962 (2)	0.0143 (5)
C15	0.1158 (3)	0.8874 (2)	0.5574 (2)	0.0139 (5)
C16	0.2588 (4)	0.9103 (2)	0.6079 (2)	0.0180 (5)
C17	0.4154 (4)	0.9017 (2)	0.5680 (2)	0.0224 (6)
C18	0.4307 (4)	0.8694 (2)	0.4768 (2)	0.0231 (6)
C19	0.2885 (4)	0.8454 (2)	0.4260 (2)	0.0227 (6)
C20	0.1324 (4)	0.8546 (2)	0.4657 (2)	0.0171 (5)

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

O1—C7	1.239 (3)	C8—C9	1.421 (3)
O2—C14	1.225 (3)	C9—C10	1.406 (3)
O3—C9	1.351 (3)	C10—C11	1.398 (4)
O4—C12	1.363 (3)	C10—C14	1.502 (3)
C1—C6	1.389 (4)	C11—C12	1.388 (4)
C7—C8	1.479 (4)	C12—C13	1.395 (4)
C8—C13	1.403 (4)	C14—C15	1.484 (4)
C6—C1—C2	120.0 (2)	C9—C10—C14	123.2 (2)
O1—C7—C8	120.7 (2)	C12—C11—C10	121.1 (2)
O1—C7—C1	118.1 (2)	O4—C12—C11	117.1 (2)
C8—C7—C1	121.2 (2)	O4—C12—C13	123.2 (2)
C13—C8—C9	119.7 (2)	C11—C12—C13	119.7 (2)
C13—C8—C7	121.1 (2)	C12—C13—C8	120.5 (2)
C9—C8—C7	119.1 (2)	O2—C14—C15	121.1 (2)
O3—C9—C10	118.4 (2)	O2—C14—C10	118.1 (2)
O3—C9—C8	122.4 (2)	C15—C14—C10	120.7 (2)
C10—C9—C8	119.1 (2)	C16—C15—C20	119.0 (3)
C11—C10—C9	119.8 (2)	C16—C15—C14	121.8 (2)
C11—C10—C14	116.9 (2)	C20—C15—C14	119.1 (2)

Data collection: *MADNES* (Enraf–Nonius, 1990). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1231). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Balancing Conjugational Stabilization and Torsional Strain. The Solid-State Structure of a 2-Thioalkyl-Substituted Pyridine *N*-Oxide

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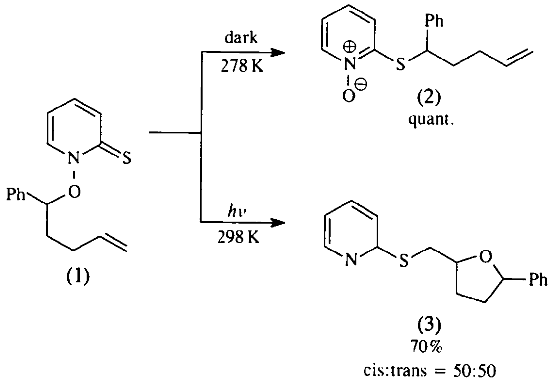
Abstract

The solid-state geometry of 2-(1-phenyl-4-penten-1-ylthio)pyridine *N*-oxide, $C_{16}H_{17}NOS$, provides an insight into the spatial arrangement of the 2-thioalkyl side chain. The N2—C7—S8 bond angle [112.0 (2)°] shows a significant and unprecedented distortion from the expected value of 120° towards the pyridine *N*-oxide O atom. The substituents of the thioether are arranged to allow conjugational interaction of the lone pairs on sulfur and the heteroaromatic nucleus on one side, and a minimization of conformational strain between the pyridyl and the alkenyl groups on the other side.

Comment

Recent findings on the utility of *O*-alkylated 1-hydroxypyridine-2(1*H*)-thiones, *e.g.* (1), as alkoxyl radical precursors in synthetic radical chemistry (Hartung & Gallou, 1995) were paralleled by the discovery of an unexpected efficient isomerization of the pyridinethione (1) which afforded the *N*-oxide (2) in quantitative yield (Hartung, Hiller & Schmidt, 1996). This transformation has to pursue a reaction channel which is clearly different from the visible-light-induced N—O cleavage in *O*-alkylpyridinethiones. The latter leads to the phenyl-substituted tetrahydrofuran (3) *via* an efficient and fast 5-*exo*-trig radical reaction (Baldwin, 1976; Hartung *et al.*, 1996). In order to rationalize both the mechanistic details of the pyridinethione *S*-alkylpyridine *N*-oxide rearrangement and its driving forces by computational methods, the choice of an appropriate wavefunction which describes pivotal elements of the geometry and hence the relative energy values properly is fundamental. In view of the sparse crystallographic data of non-coordinated non-hydrogen-bonded 2-substituted pyridine *N*-oxides in general and 2-thioalkyl-substituted derivatives in particular, 2-(1-phenyl-4-penten-1-ylthio)pyridine *N*-oxide (2) was investigated by X-ray diffraction.



The geometry of the pyridine *N*-oxide (2) in the solid state is shown in Fig. 1. The unit cell contains both enantiomers of (2) with respect to its chiral centre at C9. The S and O substituents are bound to an almost regular heterocyclic planar hexagon. The N2—C3 bond [1.348 (4) Å] is slightly shorter than the opposite N2—C7 distance [1.360 (3) Å] while the average bond length in the pyridine ring is 1.36 (2) Å. According to the measured bond angles, the S atom is bent significantly towards the *N*-oxide O atom [N2—C7—S8 = 112.0 (2), O1—N2—C7 = 117.8 (2), O1—S8—C9 = 160.5 (1)°] and the distance between S8 and O1 is reduced to 2.661 (2) Å. Similar findings have been reported for 2-[(hydroxymethoxy)methylthio]pyridine *N*-oxide which is the only known 2-thioalkylpyridine *N*-oxide according to a CSD search (Haugwitz, Toeplitz & Gougoutas, 1980). The N2—O1 bond in (2) measures 1.308 (3) Å, which is in accord with the range of 1.301 (4)–1.308 (2) Å for 2-substituted pyridine *N*-oxides (Möhrle, Trösler, Linden, Mootz & Wunderlich, 1981; Olszak, Sobczyński, Brzozowski, Grabowski & Gwoździński, 1995) that serve neither as monodentate ligands nor as hydrogen-bond acceptors. The alkenyl side chain is aligned in an antiperiplanar arrangement with the phenyl ring twisted towards the heterocyclic core and the pentenyl substituent pointing into the opposite direction of the pyridine *N*-oxide group [C7—S8—C9—C10 = −172.5 (2), C7—S8—C9—C14 = 65.2 (2)°]. The position of the phenyl group can be best rationalized as a balance between favourable electronic interactions and torsional strain. One of the lone pairs on the S atom tends to align itself orthogonal to the nodal plane of the heterocycle in (2) in order to optimize conjugational interactions [C6—C7—S8—C9 = 5.1 (3)°]. The alkenyl group adopts a conformation which allows a minimization in torsional strain between the pyridyl and the alkenyl substituent on the S atom. Thus the smallest group on C9, the H atom, points towards H6, the bigger phenyl group is twisted out of the heterocyclic plane and the biggest substituent, the pentenyl chain, is arranged antiperiplanar with respect to the pyridine *N*-oxide substituent. In conclusion, the characteristic bond angles at the S atom with its distortion towards the pyridine *N*-oxide O atom in (2) and the conformation of the 1-phenyl-4-pentenyl side chain give valuable insights into structural properties of this class of compounds. This study forms the basis for further experimental studies on the solution structure of (2) and theoretical studies related to the structures of 2-thioalkyl pyridine *N*-oxides and their pyridinethione isomers.

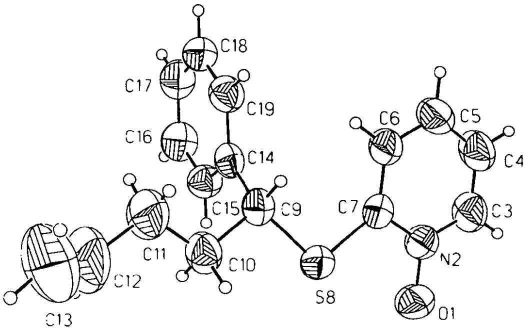


Fig. 1. Molecular structure of the 2-thioalkylpyridine *N*-oxide (2). Displacement ellipsoids are plotted at the 50% probability level.

Experimental

2-(1-Phenyl-4-penten-1-ylthio)pyridine *N*-oxide, (2), was prepared as a racemic mixture from 2-mercaptopyridine *N*-oxide tetraethylammonium salt and 1-chloro-1-phenyl-4-pentene in anhydrous DMF (Hartung *et al.*, 1996). Crystals (m.p. 380–381 K) were obtained by isothermal evaporation of the methyl *tert*-butyl ether solvent from a concentrated solution of (2).

Crystal data

$C_{16}H_{17}NOS$
$M_r = 271.37$
Triclinic
$P\bar{1}$
$a = 5.8303\,(7)$ Å
$b = 8.0390\,(10)$ Å
$c = 16.026\,(2)$ Å
$\alpha = 84.550\,(10)^\circ$
$\beta = 82.820\,(10)^\circ$
$\gamma = 81.910\,(10)^\circ$
$V = 735.5\,(2)$ Å^3
$Z = 2$
$D_x = 1.225$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.57$–12.03°
$\mu = 0.212$ mm^{-1}
$T = 297\,(2)$ K
Needle
$0.63 \times 0.15 \times 0.05$ mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical, ψ-scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.9246$, $T_{\max} = 0.9975$
2965 measured reflections
2054 independent reflections

1562 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0326$
$\theta_{\max} = 22.98^\circ$
$h = -2 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: −14.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0426$
$wR(F^2) = 0.1257$
$S = 1.038$
2054 reflections
172 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.3106P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.260$ e Å^{-3}
$\Delta\rho_{\min} = -0.179$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
O1	0.4123 (4)	0.5901 (3)	0.38128 (13)	0.0754 (6)
N2	0.2239 (4)	0.6601 (3)	0.42439 (14)	0.0578 (6)
C3	0.2140 (6)	0.6712 (4)	0.5082 (2)	0.0723 (9)
C4	0.0173 (6)	0.7432 (5)	0.5524 (2)	0.0801 (10)
C5	−0.1750 (6)	0.8024 (5)	0.5119 (2)	0.0782 (10)
C6	−0.1656 (5)	0.7876 (4)	0.4268 (2)	0.0643 (8)
C7	0.0364 (5)	0.7175 (3)	0.3822 (2)	0.0504 (7)
S8	0.09372 (13)	0.68728 (9)	0.27522 (4)	0.0572 (3)
C9	−0.1741 (5)	0.7901 (3)	0.2335 (2)	0.0523 (7)
C10	−0.1440 (6)	0.7453 (4)	0.1414 (2)	0.0659 (8)
C11	−0.3601 (7)	0.8022 (6)	0.0979 (2)	0.0963 (12)
C12	−0.3302 (11)	0.7686 (7)	0.0077 (3)	0.131 (2)
C13	−0.4538 (13)	0.7177 (8)	−0.0337 (3)	0.161 (2)
C14	−0.2170 (4)	0.9773 (3)	0.24009 (15)	0.0473 (6)
C15	−0.0483 (5)	1.0801 (4)	0.2118 (2)	0.0575 (7)
C16	−0.0953 (6)	1.2523 (4)	0.2156 (2)	0.0671 (8)
C17	−0.3098 (6)	1.3242 (4)	0.2493 (2)	0.0676 (8)
C18	−0.4783 (6)	1.2259 (4)	0.2774 (2)	0.0638 (8)
C19	−0.4331 (5)	1.0531 (4)	0.2730 (2)	0.0578 (7)

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

O1—N2	1.308 (3)	C9—C10	1.536 (4)
N2—C3	1.348 (4)	C10—C11	1.509 (5)
N2—C7	1.360 (3)	C11—C12	1.479 (6)
C3—C4	1.357 (5)	C12—C13	1.175 (6)
C4—C5	1.371 (5)	C14—C15	1.379 (4)
C5—C6	1.372 (4)	C14—C19	1.384 (4)
C6—C7	1.377 (4)	C15—C16	1.379 (4)
C7—S8	1.739 (3)	C16—C17	1.370 (4)
S8—C9	1.834 (3)	C17—C18	1.354 (4)
C9—C14	1.502 (4)	C18—C19	1.383 (4)
O1—N2—C3	121.1 (2)	N2—C7—C6	118.7 (2)
O1—N2—C7	117.8 (2)	N2—C7—S8	112.0 (2)
C3—N2—C7	121.1 (3)	C6—C7—S8	129.3 (2)
N2—C3—C4	120.7 (3)	C7—S8—C9	102.76 (12)
N2—C3—H3*A*	119.7 (2)	C14—C9—C10	111.9 (2)
C3—C4—C5	119.7 (3)	C14—C9—S8	113.9 (2)
C4—C5—C6	119.4 (3)	C10—C9—S8	104.3 (2)
C5—C6—C7	120.4 (3)		
O1—N2—C3—C4	−179.6 (3)	C6—C7—S8—C9	5.1 (3)
C7—N2—C3—C4	−1.3 (5)	C7—S8—C9—C14	65.2 (2)
O1—N2—C7—S8	−1.2 (3)	C7—S8—C9—C10	−172.5 (2)
C3—N2—C7—S8	−179.6 (2)		

Data collection: *Diffractometer Control Software* (Enraf–Nonius, 1993). Cell refinement: *Diffractometer Control Software*. Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal* (Hall, Flack & Stewart, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1196). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Three 1,4-*trans*-Substituted Cyclohexanes

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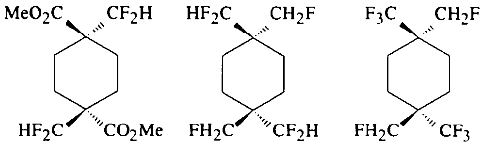
Abstract

The crystal structure determinations of *trans*-dimethyl 1,4-bis(difluoromethyl)-1,4-cyclohexanedicarboxylate, $C_{12}H_{16}F_4O_4$, *trans*-1,4-bis(difluoromethyl)-1,4-bis(fluoromethyl)cyclohexane, $C_{10}H_{14}F_6$, and *trans*-1,4-bis(fluoromethyl)-1,4-bis(trifluoromethyl)cyclohexane, $C_{10}H_{12}F_8$, confirmed the *trans* assignment for each of the 1,4-disubstituted cyclohexanes.

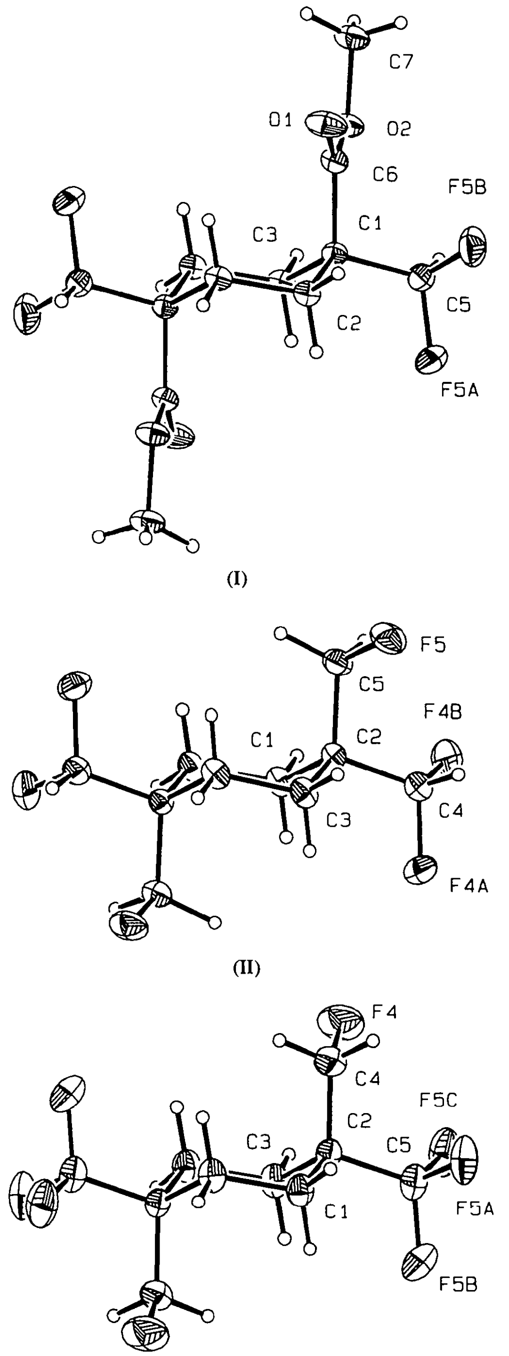
Comment

Stereoselective reduction of tetramethyl 1,1,4,4-cyclohexanetetracarboxylate with diisobutyl aluminium hydride yields *trans*-1,4-dialdehyde as the major product (90:10, 63% yield). Fluorination and additional elaboration provides a convenient synthesis of 1,1,4,4-tetrasubstituted cyclohexanes containing trifluoromethyl, difluoromethyl and fluoromethyl groups (Davis, Swenson & Burton, 1993). These compounds should have further application as intermediates of other selectively fluorinated compounds. The crystal structures of three of these compounds [*trans*-dimethyl 1,4-bis(difluoromethyl)-1,4-cyclohexanedicarboxylate, (I), *trans*-1,4-bis(difluoromethyl)-1,4-bis(fluoromethyl)cyclohexane, (II), and *trans*-1,4-bis(trifluoromethyl)-1,4-bis(fluoromethyl)cyclohexane, (III)] were determined in order to confirm the conformations.



(I) (II) (III)

The cyclohexane rings of (I) and (III) are centered on an inversion center. A twofold axis passes through the centers of the C1—C1^{i} and C3—C3^{i} bonds in (II) [(i) = 1 − x, y, 1/2 − z)]. The cyclohexane ring of each compound adopts a chair conformation. The 1,4-substituents are arranged in a *trans* conformation with the more highly fluorinated substituent occupying the equatorial position in each case. Fig. 2 shows the packing in the crystals of the title compounds.



(I)

(II)

(III)

Fig. 1. Views and numbering schemes of compounds (I), (II) and (III). Thermal displacement ellipsoids are drawn at the 35% probability level. H atoms are drawn with equal arbitrary radius.