Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^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}
C1	0.68273 (8)	0.15250 (14)	0.65165 (10)	0.0274 (2)
C2	0.65981 (7)	0.05648 (14)	0.74675 (9)	0.0259 (2)
C3	0.72487 (8)	0.03463 (15)	0.83931 (9)	0.0267 (2)
C4	0.81175 (7)	0.1071 (2)	0.84020 (9)	0.0280 (2)
C5	0.82361 (8)	0.2367 (2)	0.75984 (11)	0.0310 (2)
C6	0.76004 (8)	0.25912 (14)	0.66755 (10)	0.0304 (2)
C7	0.63974 (10)	0.1257 (2)	0.53202 (11)	0.0379 (3)
C8	0.67785 (13)	−0.0432 (2)	0.47417 (13)	0.0496 (4)
C9	0.76203 (10)	−0.1165 (2)	0.53935 (11)	0.0370 (3)
C10	0.75468 (10)	−0.2424 (2)	0.62424 (12)	0.0370 (3)
C11	0.82170 (10)	−0.2579 (2)	0.71410 (11)	0.0361 (3)
C12	0.89799 (9)	−0.1487 (2)	0.72201 (11)	0.0349 (3)
C13	0.91427 (10)	−0.0547 (2)	0.62481 (12)	0.0376 (3)
C14	0.84738 (11)	−0.0386 (2)	0.53487 (11)	0.0390 (3)
C15	0.94745 (11)	−0.1035 (3)	0.83575 (14)	0.0484 (4)
C16	0.89244 (9)	0.0251 (2)	0.90810 (12)	0.0378 (3)
C17	0.57123 (9)	−0.0395 (2)	0.74588 (12)	0.0356 (3)
C18	0.52467 (11)	−0.0402 (2)	0.8536 (2)	0.0460 (4)
O1	0.53722 (9)	−0.1125 (2)	0.66124 (10)	0.0608 (4)

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

C1—C6	1.397 (2)	C7—C8	1.585 (2)
C1—C2	1.409 (2)	C9—C10	1.401 (2)
C1—C7	1.513 (2)	C10—C11	1.390 (2)
C2—C3	1.399 (2)	C11—C12	1.395 (2)
C2—C17	1.495 (2)	C12—C13	1.395 (2)
C3—C4	1.393 (2)	C12—C15	1.512 (2)
C4—C5	1.393 (2)	C13—C14	1.389 (2)
C4—C16	1.509 (2)	C15—C16	1.574 (2)
C5—C6	1.384 (2)	C17—O1	1.214 (2)
C6—C1—C2	116.42 (11)	C14—C9—C8	121.66 (14)
C6—C1—C7	118.14 (11)	C10—C9—C8	120.54 (14)
C2—C1—C7	124.64 (11)	C11—C10—C9	120.82 (13)
C3—C2—C1	119.45 (10)	C10—C11—C12	120.85 (12)
C3—C2—C17	118.84 (10)	C11—C12—C13	116.65 (13)
C1—C2—C17	121.35 (11)	C11—C12—C15	121.06 (13)
C4—C3—C2	121.48 (10)	C13—C12—C15	120.90 (14)
C3—C4—C5	116.59 (11)	C14—C13—C12	121.01 (13)
C3—C4—C16	121.22 (12)	C13—C14—C9	120.81 (12)
C5—C4—C16	121.09 (11)	C12—C15—C16	113.37 (11)
C6—C5—C4	120.62 (10)	C4—C16—C15	112.77 (11)
C5—C6—C1	121.29 (11)	O1—C17—C2	121.64 (13)
C1—C7—C8	112.33 (11)	O1—C17—C18	120.93 (13)
C9—C8—C7	112.73 (12)	C2—C17—C18	117.43 (12)
C14—C9—C10	116.54 (13)		
C3—C4—C16—C15	94.8 (2)	C8—C7—C1—C6	92.50 (15)
C4—C16—C15—C12	−12.3 (2)	C9—C10—C11—C12	−0.1 (2)
C16—C15—C12—C11	−71.7 (2)	C10—C11—C12—C13	−14.6 (2)
C10—C9—C8—C7	89.8 (2)	C11—C12—C13—C14	14.7 (2)
C9—C8—C7—C1	−12.8 (2)	C12—C13—C14—C9	−0.1 (2)
C8—C7—C1—C2	−76.9 (2)	C1—C2—C3—C4	0.6 (2)
C5—C4—C16—C15	−72.9 (2)	C2—C3—C4—C5	15.7 (2)
C16—C15—C12—C13	94.4 (2)	C3—C4—C5—C6	−15.8 (2)
C14—C9—C8—C7	−77.0 (2)	C4—C5—C6—C1	−0.4 (2)

Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: HU1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Lindeman, S. V., Maleev, A. V., Struchkov, Yu. T. & Guryshev, V. N. (1990). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 588–590.

Lindeman, S. V., Struchkov, Yu. T. & Guryshev, V. N. (1976). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 2007–2010.

Sheldrick, G. M. (1989). *SHELXTL-Plus.* PC version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Acta Cryst. (1994). **C50**, 1749–1753

Molecular Structure and Electronic Properties of a 1-Sulfonylindolizine Derivative, 2-Isopropyl-1-methylsulfonylindolizine

VÉRONIQUE GIBON, CATHERINE POTY, GUY EVRARD, DANIEL P. VERCAUTEREN AND FRANÇOIS DURANT

Laboratoire de Chimie Moléculaire Structurale, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium

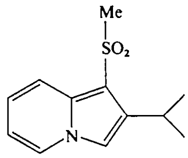
Abstract

For the title compound, $C_{12}H_{15}NO_2S$, both the crystallographic data and theoretical results (*ab initio* molecular-orbital calculations) indicate a stabilization of the symmetrical conformation of the sulfone group with respect to the indolizinic bicycle. The crystal packing and the topology of the frontier orbitals clearly suggest a charge-transfer process from the five-membered ring towards the six-membered ring of the indolizine for two adjacent molecules.

Comment

Derivatives of 1-sulfonylindolizines are being studied increasingly because of their importance as a new variety of *L*-type calcium-channel blocker and the recognition the potential impact of this class of compound on the treatment of ischemic heart disease and hypertension. The biochemical studies carried out up to now indeed indicate a new binding site for these molecules associated with the *L*-type calcium channel (Nokin *et al.*, 1989, 1990; Schmid, Romey, Barhanin & Lazdunski, 1989; Polster, Christophe, Van Damme, Houliche & Chatelain, 1990; Chatelain, Baufort, Meysmans & Clinet, 1990; Chatelain, Gubin, Manning & Sissman, 1991; Bois, Romey & Lazdunski, 1991; Gubin *et al.*, 1992; Gibon, Norberg, Vercauteren, Evrard & Durant, 1992; Kenny, Fraser & Spedding, 1993), in addition to the three sites (1,4-dihydropyridines, verapamil and diltiazem) described previously (Glossmann, Ferry, Goll, Striessnig & Zernig, 1985).

We report here the molecular structure and some electronic properties of a 2-isopropyl-1-methylsulfonylindolizine derivative, (I). This compound was synthesized by Sanofi Research* as part of a global search for new calcium-channel blockers. It exhibits some elements of the pharmacophore of this class of anticalcic molecule (Gubin *et al.*, 1992).



(I)

Fig. 1 shows a perspective view of the molecule (Johnson, 1976) and the crystal packing is presented in Fig. 2. In the observed conformation, the O atoms are located nearly symmetrically with respect to the indolizinic bicycle [O3—S1—C4—C5 −33.8 (3), O2—S1—C4—C12 20.7 (3)°]. Consequently, the O2 and O3 lone pairs can participate in intramolecular interactions [O2···H131 2.375 (2), O3···H13 2.545 (3)Å] leading to the formation of two pseudo-six-membered rings. The bond lengths in the indolizinic ring are not equivalent: alternation of single- and double-bond character is observed for the bonds from C5 to C9; C4—C5 is longer than C11—C12. S1—C4 is quite short with respect to the standard C—S single bond and the two O atoms are equidistant from the S atom. This could be the result of delocalization between the SO_2 group and the aromatic heterocycle.

* Sanofi Research Center, 1 avenue de Béjar, 1120 Bruxelles.

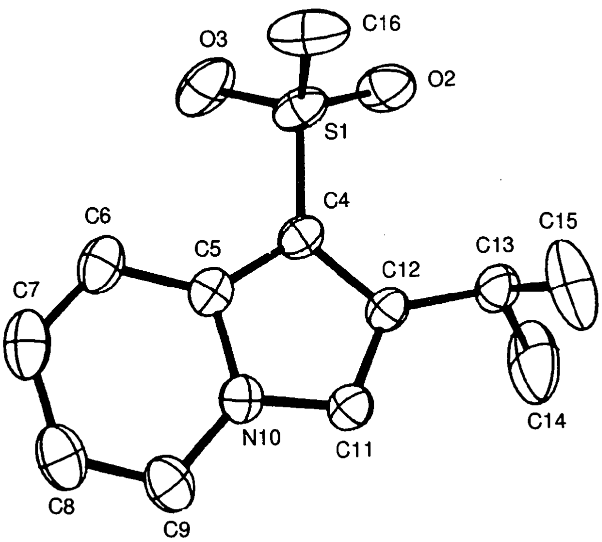


Fig. 1. View of the title molecule (30% probability ellipsoids) with atomic numbering scheme.

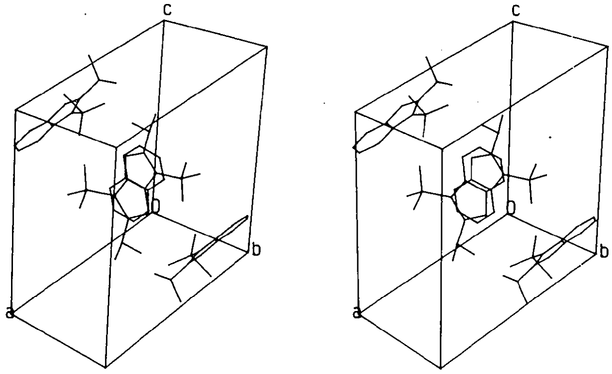


Fig. 2. Stereoscopic view of the molecular packing of the title compound.

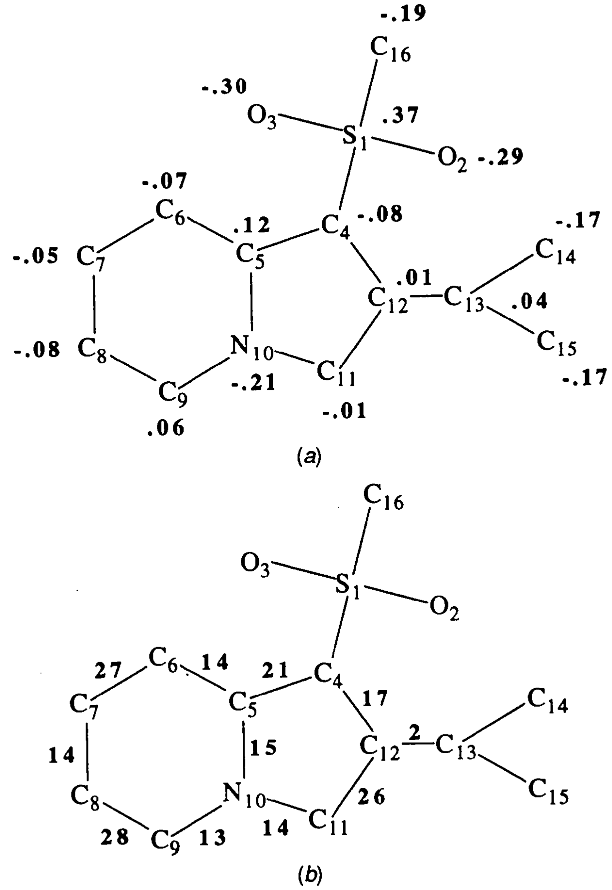


Fig. 3. (*a*) Atomic charges (e) and (*b*) π contributions (%) of the interatomic overlap populations. (*Ab initio* molecular orbital *STO-3G** results.)

Ab initio molecular-orbital calculations performed on the molecule in its crystalline conformation show (Fig. 3): (i) localized single and double bonds in the six-membered ring of the bicycle; (ii) a tendency to uniformity of the overlap values within the five-membered ring with a relatively low π-interatomic overlap population for the C4—C5 bond and an important one for C3—C12; (iii) an important π-interatomic overlap population for the C3—S1 bond; (iv) an alternation of negative and positive atomic charges from N10 to O2 or O3 through C5 and C4; (v) quasi-identical and strongly negative atomic charges for O2 and O3; (vi) a relatively important dipole moment (5.6 D) oriented along a line from N10 to the sulfone group. Calculation of the total interatomic overlap for O2···H131 and O3···H6 gives positive, though quite weak, values of 0.0015 and 0.0005 e, respectively.

Both crystallographic and theoretical results thus indicate a stabilization of the symmetrical conformation of the sulfone group with respect to the indolizine bicyclic ring by favourable intramolecular contacts between the sulfonic O atoms (O2 and O3) and H atoms of the heteroatomic ring (H131 and H6), and by electron delocalization from the bicyclic ring to the sulfone group. It is worth noting that the differences between the overlap population values [points (i) and (ii) above] are not marked but do indicate a clear tendency to delocalization. However, one has to be aware that the molecular conformation obtained by X-ray diffraction can be influenced greatly by the crystal packing. Variation of the relative total energy (*ab initio* molecular-orbital calculations) computed as a function of the O3—S1—C4—C5 torsion angle (all other parameters being constant) is presented in Fig. 4. The most stable conformation corresponds to that observed in the crystal with a symmetrical orientation of the sulfone group with respect to the aromatic ring; the energetic barrier is large enough (9 kcal mol^{-1}; 1 kcal = 4.184 kJ) to prevent any rotation around the S1—C4 bond. The observed disposition of the methanesulfonyl group represents nothing more than a convenient way to park the methyl group. In addition, the molecules stack in pairs side by side, the five-membered part of the indolizinic ring system in front of the six-membered part of another molecule with an intermolecular distance of about 3.6 Å between two adjacent aromatic entities (Fig. 2). Calculation of the topology of the frontier orbitals (Fig. 5) shows that large iso-electron density values are observed within the five-membered ring for the HOMO (highest occupied molecular orbital) and the six-membered one for the LUMO (lowest unoccupied molecular orbital); this suggests that a charge-transfer process from the five-membered ring of one molecule to the six-membered one of an adjacent molecule could sustain part of the molecular packing.

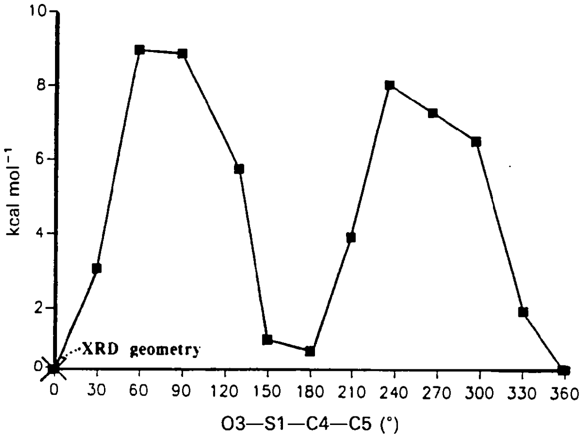


Fig. 4. Variation of the total energy (kcal mol^{-1}; 1 kcal = 4.184 kJ) with respect to the O3—S1—C4—C5 torsion angle in steps of 30° starting from the crystalline geometry (×). (*Ab initio* molecular orbital *STO-3G** results.)

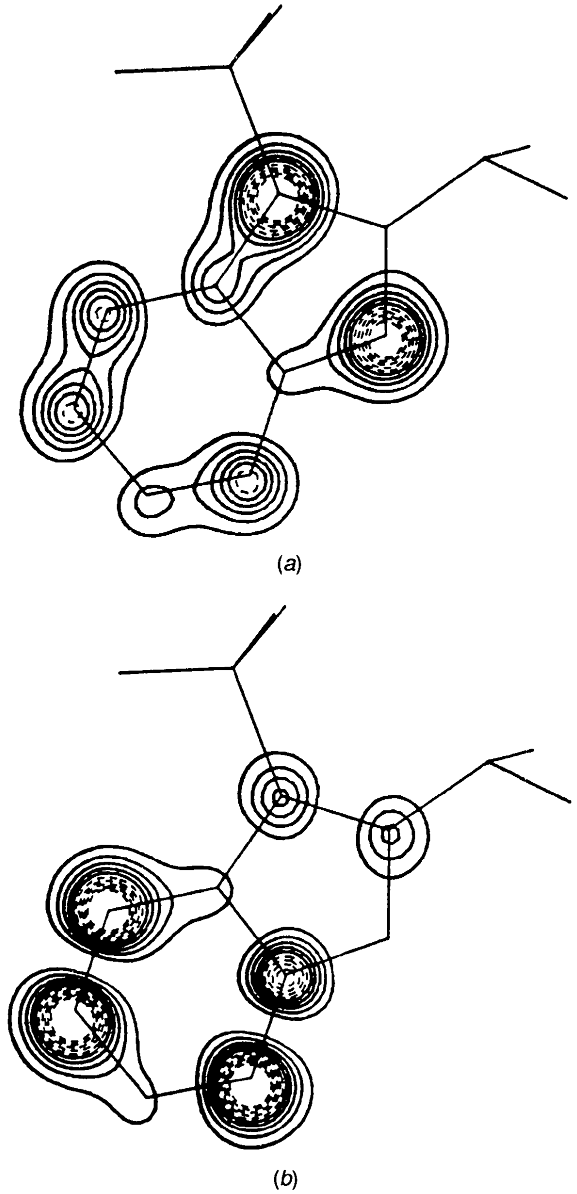


Fig. 5. Topology of the (*a*) HOMO and (*b*) LUMO frontier orbitals of the title molecule. The iso-electron-density maps are drawn as solid lines from 0.005 to 0.025 e Å^{-3} and dotted lines from 0.03 to 0.05 e Å^{-3}. (*Ab initio* molecular orbital *STO-3G** results.)

Experimental

Crystal data

$C_{12}H_{15}NO_2S$
$M_r = 237.3$
Monoclinic
$P2_1/n$
$a = 12.307$ (2) Å
$b = 8.305$ (1) Å
$c = 12.516$ (2) Å
$\beta = 108.29$ (5)°
$V = 1214.9$ (3) Å^3
$Z = 4$
$D_x = 1.297$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 16.6$–31.8°
$\mu = 2.21$ mm^{-1}
$T = 293$ K
Needle
0.30 × 0.10 × 0.06 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans [width (0.7 + 0.15tanθ)°]
Absorption correction: none
2566 measured reflections
2389 independent reflections
1810 observed reflections [$I \geq 2.5\sigma(I)$]

$R_{int} = 0.011$
$\theta_{max} = 72°$
$h = -15 \rightarrow 15$
$k = -8 \rightarrow 10$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.048$
$wR = 0.066$
$S = 0.89$
1810 reflections
145 parameters
$w = 1/[\sigma^2(F) + 0.01F^2]$
$(\Delta/\sigma)_{max} = 0.321$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
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)

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

	x	y	z	U_{eq}
S1	0.60980 (10)	0.07250 (10)	0.81980 (10)	0.0676 (3)
O2	0.5155 (2)	0.1586 (3)	0.8363 (2)	0.0880 (8)
O3	0.6097 (2)	0.0443 (3)	0.7068 (2)	0.0985 (10)
N10	0.9229 (2)	0.2212 (2)	0.9493 (2)	0.0513 (6)
C4	0.7363 (2)	0.1645 (3)	0.8924 (2)	0.0515 (6)
C5	0.8393 (2)	0.1314 (3)	0.8717 (2)	0.0508 (7)
C6	0.8754 (3)	0.0298 (3)	0.7979 (2)	0.0665 (9)
C7	0.9886 (3)	0.0229 (4)	0.8066 (3)	0.0767 (10)
C8	1.0691 (3)	0.1183 (4)	0.8863 (3)	0.0728 (10)
C9	1.0363 (2)	0.2165 (4)	0.9559 (2)	0.0645 (9)
C11	0.8737 (2)	0.3059 (3)	1.0174 (2)	0.0564 (7)
C12	0.7597 (2)	0.2731 (3)	0.9860 (2)	0.0514 (7)
C13	0.6791 (2)	0.3372 (4)	1.0447 (2)	0.0666 (9)
C14	0.6866 (6)	0.5140 (6)	1.0596 (5)	0.146 (3)
C15	0.7011 (5)	0.2520 (7)	1.1563 (4)	0.129 (2)
C16	0.6169 (3)	−0.1184 (4)	0.8837 (4)	0.1051 (16)

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

S1—O2	1.432 (3)	C5—C6	1.421 (4)
S1—O3	1.433 (3)	C6—C7	1.364 (5)
S1—C4	1.717 (3)	C7—C8	1.409 (5)
S1—C16	1.765 (4)	C8—C9	1.344 (5)
N10—C5	1.390 (3)	C11—C12	1.361 (4)
N10—C9	1.373 (4)	C12—C13	1.505 (4)
N10—C11	1.383 (3)	C13—C14	1.479 (6)
C4—C5	1.399 (4)	C13—C15	1.513 (6)
C4—C12	1.434 (3)		
O2—S1—O3	118.29 (16)	N10—C5—C6	117.3 (2)
O2—S1—C4	110.07 (14)	C4—C5—C6	136.3 (3)
O2—S1—C16	108.06 (18)	C5—C6—C7	119.5 (3)
O3—S1—C4	108.36 (15)	C6—C7—C8	120.5 (3)
O3—S1—C16	106.56 (18)	C7—C8—C9	120.8 (3)
C4—S1—C16	104.60 (17)	N10—C9—C8	119.0 (3)
C5—N10—C9	122.9 (2)	N10—C11—C12	109.4 (2)
C5—N10—C11	109.4 (2)	C4—C12—C11	106.6 (2)
C9—N10—C11	127.7 (2)	C4—C12—C13	128.8 (2)
S1—C4—C5	122.62 (19)	C11—C12—C13	124.5 (2)
S1—C4—C12	129.0 (2)	C12—C13—C14	112.8 (3)
C5—C4—C12	108.3 (2)	C12—C13—C15	109.3 (3)
N10—C5—C4	106.3 (2)	C14—C13—C15	111.2 (4)

Lorentz and polarization corrections were applied to intensity data. The phase problem was solved by direct methods using *SHELX*86 (Sheldrick, 1986). Full-matrix least-squares refinement was performed using *SHELX*76 (Sheldrick, 1976); all H atoms were located on a difference Fourier map. Anisotropic temperature factors (U_{ij}) were used for the heavy atoms and isotropic ones for H atoms (isotropic temperature factors of the carrier atoms incremented by 0.02). Structural analysis was performed using *XRAY*76 (Stewart *et al.*, 1976). Views of the molecular conformation and molecular packing were drawn using *ORTEP* (Johnson, 1976) and *PACKER* (*NRCVAX*; Gabe, Le Page, Charland, Lee & White, 1989), respectively.

Theoretical calculations were performed at the restricted Hartree–Fock–Roothaan level of electronic theory (Roothaan, 1951). Within this framework, calculations have been performed at the *STO-3G** degree of sophistication in the LCAO (linear combination of atomic orbitals) expansion of the molecular orbital (Collins, Schleyer, Binkley & Pople, 1976). The *STO-3G** basis set, which includes five d orbitals (the title molecule possesses a second-row-element atom, S), was choosen in order to make a good compromise between the cost of calculation and the quality of the results. The atomic coordinates of the heavy atoms considered in the calculations were those obtained by crystallographic analysis; all H atoms were located at standard positions (distances, bond and torsion angles) relative to their carrier atoms, depending of their hybridization. The electron distribution was computed by the widely adopted Mulliken (1955) population analysis which allows a good relation with very common chemical concepts such as bond properties, polarization, delocalization, mesomeric and inductive effects. The indolizine bicyclic ring was placed in the xz plane in order to differentiate easily between the total and the π-overlap ($2p_y$) electronic contributions. All computations were carried out using *GAUSSIAN*86 (Frisch *et al.*, 1988) adapted for an IBM 9377/90 FPS M64 computer system (running under VM/CMS). The bi-electronic integral cutoff and convergence on the density matrix thresholds were fixed at 10^{-10} and 10^{-9} a.u., respectively. The electron charge-density iso-contour maps were generated using *MOPPLOT* (Hinde, Luken & Chin, 1988). Beside the wavefunction, the input consists of the desired molecular orbitals (all of them, or a particular desired one such as the HOMO or the LUMO) and the value of the iso-electron charge-density surface or contours (range 0.005–0.050 in steps of 0.005 e Å^{-3}). The iso-electron density was drawn using *CPS* (Baudoux & Vercauteren, 1989).

The authors acknowledge Drs P. Chatelain and J. Gubin (Sanofi Research Center, Bruxelles, Belgium) for providing the title compound and are grateful to the Fonds National pour la Recherche Scientifique (FNRS), IBM-Belgium, and the Facultes Universitaires Notre-Dame de la Paix (FUNDP) for the use of the Namur Scientific Computing Facility. VG and CP thank Sanofi Research and the Institut pour l'Encouragement à la Recherche Scientifique dans l'Industrie et l'Agriculture (IRSIA) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL566). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Baudoux, G. & Vercauteren, D. P. (1989). *CPS. Program for Contour Plotting*. Univ. of Namur, Belgium.
Bois, P., Romey, G. & Lazdunski, M. (1991). *Eur. J. Phys.* **419**, 651–656.
Chatelain, P., Beaufort, P., Meysmans, L. & Clinet, M. (1990). *Mol. Pharmacol.* **39**, 64–71.
Chatelain, P., Gubin, J., Manning, A. & Sissman, J. (1991). *Cardiovasc. Drug Rev.* **9**, 123–146.
Collins, J., Schleyer, P., Binkley, J. S. & Pople, J. A. (1976). *J. Chem. Phys.* **64**, 5142–5151.
Frisch, M. J., Binkley, J. S., Schlegel, H. B., Raghavachari, K., Melius, C. F., Martin, R. L., Stewart, J. J. P., Bobrowicz, F. W., Rohlfing, C. M., Kahn, L. R., Defrees, D. J., Suger, R., Whiteside, R. A., Fox, D. J., Fleuder, E. M. & Pople, J. A. (1988). *GAUSSIAN86. Program for ab initio Molecular Orbital Calculations*. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, USA.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Gibon, V., Norberg, B., Vercauteren, D. P., Evrard, G. & Durant, F. (1992). *Eur. J. Med. Chem.* **27**, 485–493.
Glossmann, H., Ferry, D. R., Goll, A., Striessnig, J. & Zernig, G. (1985). *Arzneim.-Forsch.* **35**, 1917–1935.
Gubin, J., Lucchetti, J., Mahaux, J., Lisato, D., Rosseels, G., Clinet, M., Polster, P. & Chatelain, P. (1992). *J. Med. Chem.* **35**, 981–988.
Hinde, R. J., Luken, W. L. & Chin, S. (1988). *MOPLOT. Program for Molecular Orbital Plot*. IBM Kingston Technical Report, KEN-141, New York.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kenny, B., Fraser, S. & Spedding, M. (1993). *Br. J. Pharmacol.* **108**, 93–99.
Mulliken, R. S. (1955). *J. Chem. Phys.* **23**, 1833–1840.
Nokin, P., Clinet, M., Beaufort, P., Meysmans, L., Laruel, R. & Chatelain, P. (1990). *J. Pharmacol. Exp. Ther.* **255**, 600–607.
Nokin, P., Clinet, M., Polster, P., Beaufort, P., Meysmans, L., Gougat, J. & Chatelain, P. (1989). *Naunyn-Schmiedeberg's Arch. Pharmacol.* **339**, 31–36.
Polster, P., Christophe, B., Van Damme, M., Houliche, A. & Chatelain, P. (1990). *J. Pharmacol. Exp. Ther.* **255**, 593–599.
Roothaan, C. C. J. (1951). *Rev. Mod. Phys.* **23**, 69–89.
Schmid, A., Romey, G., Barhanin, J. & Lazdunski, M. (1989). *Mol. Pharmacol.* **35**, 766–773.
Sheldrick, G. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. (1986). *SHELX86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Acta Cryst. (1994). C**50**, 1753–1756

5-Acetyl-4-methyl-2-pyrimidinylhydrazine and 5-(1-Hydrazonoethyl)-4-methyl-2-pyrimidinylhydrazine, $C_7H_{10}N_4O$ and $C_7H_{12}N_6$

ALAIN COUSSON

Laboratoire Léon Brillouin (CEA - CNRS), CE Saclay, 91191 Gif-sur-Yvette CEDEX, France

FRANÇOISE NECTOUX

Institut Curie, Section de Physique et Chimie, UA CNRS 448, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France

BERNARD BACHET

Laboratoire de Minéralogie et Cristallographie, LA CNRS 09, Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris CEDEX 05, France

BRUNO KOKEL AND MICHEL HUBERT-HABART

Institut Curie, Section de Physique et Chimie, Chercheurs INSERM, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France

(*Received* 23 *September* 1993; *accepted* 16 *February* 1994)

Abstract

5-Acetyl-4-methyl-2-pyrimidinylhydrazine is planar but its hydrazone is not. Distortions observed in the hydrazone are due to the presence of two methyl groups on the same side of the molecule.

Comment

5-Acetyl-4-methyl-2-methylthiopyrimidine (1) reacted with an excess of hydrazine in methanolic solution at room temperature to form 5-acetyl-4-methyl-2-pyrimidinylhydrazine (2). This is insoluble in methanol at this temperature and therefore cannot be transformed directly into its hydrazone, 5-(1-hydrazonoethyl)-4-methyl-2-pyrimidinylhydrazine (3). However, the reaction of (1) with hydrazine at 338 K led directly to (3); this could also be prepared