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1-Methyl-5,6-diphenylpyrazine-2(1*H*)-thione

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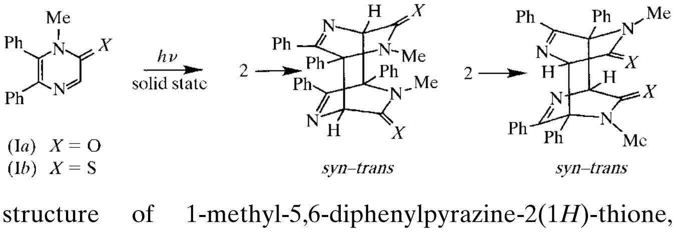
The title compound, $C_{17}H_{14}N_2S$, crystallizes in a triclinic unit cell, with two crystallographically independent molecules in the asymmetric unit. The two independent molecules pack in the same sense and form segregated layers along the *c* axis. The crystal is light-stable and no dimers are formed under irradiation. The intermolecular distances between the potential reactive centers (the C-3 and C-5 ring positions) are 4.093 (4) and 5.643 (4) Å for molecule *A*, and 4.081 (4) and 5.614 (4) Å for molecule *B*.

Comment

1-Methyl-5,6-diphenylpyrazin-2(1*H*)-one, (I*a*) (Nishio *et al.*, 1980), crystallizes in two different polymorphic forms, namely a light-sensitive form and a light-stable form. The crystal of the light-sensitive modification is chiral (space group $P2_1$), with two crystallographic independent molecules in the asymmetric unit; the two molecules are related by pseudo-twofold symmetry. Kaftory (1984) discussed the possibility that the photoreaction will be enantioselective, yielding one of two enantiomers (shown in the *Scheme* below). One way to explore this assumption is by determination of the absolute structures of the crystal of the parent compound and that of the dimer obtained by irradiation of the same crystal. Unfortunately, we could not unequivocally determine the absolute structure of the parent compound. An attempt to improve the ability to determine the absolute structure by replacing the O atom by an S atom failed. It was found that the crystal structure of 1-methyl-5,6-diphenylpyrazine-2(1*H*)-thione, (I*b*), is not isomorphous with that of 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one. An alternative method to resolve the question is discussed elsewhere (Kaftory *et al.*, 2002). We discuss here the crystal structure of (I*b*).



(I*a*) $X = O$
(I*b*) $X = S$

syn–trans *syn–trans*

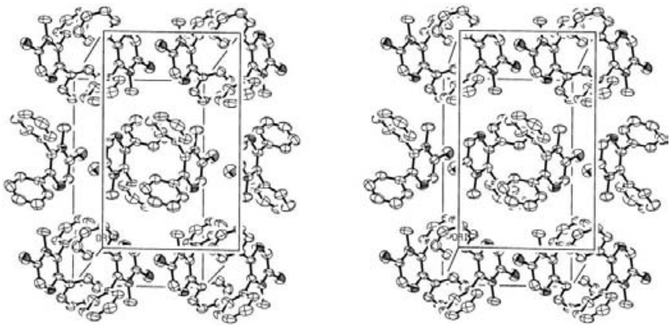


Figure 1
A stereoview of the packing of (I*b*) in the unit cell down the *b* axis, with the *a* axis to the left and the *c* axis pointing upwards (*ORTEP*-3; Farrugia, 1997).

Molecules of 1-methyl-5,6-diphenylpyrazine-2(1*H*)-thione crystallize in a triclinic unit cell, with two crystallographically independent molecules in the asymmetric unit. They are arranged in pairs related by inversion centers (see Fig. 1). The different molecules (*A* and *B*) form segregated layers along the *c* axis. The crystal is light-stable and no dimers are formed. The intermolecular distances between the potential reactive centers (C2 and C4) are 4.093 (4) and 5.643 (4) Å for molecule *A*, and 4.081 (4) and 5.614 (4) Å for molecule *B* (see Figs. 2 and 3). It is, perhaps, not surprising that although formally the two pairs where the proximity between the reaction centers is *ca* 4.1 Å may be considered as being close enough to allow a topochemically controlled photochemical reaction to proceed (Schmidt, 1971), the reaction does not take place. One of the

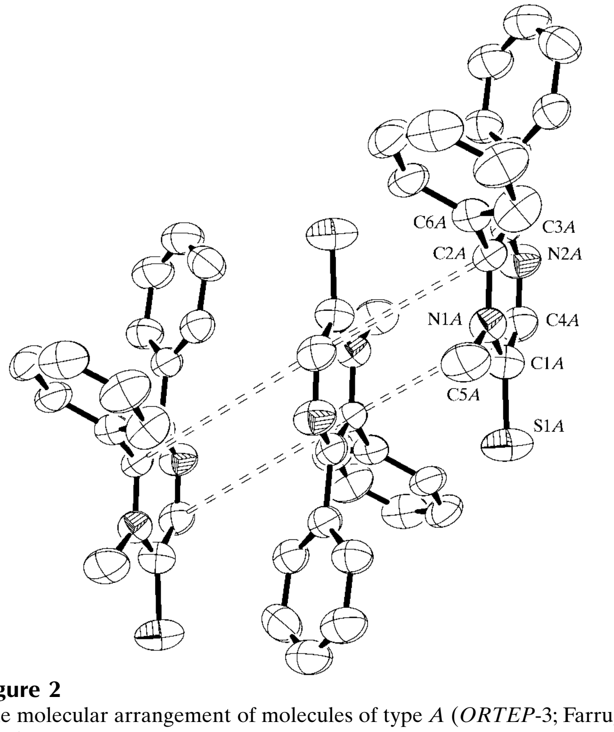


Figure 2
The molecular arrangement of molecules of type *A* (*ORTEP*-3; Farrugia, 1997).

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reasons is that the reacting centers are shifted from each other. The efficiency of the orbital overlap using the definition given by Kearsley (1987) is poor. The separations between each of the two planes of the central rings related by inversion centers are 3.632 and 3.672 Å (for the pairs consisting of *A* and *B* molecules, respectively), and the distances between the two lobes are 1.887 and 1.781 Å for the same two pairs, respectively. For comparison, the distances between the lobes in light-sensitive 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one are in the range 1.285–1.487 Å.

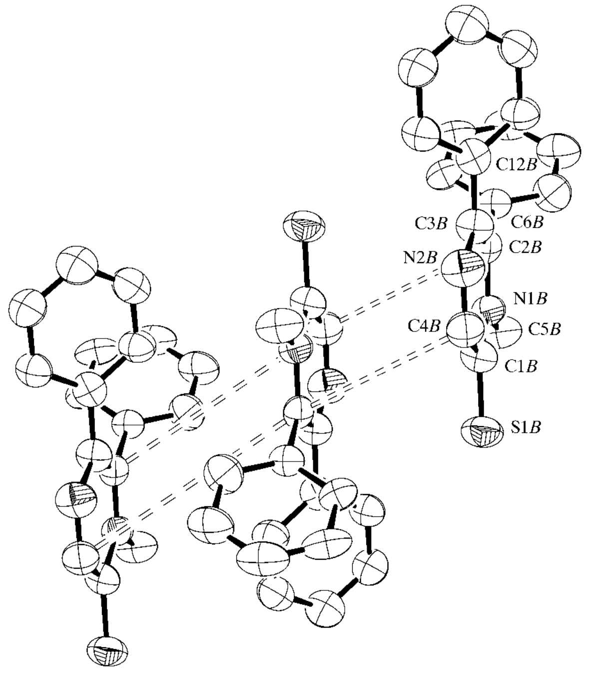

Figure 3
The molecular arrangement of molecules of type *B* (*ORTEP*-3; Farrugia, 1997).

In both compounds, the phenyl rings are rotating in a propeller sense with respect to the central pyrazinone (or pyrazinethione) ring. However, while the rotations of the two phenyl rings in 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one are similar (68.2 and 57.3° in molecule *A*, and 65.8 and 59.6° in molecule *B*), the differences in the rotations of the two phenyl rings in the present compound are much more significant [73.6 (1) and 52.5 (1)° in molecule *A*, and 76.0 (1) and 48.1 (1)° in molecule *B*]. The rotations closer to 90° cause an increase of the distances between the pyrazinoethione planes of molecules related by inversion centers.

A comparison of relevant geometry, such as bond lengths and angles of the pyrazinethione moiety, in the present compound (molecules *A* and *B*) with the geometry of the pyrazinone moiety of the light-sensitive (I*a*) (molecules *A* and *B*) and the light-stable (I*c*) modifications of 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one (Kaftory, 1984) is given in Table 1. It can be seen that replacement of the O atom by an S atom does not impose significant changes on the geometric parameters of the pyrazinone moiety.

Experimental

1-Methyl-5,6-diphenylpyrazin-2(1*H*)-one (0.5 g, 1.9 mmol) and an excess of Lawesson's reagent (1.2 g, 3 mmol, Aldrich) in dry toluene (40 ml) was refluxed for 4 h. The toluene was then distilled out under reduced pressure and the residue was chromatographed with 10% diethyl ether in petroleum ether (*v*/*v*) to give the product (0.3 g, 57% yield). Yellow needles were obtained after recrystallization from acetone (m.p. 441–443 K, literature 436.0–437.5 K).

Crystal data

$C_{17}H_{14}N_2S$
$M_r = 278.37$
Triclinic, $P\overline{1}$
$a = 9.583\ (2)$ Å
$b = 10.740\ (2)$ Å
$c = 15.247\ (3)$ Å
$\alpha = 106.79\ (3)^\circ$
$\beta = 90.65\ (2)^\circ$
$\gamma = 104.09\ (3)^\circ$
$V = 1451.5\ (5)$ Å^3
$Z = 4$
$D_x = 1.274$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4052 reflections
$\theta = 1.4$–14.9°
$\mu = 0.21$ mm^{-1}
$T = 293\ (2)$ K
Prism, yellow
$0.28 \times 0.18 \times 0.12$ mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: numerical (*maXus*; Mackay *et al.*, 1998)
$T_{\min} = 0.942$, $T_{\max} = 0.975$
14 392 measured reflections
5053 independent reflections
2222 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$
$\theta_{\max} = 25.3^\circ$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.107$
$S = 0.81$
5053 reflections
362 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0053 (10)

Table 1
Comparison of bond lengths (Å) and angles (°) in pyrazinones.

	(I*b*)[a] Molecule *A*	(I*b*) Molecule *B*	(I*a*)[b] Molecule *A*	(I*a*) Molecule *B*	(I*c*)[c]
N1—C1	1.372 (3)	1.372 (3)	1.393 (4)	1.389 (4)	1.385 (4)
N1—C2	1.387 (3)	1.385 (3)	1.391 (4)	1.391 (3)	1.378 (3)
N2—C4	1.305 (3)	1.294 (3)	1.291 (4)	1.297 (4)	1.299 (4)
N2—C3	1.372 (3)	1.374 (3)	1.361 (3)	1.362 (4)	1.372 (4)
C1—C4	1.424 (4)	1.428 (4)	1.437 (4)	1.440 (4)	1.437 (4)
C2—C3	1.366 (3)	1.367 (3)	1.361 (3)	1.362 (4)	1.372 (4)
C1—N1—C2	122.3 (2)	121.9 (2)	121.2 (3)	121.9 (3)	121.9 (2)
C4—N2—C3	117.8 (3)	117.8 (3)	117.6 (3)	118.3 (3)	118.0 (2)
S1/O1—C1—N1	124.7 (2)	123.9 (2)	121.8 (3)	122.2 (3)	121.4 (3)
S1/O1—C1—C4	121.3 (3)	122.4 (2)	124.5 (3)	124.1 (3)	124.6 (3)
N1—C1—C4	113.9 (3)	113.6 (3)	113.7 (3)	113.8 (3)	114.0 (2)
C3—C2—N1	118.6 (3)	119.3 (2)	119.4 (2)	118.8 (2)	119.2 (2)
C2—C3—N2	121.7 (3)	121.0 (3)	121.7 (2)	121.7 (3)	121.4 (2)
N2—C4—C1	125.5 (3)	126.3 (3)	126.2 (2)	125.3 (2)	125.4 (3)

Notes: (*a*) (I*b*) is the title compound; (*b*) (I*a*) is 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one (Kaftory, 1984); (*c*) (I*c*) is the light-stable modification of (I*a*).

The H atoms were located in a difference Fourier map. During the refinement, the H-atom coordinates were recalculated and allowed to ride on their bonded atoms (C—H = 0.93 and 0.96 Å), while their isotropic displacement parameters were fixed [$U_{\rm iso} = 1.5U_{\rm eq}$(C)].

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97

(Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1129). Services for accessing these data are described at the back of the journal.

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