

1-Methyl-5,6,7,8-tetrahydroquinoxalin-2(1H)-one

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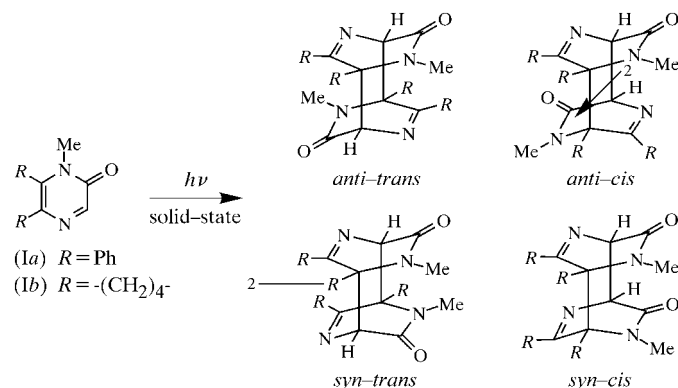
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The title compound, $C_9H_{12}N_2O$, crystallizes in a triclinic unit cell, with two crystallographically independent molecules in the asymmetric unit. The two independent molecules adopt different modes of packing. One type of molecule is arranged in infinite columns, while the other type packs as dimers, forming spacers between the parallel columns. Each type of molecule is arranged in pairs related by inversion centers. The distances between potential reaction centers are 3.395 (2), 3.457 (2) and 3.522 (2) Å. As a result of the symmetry of the pairs and the close distances between the potential photo-reactive centers, it is expected that the dimer will be the *anti-trans* isomer.

Comment

There is confusion regarding the solid-state photodimerization of some pyrazin-2(1H)-ones. The present study intends to clear up some of the misinterpretations regarding the photochemical product. It was reported (Nishio *et al.*, 1980) that 1-methyl-5,6-diphenylpyrazin-2-one and 1-methyl-5,6,7,8-tetrahydro-2(1H)-quinoxalinone [(1a) and (1b), respectively]



were inert to photolysis in benzene or methanol solution; however, irradiation of the methyl derivative (1a) in the solid

state gave the [4+4] dimer. In principle, four different cyclo-dimers may be anticipated, as shown in the *Scheme* below. The solid-state photoreaction, however, led to a single isomer, assigned by the authors as the *anti-trans* dimer. The solid-state

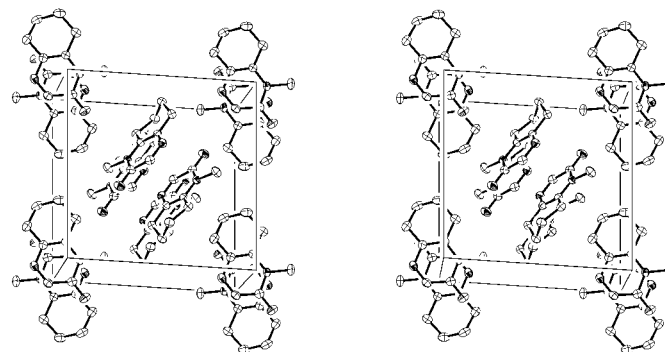


Figure 1
View of the packing of (1b) in the unit cell (ORTEP-3; Farrugia, 1997).

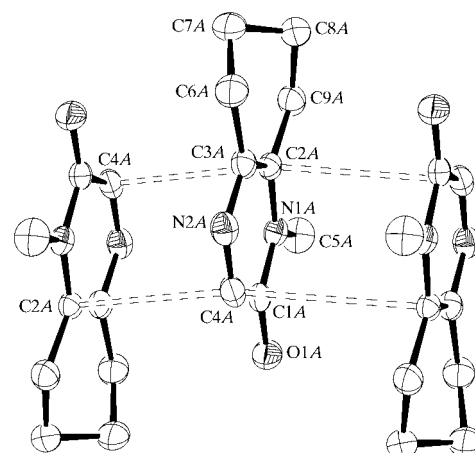


Figure 2
The two possible dimers formed by molecules of type A (ORTEP-3; Farrugia, 1997).

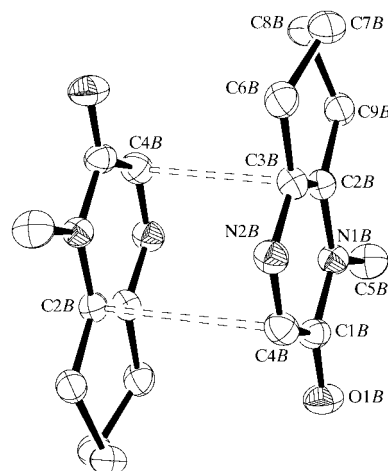


Figure 3
The dimer formed by molecules of type B (ORTEP-3; Farrugia, 1997).

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

	(Ib) ^a Molecule A	(Ib) Molecule B	(Ia) ^b Molecule A	(Ia) Molecule B	(Ic) ^c	TANNEB ^d	TANNIF ^d
O1—C1	1.239 (3)	1.239 (2)	1.228 (4)	1.235 (3)	1.233 (4)	1.239	1.226
N1—C1	1.386 (3)	1.376 (3)	1.393 (4)	1.389 (4)	1.385 (4)	1.386	1.391
N1—C2	1.384 (3)	1.388 (3)	1.391 (4)	1.391 (3)	1.378 (3)	1.383	1.386
N2—C4	1.301 (3)	1.303 (3)	1.291 (4)	1.297 (4)	1.299 (4)	1.290	1.297
N2—C3	1.379 (3)	1.371 (3)	1.361 (3)	1.362 (4)	1.372 (4)	1.384	1.375
C1—C4	1.440 (3)	1.444 (3)	1.437 (4)	1.440 (4)	1.437 (4)	1.428	1.439
C2—C3	1.361 (3)	1.365 (3)	1.361 (3)	1.362 (4)	1.372 (4)	1.361	1.380
C1—N1—C2	122.3 (2)	122.1 (2)	121.2 (3)	121.9 (3)	121.9 (2)	120.8	121.6
C4—N2—C3	118.6 (2)	118.6 (2)	117.6 (3)	118.3 (3)	118.0 (2)	118.6	118.9
O1—C1—N1	121.9 (2)	122.2 (2)	121.8 (3)	122.2 (3)	121.4 (3)	120.6	121.8
O1—C1—C4	124.4 (2)	123.5 (2)	124.5 (3)	124.1 (3)	124.6 (3)	124.6	124.3
N1—C1—C4	113.7 (2)	114.3 (2)	113.7 (3)	113.8 (3)	114.0 (2)	114.9	113.8
C3—C2—N1	119.1 (2)	118.8 (2)	119.4 (2)	118.8 (2)	119.2 (2)	119.9	119.4
C2—C3—N2	121.3 (2)	121.7 (2)	121.7 (2)	121.7 (3)	121.4 (2)	120.8	120.6
N2—C4—C1	124.9 (2)	124.5 (2)	126.2 (2)	125.3 (3)	125.4 (3)	125.0	125.4

Notes: (a) present work; (b) (Ia) is 1-methyl-5,6-diphenylpyrazin-2(1H)-one (Kaftory, 1984); (c) (Ic) is 1-ethyl-5,6-diphenylpyrazin-2(1H)-one (Kaftory, 1984); (d) Mori *et al.* (1992).

photochemical dimerization of 1-methyl-5,6-diphenylpyrazin-2-one, (Ia), was discussed in a publication by Kaftory (1984). The compound crystallizes in two different polymorphic forms, *viz.* a light-sensitive and a light-stable form. The crystal of the light-sensitive modification is chiral (space group $P2_1$), with two crystallographically independent molecules in the asymmetric unit. The two molecules are related by pseudo-twofold symmetry. The mutual orientation and the short distances between the two molecules suggest that irradiation of the crystal will lead to the formation of the *syn-trans* isomer. The crystal structure of the product proves that this expectation was correct. These results led Nishio *et al.* (Nishio, Nakajima, Kondo, Omote & Kaftory, 1984; Nishio, Nakajima, Kondo & Omote, 1984) to publish a paper with a structural revision of the photoproduct of (Ia). Unfortunately, Nishio *et al.* also revised the structure of the photoproduct of (Ib) and suggested that it should also be the *syn-trans* isomer. The crystal structure of (Ib), which is described here, shows undoubtedly that irradiation of the crystalline material should lead to the *anti-trans* isomer.

The title compound crystallizes in the triclinic unit cell (space group $P\bar{1}$), with two crystallographically independent molecules. The packing of the molecules in the unit cell is very special (see Fig. 1). Molecules of type A are packed in columns running along the *a* axis, while molecules of type B are arranged in pairs inclined by 62.8 (1)° to the columns and blocked by them. As a result, there are three different pairs that may be photochemically dimerized. The two B molecules are related by an inversion center (see Fig. 2), with distances between the reacting centers (C2A...C4A) of 3.395 (2) Å. The molecules of type A that are arranged in infinite columns show two different pairs (see Fig. 3). In each pair, the molecules are related by inversion centers and the photodimer is therefore expected to be the *anti-trans* isomer. The distances between the reacting centers of the two different pairs are 3.457 (2) and 3.522 (2) Å. In all the pairs mentioned above, the distances between the reacting centers are much smaller than the upper limit of the distances between potential photo-

reactive centers that enable the execution of solid-state photodimerization, as discussed by Schmidt (1971). In Table 1, the bond lengths and angles of the pyrazinone ring of the present work are compared with those found in 1-methyl-, (Ia), and 1-ethyl-5,6-diphenylpyrazin-2(1H)-one, (Ic), in 1-(2-hydroxyethyl)-5,6-diphenylpyrazin-2(1H)-one (TANNEB; Mori *et al.*, 1992) only in 1-(3-hydroxypropyl)-5,6-diphenylpyrazin-2(1H)-one (TANNIF; Mori *et al.*, 1992) [the codes are Cambridge Structural Database (2001) reftcodes]. Some bond angles should be noted. The inner-ring bond angle at the carbonyl C atom (C1) is significantly smaller [113.7 (2)–114.9°] than that expected for a Csp^2 atom. The calculated average value obtained from 141 compounds possessing the pyridone moiety taken from the Cambridge Structural Database (2001) is 115.3 (13)°. Also to be noted is the significantly larger inner-ring bond angle at C4 [124.9 (2) and 124.5 (2)°] compared with that at C3 [121.3 (2) and 121.7 (2)°]. The calculated average values for the same bond angles in pyridones are 121.0 (14) and 118.9 (13)°, respectively. There is a significant difference between the outer-ring bond angles at C1 [121.9 (2) and 122.2 (2)° for O1—C1—N1 compared with 124.4 (2) and 123.5 (2)° for O1—C1—C4]. Similar differences were found in the geometry of pyridones where the average of the comparable bond angles are 119.6 (12) and 125.1 (13)°.

Experimental

The title compound was synthesized according to the procedure of Brill *et al.* (1964).

Crystal data

$C_9H_{12}N_2O$	$Z = 4$
$M_r = 164.21$	$D_x = 1.326 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.791 (1) \text{ \AA}$	Cell parameters from 3833 reflections
$b = 11.170 (2) \text{ \AA}$	$\theta = 1.7\text{--}26.4^\circ$
$c = 11.246 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 93.75 (3)^\circ$	$T = 140 \text{ K}$
$\beta = 97.13 (3)^\circ$	Plate, colorless
$\gamma = 102.56 (2)^\circ$	$0.20 \times 0.15 \times 0.08 \text{ mm}$
$V = 822.4 (3) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.055$
φ and ω scans	$\theta_{\text{max}} = 27.8^\circ$
8459 measured reflections	$h = 0 \rightarrow 8$
3751 independent reflections	$k = -14 \rightarrow 14$
2056 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.169$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 0.91$	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{\AA}^{-3}$
3751 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e } \text{\AA}^{-3}$
314 parameters	Extinction correction:
All H-atom parameters refined	<i>SHELXL97</i>
	Extinction coefficient: 0.060 (9)

H atoms were located in a difference Fourier map. The coordinates and isotropic displacement parameters were refined [C–H = 0.96 (3)–1.05 (3) Å].

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1127). Services for accessing these data are described at the back of the journal.

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