Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.138$
$S = 0.884$
10 384 reflections
584 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0063 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1*A*—C9*A*	1.377 (2)	O1*B*—C9*B*	1.373 (2)
O1*A*—C1*A*	1.450 (2)	O1*B*—C1*B*	1.453 (2)
O2*A*—C12*A*	1.442 (2)	O2*B*—C11*B*	1.440 (2)
O2*A*—C11*A*	1.443 (2)	O2*B*—C12*B*	1.446 (2)
O3*A*—C20*A*	1.368 (2)	O3*B*—C20*B*	1.366 (2)
O3*A*—C21*A*	1.386 (2)	O3*B*—C21*B*	1.408 (2)
O4*A*—C27*A*	1.376 (2)	O4*B*—C27*B*	1.375 (2)
O4*A*—C28*A*	1.397 (3)	O4*B*—C28*B*	1.393 (2)
C2*A*—C3*A*	1.325 (2)	C2*B*—C3*B*	1.325 (2)
C7*A*—C10*A*	1.508 (2)	C7*B*—C10*B*	1.510 (2)
C8*A*—C13*A*	1.501 (2)	C8*B*—C13*B*	1.501 (2)
C10*A*—C11*A*	1.486 (3)	C10*B*—C11*B*	1.490 (3)
C11*A*—C12*A*	1.456 (3)	C11*B*—C12*B*	1.445 (3)
C12*A*—C13*A*	1.483 (3)	C12*B*—C13*B*	1.491 (2)
C12*A*—O2*A*—C11*A*	60.6 (1)	C11*B*—O2*B*—C12*B*	60.1 (1)
C21*A*—O3*A*—C20*A*—C19*A*	−14.4 (3)		
C28*A*—O4*A*—C27*A*—C26*A*	−30.6 (3)		
C21*B*—O3*B*—C20*B*—C19*B*	6.3 (3)		
C28*B*—O4*B*—C27*B*—C26*B*	−1.4 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12*A*—H12*A*···O2*B*	0.98	2.52	3.261 (2)	132

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 3 cm and the detector swing angle was −20°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. After checking their presence in the difference map, all the H atoms were placed at geometrically calculated positions and a riding model was used for their refinement; rotating group refinement was used for the methyl groups.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1398). Services for accessing these data are described at the back of the journal.

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4-(*p*-Methoxyphenyl)-3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole

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Abstract

In the title molecule, $C_{19}H_{15}N_5O$, the dihedral angle between the phenyl and the triazole rings is 59.30 (7)°. The triazole ring forms dihedral angles of 47.90 (8) and 26.91 (8)° with the two pyridyl rings. In the crystal, the molecules exist as centrosymmetrically C—H···N intermolecular hydrogen-bonded dimers. The glide-related molecules translated a unit along the *b* axis are linked by weak C—H···N hydrogen bonds to form an infinite chain along the *c* axis which is further stabilized by C—H···π interactions.

Comment

Extensive studies have been carried out on the substituted 1,2,4-triazole ligands (Cornelissen *et al.*, 1992; Gupta & Bhargava, 1978; Kunkeler *et al.*, 1996). It

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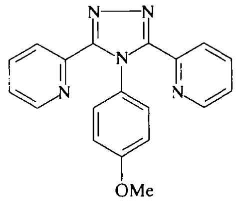
is of interest that some iron(II) complexes containing substituted 1,2,4-triazole ligands are the spin-crossover materials which could be used as molecular-based memory devices, displays and optical switches (Garcia *et al.*, 1997; Kahn & Martinez, 1998). We have recently synthesized the title molecule, (I), which can act as a potentially dinucleating ligand. The X-ray structure determination was carried out in order to elucidate the molecular conformation.



(I)

Bond lengths and angles in the structure are comparable with those reported for related structures (Wang *et al.*, 1998; Chen *et al.*, 1998). The substituted pyridyl groups and the phenyl ring lie in a propeller arrangement around the central 1,2,4-triazole ring. The dihedral angle between the phenyl and triazole rings is 59.30 (7)°. The two pyridyl rings form dihedral angles of 47.90 (8) and 26.91 (8)° with the triazole ring. In the crystal, the molecules exist as centrosymmetrically C7—H7···N2($-x$, $1-y$, $1-z$) hydrogen-bonded dimers (Table 2). The triazole and one of the pyridyl rings (N5) of the glide-related molecules translated a unit along the b axis are stacked along the c direction, with a perpendicular distance of 3.301 (2) Å. The possibility of π–π stacking interactions involving these rings is reduced as these planes are inclined at an angle of 27°. However, these molecules are linked by weak C12—H12···N4(x, $\frac{3}{2}-y$, $z-\frac{1}{2}$) hydrogen bonds to form an infinite chain along the c axis. This arrangement is further stabilized by C—H···π interactions involving (i) H14 and the phenyl ring at (x, $\frac{3}{2}-y$, $z+\frac{1}{2}$), and (ii) H18 and a pyridyl ring (N5) at (x, $\frac{3}{2}-y$, $z-\frac{1}{2}$). The geometry of these interactions are listed in Table 2.

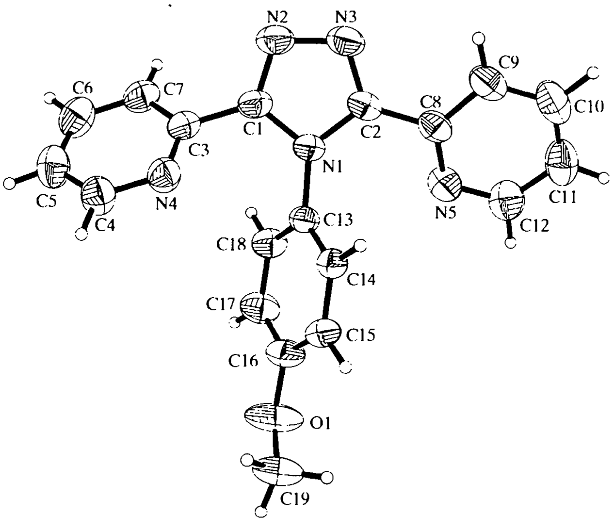


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

The title compound was synthesized by the reaction of equivalent amounts of 4,4′-methoxyphenylphosphazoanilide and N,N'-dipyridoylhydrazine in N,N-dimethylaniline for 3 h at 463–473 K (Grimmel *et al.*, 1946; Klingsberg, 1958). Single crystals suitable for X-ray diffraction analysis were obtained from acetone.

Crystal data

$C_{19}H_{15}N_5O$
$M_r = 329.36$
Monoclinic
$P2_1/c$
$a = 11.5436\ (4)$ Å
$b = 18.2820\ (6)$ Å
$c = 8.2935\ (3)$ Å
$\beta = 107.141\ (1)°$
$V = 1672.5\ (1)$ Å^3
$Z = 4$
$D_x = 1.308$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6971 reflections
$\theta = 2.16$–$38.60°$
$\mu = 0.086$ mm^{-1}
$T = 293\ (2)$ K
Plate
$0.50 \times 0.32 \times 0.14$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
13 978 measured reflections
4831 independent reflections
3310 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 30°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.120$
$S = 1.029$
4831 reflections
287 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.2459P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.017 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C16	1.369 (2)	N2—N3	1.384 (2)
O1—C19	1.406 (2)	N3—C2	1.316 (2)
N1—C1	1.369 (2)	N4—C4	1.336 (2)
N1—C2	1.373 (2)	N4—C3	1.341 (2)
N1—C13	1.442 (1)	N5—C12	1.335 (2)
N2—C1	1.311 (2)	N5—C8	1.339 (2)
N2—C1—C3—C7	48.1 (2)	C1—N1—C13—C18	57.1 (2)
N3—C2—C8—C9	26.8 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N2^{i}	0.94 (2)	2.56 (2)	3.318 (2)	137 (1)
C12—H12···N4^{ii}	1.01 (2)	2.60 (2)	3.382 (2)	134 (2)
C14—H14···π(phenyl^{iii})	0.98 (2)	3.06 (2)	3.876 (2)	141 (2)
C18—H18···π(pyridyl^{ii})	0.99 (2)	2.87 (2)	3.682 (2)	140 (2)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 3 cm and the detector swing angle was −40°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference map and refined isotropically.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1269). Services for accessing these data are described at the back of the journal.

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2-Ethyl-2-(3-oxobutyl)cycloheptane-1,3-dione

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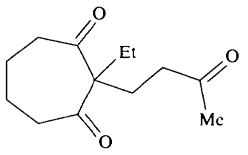
Abstract

In the title compound, $C_{13}H_{20}O_3$, the cycloheptane ring adopts a twist-chair conformation. The molecules are packed as layers parallel to the ($\bar{2}02$) plane. The planar oxobutyl group forms a dihedral angle of 48.3 (1)° with the best plane through the cycloheptane ring.

Comment

The title compound, (I), is the first solid prochiral triketone system in carbocyclic chemistry. It serves as an important precursor for the synthesis of homo-Wieland Miescher ketone which is a potential building block for the synthesis of terpenes (Ireland & Aristoff, 1979) and other natural-product intermediates. It can also be used for the study of oxy-cope rearrangement (Selvarajan, 1966) and synthesis of optically active carbocyclic intermediates (Rajagopal & Swaminathan, 1998). The X-ray structure determination of the compound was carried out to study the molecular conformation.



(I)

Some of the bond lengths and intra-annular valence angles in the cycloheptane ring that deviate significantly from the reported mean values (Allen *et al.*, 1993) may be due to the presence of the extended oxobutyl substituent at C1, and Csp^2 atoms C2 and C7. The cycloheptane ring adopts a twist-chair conformation with a twofold axis running through C1 and the mid-point of the C4—C5 bond. The Cremer & Pople puckering parameters (Cremer & Pople, 1975) are $q_2 = 0.540(2)$ Å,

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