Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 4-Oxo-2,3,5,6-tetraphenylpiperidine-1-carbonitrile ethyl acetate hemisolvate

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**Key indicators**

Single-crystal X-ray study
*T* = 105 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
*R* factor = 0.067
*wR* factor = 0.188
Data-to-parameter ratio = 18.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

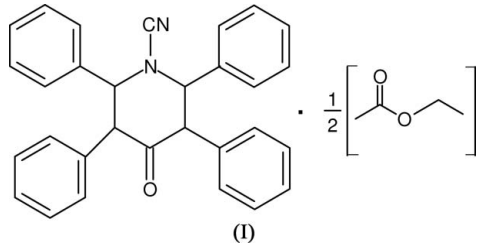


Received 24 January 2006
Accepted 3 March 2006

In the title compound, $C_{30}H_{24}N_2O\cdot0.5C_4H_8O_2$, the piperidone ring adopts the chair conformation and all the phenyl rings are equatorially oriented. The ethyl acetate molecule is present as a space filler and does not participate in the hydrogen-bonding network. The crystal structure is stabilized through C—H···N and C—H···O hydrogen bonds. No significant C—H···$\pi$ and $\pi$–$\pi$ interactions are observed.

## Comment

Piperidinone derivatives have a variety of biological roles to play, such as bactericidal, fungicidal and herbicidal (Mobio *et al.*, 1989; Dimmock *et al.*, 1992, 1994; Rameshkumar *et al.*, 2003). They have also been regarded as precursors for a host of biologically active compounds and natural alkaloids, prior to their conversion to piperidines. Piperidinone derivatives act as potential inhibitors of human placental aromatase *in vitro* (Baroudi *et al.*, 1996). In particular, *N*-cyano compounds have been found as activators of ATP-sensitive potassium channels and inhibitors of insulin release (Manley *et al.*, 1993; Tagmose *et al.*, 2004; Yoshiizumi *et al.*, 1997). This has prompted us to carry out accurate determinations of the crystal structures of a host of *N*-cyano-substituted piperidinone derivatives. Details of the molecular conformations of such compounds at atomic resolution are expected to shed light on modelling a host of similar biologically important compounds. This paper deals with the structure of the title compound, (I), a cyano-piperidinone derivative with an ethyl acetate solvent molecule incorporated in the crystal structure. Recently, in our laboratory, we have elucidated the crystal structures of a few nitroso-piperidinone derivatives with varying substituents in the phenyl rings at the 2,6-positions of the nitroso–piperidinone ring and with unsubstituted phenyl rings at the 3,5-positions, namely the 4-methoxy (PIP1; Natarajan *et al.*, 2005), 2-methyl (PIP2; Suresh *et al.*, 2005*a*), 2-methoxy (PIP3; Suresh *et al.*, 2005*b*) and 2-chloro (PIP4; Suresh *et al.*, 2005) analogues of the title compound.




(I)

Fig. 1 illustrates the molecular structure of compound (I) and the atom-numbering scheme. The piperidinone ring

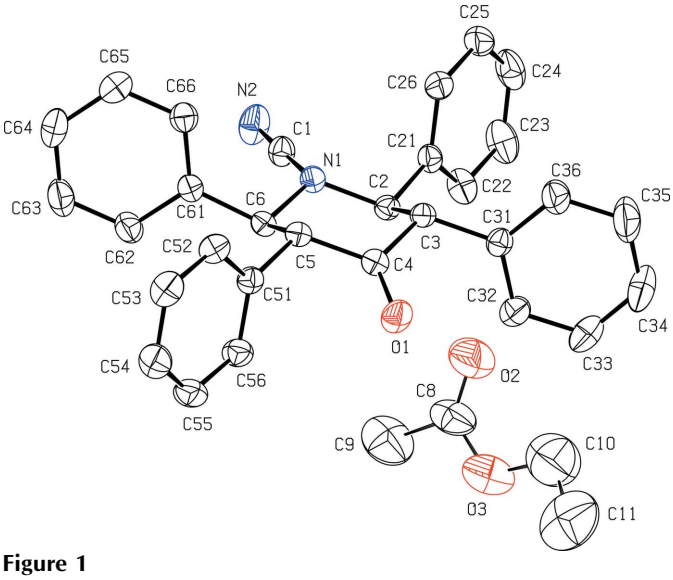



**Figure 1**
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

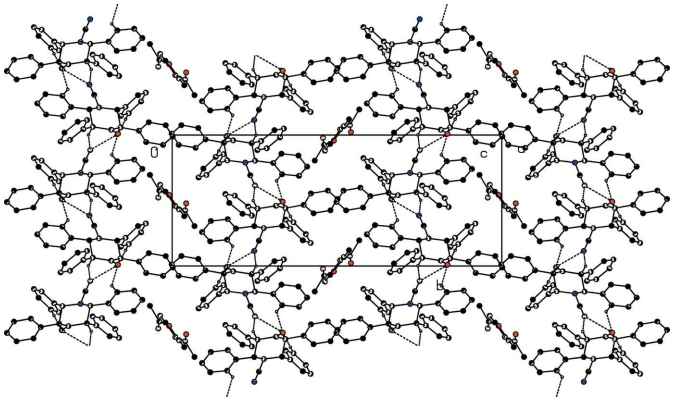


**Figure 2**
The packing of (I), viewed down the *a* axis. H atoms which do not take part in hydrogen bonding (dashed lines) have been omitted for clarity.

adopts a chair conformation. Atoms C3 and C6 deviate by 0.691 (2) and 0.663 (2) Å, respectively, from the least-squares plane defined by atoms N1, C2, C4 and C5. From this plane, atoms O1, C7 and N2 deviate on the same side by 0.458 (3), 0.220 (3) and 0.361 (4) Å, respectively. This may be attributed to the fact that both the cyano group and the O atom of the piperidinone ring participate in the hydrogen bonding as acceptors. The orientations of the aryl rings at the 2- and 3-positions and of those at the 5- and 6-positions are −56.8 (2)° (C21—C2—C3—C31) and 59.3 (2)° (C51—C5—C6—C61). The dihedral angle between the planes formed by the phenyl rings at the C2 and C3 positions is 56.5 (1)°, and that at C5 and C6 is 50.2 (1)°. These nearly equal values, and the overall geometry of (I), show that the present structure is a good example of a molecule where the competition between intra- and intermolecular interactions is apparent. Moreover, the strength of the intermolecular interactions (see Table 1), which is directly related to the tendency of the molecules to pack as densely as possible, has presumably 'steered' the molecule in lowering its symmetry. The presence of the ethyl acetate solvent as a mere space filler suggests that its contribution to the intermolecular interactions is insignificant but it has nevertheless played a role in crystallization.

Fig. 2 shows the crystal packing of moelcules of (I), viewed down the *a* axis. The crystal packing is stabilized by two-dimensional networks characterized by C—H···N and C—H···O hydrogen bonds. There is a solvent-accessible volume of about 465 Å$^3$ between these layers, surrounded by the phenyl rings, in which the ethyl acetate molecules are trapped. The solvent molecules do not participate in hydrogen bonds but have van der Waals-type interactions with the neighbouring molecules.

## Experimental

A solution of tetraphenylpiperidin-4-one (1 g, 0.002 mol) in acetone was added slowly to a solution of cyanogen bromide (0.5 g, 0.004 mol). Anhydrous potassium carbonate (0.342 g, 0.002 mol) was added to this solution and the mixture was refluxed for about 12–15 h on a water bath. After the completion of the reaction, the solvent was evaporated and the crude product was recrystallized from ethyl acetate (yield 78%).

*Crystal data*

$C_{30}H_{24}N_2O\cdot0.5C_4H_8O_2$
$M_r$ = 472.56
Monoclinic, $P2_1/c$
$a$ = 9.3887 (3) Å
$b$ = 10.6241 (4) Å
$c$ = 26.7247 (10) Å
$\beta$ = 92.232 (2)°
$V$ = 2663.67 (17) Å$^3$
$Z$ = 4
$D_x$ = 1.178 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 6611 reflections
$\theta$ = 2–23°
$\mu$ = 0.07 mm$^{-1}$
$T$ = 105 (2) K
Block, colourless
0.26 × 0.18 × 0.12 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min}$ = 0.97, $T_{max}$ = 0.99
40759 measured reflections
6596 independent reflections
5640 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040
$\theta_{max}$ = 28.3°
$h$ = −12 → 12
$k$ = −14 → 14
$l$ = −35 → 35

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.188
$S$ = 1.12
6596 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0737P)^2 + 2.1461P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.46 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.24 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C3—H3···N2$^{i}$ | 0.98 | 2.57 | 3.433 (2) | 147 |
| C5—H5···N2$^{i}$ | 0.98 | 2.42 | 3.317 (2) | 152 |
| C25—H25···O1$^{ii}$ | 0.93 | 2.47 | 3.399 (3) | 176 |
| C62—H62···O1$^{iii}$ | 0.93 | 2.44 | 3.203 (2) | 139 |

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

H atoms were placed in calculated positions and allowed to ride on their carrier atoms, with C—H = 0.93–0.98 Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(C) for $CH_2$ and CH groups or 1.5$U_{eq}$(C) for $CH_3$ groups. A suitable molecular geometry for the ethyl acetate solvent molecule could not be obtained, owing to the fact that it is disordered about an inversion centre within the unit cell; consequently, the C10—C11 bond length was restrained to a value of 1.51 (1) Å.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

The authors thank the UGC, New Delhi, for the DRS and ASIST programmes, and the DST, New Delhi, for the IRHPA project. JS thanks the UGC and the management of The Madura College, Madurai, for providing a Teacher Fellowship.

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