C2—C3—C4	101.6 (2)	101.6 (3)	101.8 (3)
C2—C3—C6	108.1 (3)	109.9 (3)	109.6 (3)
C3—C4—C5	106.1 (2)	106.4 (3)	107.2 (3)
C4—C3—C6	109.4 (2)	108.1 (3)	109.6 (3)
C11—C5—C4	115.6 (2)	114.7 (3)	115.6 (3)
C21—C2—C3	116.5 (2)	115.5 (3)	116.2 (3)
C31—C3—C6	112.5 (2)	113.9 (3)	112.8 (3)
C31—C3—C4	113.2 (2)	112.2 (3)	111.3 (3)
C31—C3—C2	111.4 (2)	110.5 (3)	111.1 (3)

The structure analysis of (I) proceeded routinely and the H atoms were located by difference syntheses and refined isotropically. For (II), systematic absences indicated the possible space groups $Pca2_1$ or $Pcam$. A satisfactory solution was obtained in the non-centrosymmetric space group with two molecules in the asymmetric unit. The C-bonded H atoms were included in geometrically calculated positions and N-bonded H atoms were found from difference Fourier maps and refined isotropically. The collection of data at low temperature was carried out in order to improve the counting statistics [using an Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986)]. In the case of (II), the absolute direction of the polar axis cannot be determined reliably since the values of anomalous dispersion for the heaviest O atoms in the case of molybdenum radiation are very small.

For both compounds, data collection: *Kuma KM-4 Software* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 Software*; data reduction: *Kuma KM-4 Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1033). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 870–872

Ethyl 3,5-Dimethyl-4-oxo-*cis*-2,6-diphenylpiperidine-1-carboxylate

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(*Received 28 April 1997; accepted 6 January 1998*)

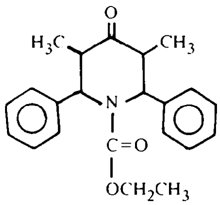
Abstract

The piperidine ring in the title compound, $C_{22}H_{25}NO_3$, adopts a distorted-boat conformation. Some conjugation of the lone pair of the N atom with the carbonyl group is observed. The two phenyl rings form dihedral angles of 88.9 (1) and 79.1 (1)° with the best plane through the piperidine ring.

Comment

Piperidine derivatives are used clinically to prevent post-operative vomiting, to speed up gastric emptying before anaesthesia or to facilitate radiological evaluation, and to correct a variety of disturbances of gastrointestinal functions (Robinson, 1973). Several 2,6-disubstituted piperidines are found to be useful as tranquilisers (Bochringer & Soehne, 1961) and possess hypotensive activity (Severs *et al.*, 1965), and a combination of stimulant and depressant effects on the central nervous system (Ganellin & Spickett, 1965), as well as bactericidal, fungicidal and herbicidal activities (Mobio *et al.*, 1990).

The torsion angles of the title compound, (I), show that the piperidine ring adopts a distorted-boat conformation. The carbonyl group of the ethoxycarbonyl moiety shows some conjugation with the N1 atom of the piperidine ring; N1—C19 1.367 (3) and C19—O20 1.204 (3) Å, the N1 atom being 0.156 (2) Å out of the C2, C6, C19 plane. The methyl groups in the 3 and 5 positions of the piperidine ring assume axial and equatorial orientations, respectively, as can be seen from the torsion angles N1—C2—C3—C24 −173.8 (2) and N1—C6—C5—C25 63.4 (2)°.



(I)

Phenyl rings *A* (C7–C12) and *B* (C13–C18) are in axial and equatorial [C4—C5—C6—C7 68.6 (2) and C4—C3—C2—C13 −173.1 (2)°] positions, respectively. Rings *A* and *B* form dihedral angles of 88.9 (1) and 79.1 (1)° with the best plane through the piperidine ring.

The molecules are packed in such a way that centrosymmetrically related phenyl rings are quite separate and create a hollow at the centre when viewed along the *b* axis. The shortest intermolecular contact is C22···O20^i: H22*B*···O20^i 2.503 (3), C22···O20^i 3.183 (3) Å and C22—H22*B*···O20^i 127° [symmetry code: (i) $-x+1$, $-y$, $-z+1$].

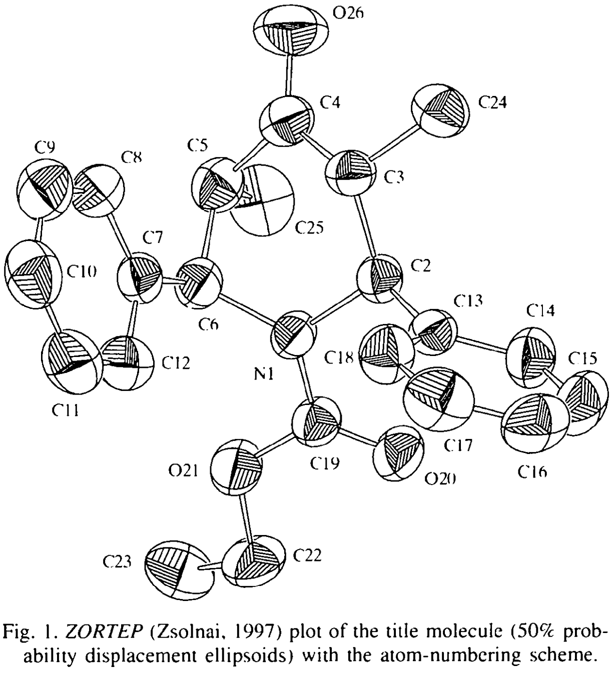


Fig. 1. *ZORTEP* (Zsolnai, 1997) plot of the title molecule (50% probability displacement ellipsoids) with the atom-numbering scheme.

Experimental

The title compound was synthesized by the condensation of an ester of acetonedicarboxylic acid with an aromatic aldehyde in the presence of ammonium acetate (Ravindran *et al.*, 1991).

Crystal data

$C_{22}H_{25}NO_3$
$M_r = 351.43$
Monoclinic
$P2_1/n$
$a = 10.404\,(2)$ Å
$b = 9.743\,(2)$ Å
$c = 19.096\,(3)$ Å
$\beta = 95.70\,(2)°$
$V = 1926.1\,(6)$ Å^3
$Z = 4$
$D_x = 1.212$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 20 reflections
$\theta = 10–18°$
$\mu = 0.639$ mm^{-1}
$T = 293\,(2)$ K
Thick plate
0.6 × 0.5 × 0.3 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: *CYLABS* (Nardelli, 1997)
$T_{min} = 0.717$, $T_{max} = 0.826$
3244 measured reflections
3058 independent reflections
2495 reflections with $I > 2\sigma(I)$

$R_{int} = 0.016$
$\theta_{max} = 62.49°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 21$
3 standard reflections every 200 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.157$
$S = 1.030$
3055 reflections
239 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.9P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.182$ e Å^{-3}
$\Delta\rho_{min} = -0.200$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0087 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C19	1.367 (3)	C19—O20	1.204 (3)
N1—C2	1.486 (2)	C19—O21	1.344 (3)
N1—C6	1.483 (3)	O21—C22	1.456 (3)
C4—O26	1.208 (3)		
C19—N1—C2	114.1 (2)	O20—C19—O21	124.2 (2)
C19—N1—C6	122.4 (2)	O20—C19—N1	123.9 (2)
C2—N1—C6	120.0 (2)	O21—C19—N1	111.9 (2)
C13—C2—C3	110.8 (2)	C19—O21—C22	115.9 (2)
C19—N1—C2—C13	−66.9 (2)	C2—N1—C6—C5	43.8 (2)
C6—N1—C2—C3	9.3 (3)	C4—C5—C6—N1	−58.0 (2)
N1—C2—C3—C4	−48.2 (2)	C4—C5—C6—C7	68.6 (2)
C13—C2—C3—C24	61.3 (2)	C2—N1—C19—O21	−176.8 (2)
C2—C3—C4—C5	33.2 (3)	N1—C19—O21—C22	178.7 (2)
C3—C4—C5—C6	20.3 (3)		

Beyond 62.49°, we could not detect a diffraction pattern and so the data collection was restricted to this value.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *PARST* (Nardelli, 1983, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1307). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 872–875

Three Cycloadducts Formed by the Reaction of Bis(phenylazo)stilbene with Acetylenic and Olefinic Dipolarophiles

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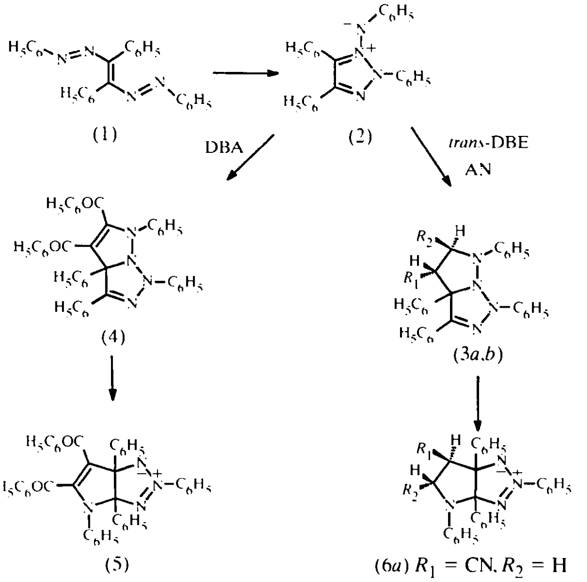
(*Received 16 June 1997; accepted 19 November 1997*)

Abstract

Bis(phenylazo)stilbene, (1), undergoes facile cycloaddition reactions with acetylenic and olefinic dipolarophiles to give the corresponding cycloadducts. The cycloadducts of (1) with dibenzoylacetylene (DBA), *trans*-1,2-dibenzoylethylene (*trans*-DBE) and acrylonitrile (AN) have been unambiguously identified through X-ray crystallographic analysis as, formally, 5,6-dibenzoyl-2,3a,4,6a-tetraphenyl-2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene [$C_{42}H_{30}N_4O_2$, (5)], 2,3a,4,6a-tetraphenyl-2,3a,4,5,6,6a-hexahydro-1,2,3,4-tetraazapentalene-6-carbonitrile [$C_{29}H_{23}N_5$, (6*a*)] and 5,6-dibenzoyl-2,3a,4,6a-tetraphenyl-2,3a,4,5,6,6a-hexahydro-1,2,3,4-tetraazapentalene [$C_{42}H_{32}N_4O_2$, (6*b*)], in each of which there is a delocalized double bond over atoms N1, N2 and N3 [N1$\cdots$N2$\cdots$N3: N1$\cdots$N2/N2$\cdots$N3 1.297 (2)/1.305 (2), 1.308 (2)/1.302 (1) and 1.298 (1)/1.298 (1) Å for (5), (6*a*) and (6*b*), respectively]. In (5), the C(O)C_6H_5 substituent on C6 is almost fully conjugated with the C5=C6 double bond [O2=C32—C6=C5 torsion angle 166.4 (2)°]. Compounds (5), (6*a*) and (6*b*) are examples of a new class of heterocyclic compounds.

Comment

Several suggestions have been made concerning the structures of the oxidation products of bisphenylhydrazones and bisbenzoylhydrazones of 1,2-diketones. These include a dihydro-1,2,3,4-tetrazine structure (von Pechman, 1897) and a bisazoolefin structure (Stolle, 1926; Grammaticakis, 1947) for the oxidation products of 1,2-diketone bisphenylhydrazones, whereas enol derivatives have been suggested as the oxidation products of bisbenzoylhydrazones of 1,2-diketones (Curtin & Alexandrou, 1963). A suggestion has also been made (Bauer *et al.*, 1964) that certain *ortho*-bisazo compounds containing electron-withdrawing groups attached to one of the azo groups exist in the meso-ionic form. It has been reported (Angadiyavar *et al.*, 1971; Sukumaran *et al.*, 1972) that the oxidation products of bisphenylhydrazones of several 1,2-diketones undergo facile 1,3-dipolar cycloaddition reactions with acetylenic and olefinic dipolarophiles to give adducts such as (4), (3*a*) and (3*b*).



(6*a*) R_1 = CN, R_2 = H
(6*b*) R_1 = R_2 = COC_6H_5