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2,9-Bis(3-nitrophenyl)-1-azaadamantan-4-one

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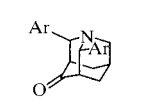
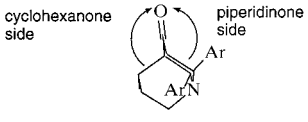
The title compound, 2,9-bis(3-nitrophenyl)-1-azatricyclo-[3.3.1.1^{3,7}]decan-4-one, $C_{21}H_{19}N_3O_5$, has a tricyclic structure. The torsion angles may be used to describe the relationship of the carbonyl group to the adjacent faces, whereby it is seen that the angles on the face of the arylpiperidinone side [122.0 (3) and −122.0 (3)°] are greater than those on the cyclohexanone side [−119.8 (4) and 119.9 (4)°]. Although these differences may explain a facial selectivity during nucleophilic addition to the carbonyl group, the presence of the aryl rings is probably also important.

Comment

Numerous investigations have shown that substitution in adamantanones and azaadamantanones may affect facial selectivity during nucleophilic addition to the carbonyl group (Kaselj *et al.*, 1999). Structural studies of azaadamantanone have been used to explain its facial selectivity; the distortion in the calculated geometry (HF/6-31G*) of azaadamantanone has been discussed by Gung & Wolf (1996). We recently designed the 2-eq-9-ax-diarylazaadamantan-4-one (eq is equatorial and ax is axial) analogues to the title compound, (I), as probes for facial selectivity in the nucleophilic addition of sodium borohydride in methanol. The highly preferential *anti* attack in the reduction of these ketones has been described; both steric and electronic effects were involved (Jiménez-Cruz *et al.*, 2000).



Ar = *m*-NO_2Ph
(I)



Ar = *m*-NO_2Ph
(I*a*)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The molecule consists of a tricyclic azaadamantanone cage with aryl rings (3-nitrophenyl) substituted at the 2 and 9 positions. Rings *A* (C11–C16) and *B* (C17–C22) are attached to atoms C2 and C9 in equatorial and axial positions, respectively, relative to the piperidinone ring. The rotation between each aryl ring and the tricyclic framework may be described by the torsion angles C3—C2—C11—C12 [−28.4 (4)°; ring *A*] and C5—C9—C17—C18 [−37.2 (4)°; ring *B*]. The aromatic rings are themselves planar [mean deviations 0.006 (2) Å for ring *A* and 0.008 (3) Å for ring *B*], and although the ring and the nitro group in pure *m*-nitroacetophenone are almost planar, with an angle between the groups of 1.8 (2)° (Feeder *et al.*, 1996), in (I), the planes of the 3-nitrophenyl groups are rotated significantly away from the planes of the rings [11.2 (6)° for ring *A* and 10.7 (2)° for ring *B*].

The average C—C bond length within the adamantane cage in (I) is 1.53 (4) Å. The bonds N1—C2, N1—C9 and N1—C8 are 1.479 (4), 1.484 (4) and 1.472 (4) Å, respectively. These values are greater than those reported for 2-phenyl-3,5,7-trimethylazaadamantane-4,10-dione, (II) (Risch *et al.*, 1991), in which the N—C distances are 1.462 (3), 1.458 (3) and 1.452 (3) Å, and are less than those described in chlorophenyloxyazaadamantane hydrochloride, (III) (Fernández *et al.*, 1989), in which the N—C distances are 1.514 (7), 1.49 (3) and 1.50 (3) Å. The C=O distance (C4—O1) is 1.214 (4) Å in (I), which is similar to the values in (II) (1.211 and 1.214 Å). The C3—C4—C5 bond angle is 112.7 (3)° in (I), which is less than the values in (II) (114.25 and 114.95°; Risch *et al.*, 1991).

The torsion angles used to describe the two faces of the other side of the cage (see Scheme above) show that the angles on the arylpiperidinone side [C9—C5—C4—O1 122.0 (3)° and C2—C3—C4—O1 −122.0 (3)°] are greater than on the cyclohexanone side [C6—C5—C4—O1 −119.8 (4)° and C10—C3—C4—O1 119.9 (4)°]. These geometrical parameters may provide some understanding of the nucleophilic addition reactions on these substrates. Although these differences imply a facial asymmetry that may explain a preferential selectivity, the presence of the aryl rings is also important in preferential attack on the cyclohexanone face.

The molecules in the crystal of (I) are linked by several weak C—H···O bonds involving the O atoms in the carbonyl ketone and the nitro groups (Table 2).

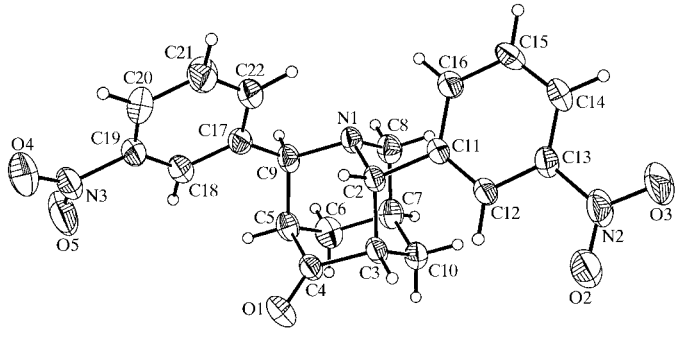


Figure 1
A molecular view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

† Deceased.

Experimental

The title compound was prepared according to the procedure described by Jiménez-Cruz *et al.* (2000). After purification *via* a chromatographic column, crystals of (I) were grown by slow evaporation of a chloroform–hexane solution at room temperature (m.p. 498–500 K).

Crystal data

$C_{21}H_{19}N_3O_5$
M_r = 393.39
Orthorhombic, *Pbca*
a = 13.318 (1) Å
b = 15.217 (2) Å
c = 17.965 (1) Å
V = 3640.8 (6) Å^3
Z = 8
D_x = 1.435 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 40 reflections
θ = 3.0–12.5°
μ = 0.10 mm^{-1}
T = 293 (2) K
Block, yellow
0.6 × 0.3 × 0.3 mm

Data collection

Siemens *P*4/PC diffractometer
$\theta/2\theta$ scans
3999 measured reflections
3185 independent reflections
1685 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25°
$h = -1 \rightarrow 15$
$k = -1 \rightarrow 18$
$l = -1 \rightarrow 21$
3 standard reflections
every 97 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.133
S = 1.00
3185 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0012 (4)

Table 1
Selected geometric parameters (Å, °).

O1—C4	1.214 (4)	C3—C4	1.517 (4)
N1—C8	1.472 (4)	C4—C5	1.507 (5)
N1—C2	1.479 (4)	C5—C9	1.548 (4)
N1—C9	1.484 (4)	C7—C8	1.528 (5)
C2—C3	1.553 (4)		
C8—N1—C2	110.4 (2)	O1—C4—C3	123.1 (3)
C8—N1—C9	109.3 (3)	C5—C4—C3	112.7 (3)
C2—N1—C9	109.7 (2)	N1—C8—C7	112.0 (3)
N1—C2—C3	111.0 (3)	N1—C9—C5	109.9 (3)
O1—C4—C5	124.1 (3)		
C10—C3—C4—O1	119.9 (4)	O1—C4—C5—C9	122.0 (3)
C2—C3—C4—O1	−122.0 (3)	C3—C2—C11—C12	−28.4 (4)
O1—C4—C5—C6	−119.8 (4)	C5—C9—C17—C18	−37.2 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O4^{i}	0.96	2.54	3.249 (4)	131
C20—H20···O1^{i}	0.96	2.44	3.300 (5)	150
C21—H21···O3^{ii}	0.96	2.53	3.263 (6)	133

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$.

The positional parameters of the H atoms were calculated geometrically and fixed, with U_{iso}(H) = 1.2U_{eq} of the parent atom.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1181). Services for accessing these data are described at the back of the journal.

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