Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Conformation of *N*-methyl-4-piperidyl 2,4-dinitrobenzoate

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Received 22 November 2002
Accepted 2 December 2002
Online 11 January 2003

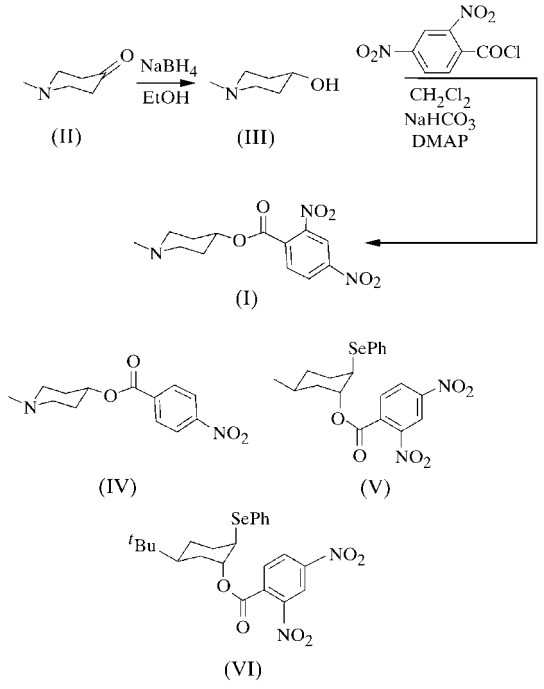
The crystal structure of *N*-methyl-4-piperidyl 2,4-dinitrobenzoate, $C_{13}H_{15}N_3O_6$, (I), at 130 (2) K reveals that, in the solid state, the molecule exists in the equatorial conformation, (Ieq). Thus, the through-bond interaction present in the axial conformation, (Iax), is not strong enough to overcome the *syn*–diaxial interactions between the axial methyl substituent and the axial H atoms on the two piperidyl ring C atoms either side of the ester-linked ring C atom. The carboxylate group in (I) is orthogonal to the aromatic ring, in contrast with other 2,4-dinitrobenzoates, which are coplanar. The piperidyl–ester C—O bond distance is 1.467 (3) Å, which is actually shorter than other equatorial cyclohexyl–ester C—O distances. This shorter piperidyl–ester C—O bond distance is due to the reduced electron demand of the orthogonal ester group.

Comment

As part of our studies of the factors influencing C—O*R* bond distances, where *R* is hydroxy, ester or ether (White & Robertson, 1992; White *et al.*, 2000; Pool *et al.*, 2000), we have determined the structure of the title compound, (I), which was prepared in two steps from 4-piperidone, (II), with an overall yield of 60%.

Compound (I) can conceivably exist in solution in two conformations, (Iax) and (Ieq), which interconvert by nitrogen inversion. Although conformation (Ieq) is expected to be favoured on steric grounds, the axial conformation, (Iax), is stabilized by a through-bond interaction between the nitrogen lone-pair electrons and the low-lying C—ODNB (ODNB is dinitrobenzoate) antibonding orbital (Fig. 1).

Previous to this study, we determined the structure of *N*-methyl-4-piperidinyl 4-nitrobenzoate, (IV) (Andrau & White, 2003), which was shown to adopt a conformation analogous to (Ieq) in the solid state, suggesting that the through-bond interaction between the nitrogen lone-pair and the C—OPNB antibonding orbital was not strong enough to overcome the steric repulsion associated with the axial methyl group in (Iax). The C—OPNB (OPNB is 4-nitrobenzoate) bond distance in (IV) is 1.4630 (16) Å, which is not significantly lengthened compared with the standard cyclohexyl C—OPNB distance (White & Robertson, 1993). The 2,4-dinitrobenzoate ester is more strongly electron demanding than the 4-nitrobenzoate ester, and this is reflected in the relative pK_a values for the parent acids; 4-nitrobenzoic and 2,4-dinitrobenzoic acids have pK_a values of 3.4 and 1.4, respectively (Dean, 1992). The stronger electron demand of the 2,4-dinitrobenzoate ester substituent would result in a stronger through-bond interaction with the nitrogen lone pair. Thus, we were interested in establishing whether (I) would adopt conformation (Iax). If this axial conformation were observed, then we would be interested in seeing the effects of the through-bond interaction on the C—ODNB distance compared with a typical cyclohexyl 2,4-dinitrobenzoate.



The crystal structure of (I) at 130 (2) K reveals, disappointingly, that ester (I) exists in the solid state in the equatorial conformation (Ieq), suggesting that the through-bond interaction in conformation (Iax) is still not sufficiently stabilizing to overcome the repulsive *syn*–diaxial interactions. However, there is an interesting aspect to this structure. Examination of the dihedral angle between the carboxyl ring and the aromatic ring [O2—C7—C8—C9 = 78.7 (3)°] reveals that these two groups are close to orthogonal, whereas in other 2,4-dinitrobenzoate esters whose structures we have determined, these two groups are essentially coplanar (Green *et al.*, 1995). This conformation brings nitro atom O3 into a close contact with carbonyl atom C7, with an O3···C7 distance of 2.599 (3) Å. Furthermore, the carbonyl C atom deviates from the plane of the attached atoms (O1, O2 and C8) by 0.043 (2) Å towards atom O3. These latter structural effects are consistent with the early stages of nucleophilic addition of the nitro O atom to the ester carbonyl group (Burgi *et al.*, 1973).

The orthogonal relationship between the aromatic ring and the carboxyl group in (I) would result in poor π overlap

  DOI: 10.1107/S0108270102022254

between the electron-deficient aromatic ring and the carboxyl group. This, in addition to the interaction with the nitro O atom discussed above, would make the ester O atom less electron-demanding. The result of decreased electron demand at the ester O atom would be twofold. Firstly, the strength of the through-bond interaction would be decreased, and secondly, the C1—O1 distance, which is sensitive to electron demand (Amos *et al.*, 1992), would be shorter than expected for a cyclohexyl 2,4-dinitrobenzoate ester. The C1—O1 distance in (I) is 1.468 (3) Å, which is in fact shorter than that observed for other equatorial cyclohexyl 2,4-dinitrobenzoate esters [1.476 (2) Å; Green *et al.*, 1994]. A similar situation arises in the structures of phenylselenyl cyclohexyl 2,4-dinitrobenzoates (V) and (VI) (White *et al.*, 2002). For example,

Figure 1
The two possible conformations of (I), illustrating the through-bond interaction present in (Iax). ODNB denotes dinitrobenzoate.

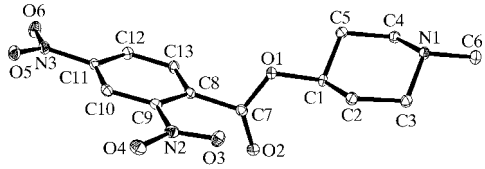


Figure 2
A view of the molecule of (I), with displacement ellipsoids drawn at the 20% probability level. H atoms have been omitted for clarity.

ester (V), which has the carboxylate group orthogonal to the aromatic ring, has a C1—O1 distance of 1.474 (2) Å, which is significantly shorter than the C1—O1 distance of 1.487 (2) Å observed in ester (VI). Notably in ester (VI), the carboxyl group is coplanar with the ring. This again demonstrates the reduced electron demand of the orthogonal carboxylate group.

Experimental

4-Piperidone, (II), was reduced to 4-piperidol, (III), using sodium borohydride in ethanol. The secondary alcohol (III) was converted into the 2,4-dinitrobenzoate ester, (I), by stirring with 2,4-nitrobenzoyl chloride in dichloromethane in the presence of sodium bicarbonate and dimethylaminopyridine, followed by aqueous work-up. Crystals of (I) were grown by slow evaporation of an ether solution.

Crystal data

$C_{13}H_{15}N_3O_6$
M_r = 309.28
Monoclinic, $P2_1/c$
a = 6.040 (3) Å
b = 13.303 (5) Å
c = 17.699 (7) Å
β = 94.096 (8)°
V = 1418.4 (10) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1163 reflections
θ = 2.3–22.5°
μ = 0.12 mm^{-1}
T = 130 (2) K
Rod, orange
0.30 × 0.12 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer
φ and ω scans
7269 measured reflections
2486 independent reflections
1840 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25°
$h = -7 \rightarrow 7$
$k = -8 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.118
S = 1.06
2486 reflections
259 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.2224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.467 (3)	C3—N1	1.468 (3)
C1—C5	1.507 (3)	C4—N1	1.465 (3)
C1—C2	1.511 (3)	C4—C5	1.525 (3)
C2—C3	1.526 (3)	C6—N1	1.466 (3)
O1—C1—C5	106.35 (18)	N1—C3—C2	111.6 (2)
O1—C1—C2	111.25 (19)	N1—C4—C5	111.16 (19)
C5—C1—C2	110.5 (2)	C1—C5—C4	109.4 (2)
C1—C2—C3	108.8 (2)		
O1—C1—C2—C3	−174.9 (2)	N1—C4—C5—C1	−57.8 (3)
C5—C1—C2—C3	−57.0 (3)	O2—C7—C8—C13	−98.2 (3)
C1—C2—C3—N1	57.7 (3)	O1—C7—C8—C13	75.8 (3)
O1—C1—C5—C4	178.15 (19)	O2—C7—C8—C9	78.7 (3)
C2—C1—C5—C4	57.3 (3)		

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*.

The authors acknowledge financial support from The University of Melbourne.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1405). Services for accessing these data are described at the back of the journal.

References

Amos, R. D., Handy, N. C., Jones, P. G., Kirby, A. J., Parker, J. M., Percy, M. D. & Su, J. (1992). *J. Chem. Soc. Perkin Trans.* 2, pp. 549–558.
Andrau, L. & White, J. M. (2003). *Acta Cryst.* E**59**, o77–o79.
Bruker (1997). *SHELXTL.* Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.
Burgi, H. B., Dunitz, J. D. & Shefter, E. (1973). *J. Am. Chem. Soc.* **95**, 5065–5067.
Dean, J. A. (1992). *Lange's Handbook of Chemistry*, 14th ed., section 8. New York: McGraw–Hill.
Green, A. J., Kuan, Y.-L. & White, J. M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2023–2024.
Green, A. J., Kuan, Y.-L. & White, J. M. (1995). *J. Org. Chem.* **60**, 2734–2738.
Pool, B. R., White, J. M. & Wolynec, P. (2000). *J. Org. Chem.* **65**, 7505–7601.
White, J. M., Giordano, J. & Green, A. J. (2000). *Aust. J. Chem.* **53**, 285–292.
White, J. M., Lambert, J. B., Spiniello, M., Jones, S. A. & Gable, R. W. (2002). *Chem. Eur. J.* **8**, 2799–2811.
White, J. M. & Robertson, G. B. (1992). *J. Org. Chem.* **57**, 4638–4644.
White, J. M. & Robertson, G. B. (1993). *Acta Cryst.* C**49**, 347–350.