

***N*-Methyl-4-piperidyl *p*-nitrobenzoate at 130 K****Laura Andrau and Jonathan White\***School of Chemistry, University of Melbourne,  
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whitejm@unimelb.edu.au**Key indicators**Single-crystal X-ray study  
 $T = 130\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.041  
 $wR$  factor = 0.097  
Data-to-parameter ratio = 11.8For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The crystal structure of the title compound,  $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4$ , (1), reveals that the molecule exists in the solid state in the equatorial conformation. Thus, the through-bond interaction present in the axial conformation is not strong enough to overcome the *syn*-diaxial interactions between the axial methyl substituent and the axial H atoms on each of the ring C atoms  $\beta$  to N. The  $\text{C}-\text{O}_{\text{PNB}}$  (PNB is *p*-nitrobenzoate) bond distance is 1.4630 (16)  $\text{\AA}$ , which is not significantly different from the corresponding  $\text{C}-\text{O}_{\text{PNB}}$  distance in 4-*tert*-butyl-cyclohexyl 4-nitrobenzoate. The structure of (1) was determined at 130 K.

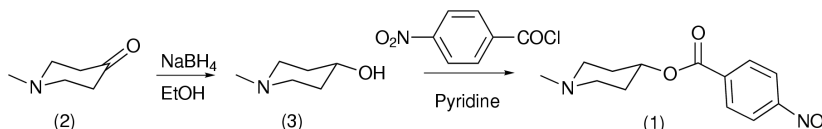
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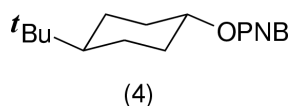
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**Comment**

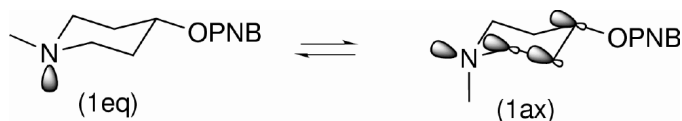
As part of our studies on the factors influencing  $\text{C}-\text{OR}$  ( $R =$  hydroxy, ester or ether) bond distances (White & Robertson, 1992; Green *et al.*, 2000; Pool *et al.*, 2000), we have determined the structure of *N*-methyl-4-piperidyl *p*-nitrobenzoate, (1). Compound (1) can conceivably exist in solution in two conformations; (1ax) and (1eq) (Fig. 1), which interconvert by nitrogen inversion. Although conformation (1eq) is expected to be favoured on steric grounds, the axial conformation (1ax) is stabilized by a through-bond interaction between the nitrogen lone-pair electrons and the low-lying  $\text{C}-\text{O}_{\text{PNB}}$  (PNB is *p*-nitrobenzoate) antibonding orbital.



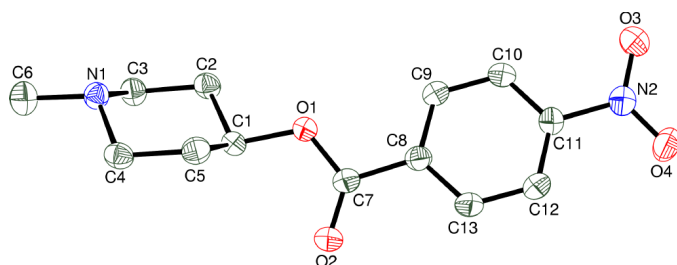
Thus, the purpose of this investigation was twofold: firstly to establish whether (1) exists as (1ax) or (1eq) in the solid state, and secondly, if the axial conformation was observed, to determine the effects of the through-bond interaction (Grob, 1969) on the  $\text{C}-\text{O}_{\text{PNB}}$  distance compared with the parent compound, 4-*tert*-butyl 4-nitrobenzoate, (4). The crystal structure of (1) (Fig. 2) reveals that the ester exists in the solid state in the equatorial conformation (1eq), suggesting that either the through-bond interaction in conformation (1ax) is



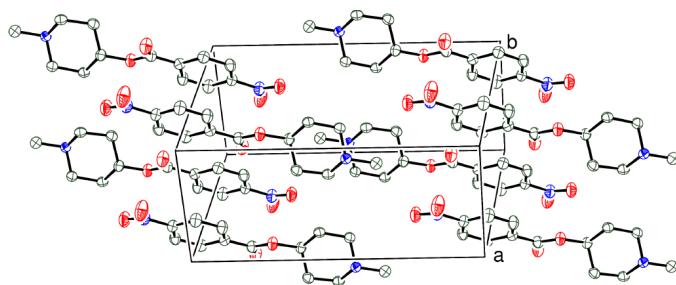
not sufficiently stabilizing to overcome the repulsive *syn*-diaxial interactions, or that more favourable packing forces exist for the equatorial conformer (1eq). The  $\text{C}-\text{O}_{\text{PNB}}$  bond distance in (1) of 1.4630 (16)  $\text{\AA}$  is not significantly different from the  $\text{C}-\text{O}_{\text{PNB}}$  distance observed in compound (4), whose two independent molecules have  $\text{C}-\text{O}_{\text{PNB}}$  distances of 1.464 (2) and 1.468 (2)  $\text{\AA}$  (White & Robertson, 1993).



**Figure 1**  
The conformations of (1) and the through-bond interaction present in (1ax).



**Figure 2**  
Displacement ellipsoid plot of (1), with ellipsoids at the 20% probability level. H atoms have been omitted.



**Figure 3**  
The  $\pi$ - $\pi$  stacking between the 4-nitrobenzoate moieties along the  $b$  axis.

79 The packing of (1) in the crystal is characterized by  $\pi$ - $\pi$  stacking between the 4-nitrobenzoate moieties along the  $b$  axis (Fig. 3). The planes of the aromatic rings are essentially parallel, with a separation of 3.535 (3) Å. The aromatic rings of one moiety are displaced relative to each other along the C8—C11 vector by *ca* 1.2 Å.

## Experimental

The title compound, (1), was prepared in two steps from 4-piperidone, (2), as outlined in the *Scheme*. Thus, 4-piperidone was reduced to 4-piperidol, (3), using sodium borohydride in ethanol. The secondary alcohol, (3), was converted into the 4-nitrobenzoate ester, (1), by stirring with 4-nitrobenzoyl chloride in pyridine followed by aqueous work-up. Plate-like crystals of (1) were grown by slow evaporation of a pentane solution.

### Crystal data

$C_{13}H_{16}N_2O_4$   
 $M_r = 264.28$   
Triclinic,  $P\bar{1}$   
 $a = 6.3348$  (8) Å  
 $b = 7.697$  (1) Å  
 $c = 13.9423$  (18) Å  
 $\alpha = 99.030$  (2)°  
 $\beta = 92.142$  (2)°  
 $\gamma = 97.528$  (3)°  
 $V = 664.43$  (15) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.321$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 1094 reflections  
 $\theta = 2.7$ – $27.5$ °  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 130.0$  (2) K  
Plate, colourless  
 $0.50 \times 0.30 \times 0.07$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $R_{int} = 0.032$   
 $\theta_{max} = 27.5$ °  
 $\varphi$  and  $\omega$  scans  
 $h = -8 \rightarrow 4$   
3614 measured reflections  
 $k = -9 \rightarrow 8$   
2787 independent reflections  
 $l = -17 \rightarrow 16$   
1915 reflections with  $I > 2\sigma(I)$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.097$   
 $S = 0.88$   
2787 reflections  
236 parameters  
All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.20$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.19$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

C1—O1	1.4630 (16)	C7—C8	1.496 (2)
C1—C2	1.5111 (18)	C8—C13	1.391 (2)
C1—C5	1.510 (2)	C8—C9	1.3969 (19)
C2—C3	1.518 (2)	C9—C10	1.378 (2)
C3—N1	1.4603 (18)	C10—C11	1.381 (2)
C4—N1	1.4616 (17)	C11—C12	1.3837 (19)
C4—C5	1.525 (2)	C11—N2	1.4761 (18)
C6—N1	1.4540 (19)	C12—C13	1.380 (2)
C7—O2	1.2101 (16)	N2—O4	1.2233 (15)
C7—O1	1.3345 (15)	N2—O3	1.2247 (15)
O1—C1—C2	105.68 (10)	C9—C10—C11	118.84 (14)
O1—C1—C5	111.02 (11)	C10—C11—C12	122.43 (14)
C2—C1—C5	110.75 (13)	C10—C11—N2	118.55 (13)
C1—C2—C3	110.17 (12)	C12—C11—N2	119.02 (12)
N1—C3—C2	111.64 (12)	C13—C12—C11	118.23 (13)
N1—C4—C5	110.73 (11)	C12—C13—C8	120.70 (14)
C1—C5—C4	109.53 (12)	C6—N1—C3	110.08 (12)
O2—C7—O1	124.42 (13)	C6—N1—C4	111.18 (12)
O2—C7—C8	124.05 (13)	C3—N1—C4	109.89 (12)
O1—C7—C8	111.52 (11)	O4—N2—O3	123.51 (13)
C13—C8—C9	119.70 (14)	O4—N2—C11	118.41 (12)
C13—C8—C7	118.99 (12)	O3—N2—C11	118.08 (12)
C9—C8—C7	121.28 (12)	C7—O1—C1	118.26 (10)
C10—C9—C8	120.10 (14)		
O1—C1—C2—C3	-174.20 (12)	N1—C4—C5—C1	-58.72 (17)
C5—C1—C2—C3	-53.88 (17)	C2—C3—N1—C6	177.42 (13)
C1—C2—C3—N1	56.30 (17)	C2—C3—N1—C4	-59.80 (15)
O1—C1—C5—C4	172.16 (11)	C5—C4—N1—C6	-176.98 (13)
C2—C1—C5—C4	55.07 (16)	C5—C4—N1—C3	60.89 (16)

All H atoms were located in a difference map and their positional and isotropic displacement parameters were refined.

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*; software used to prepare material for publication: *SHELXTL*.

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