

Cyclopropyl *m*-nitrophenyl ketone

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Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.040

w*R* factor = 0.105

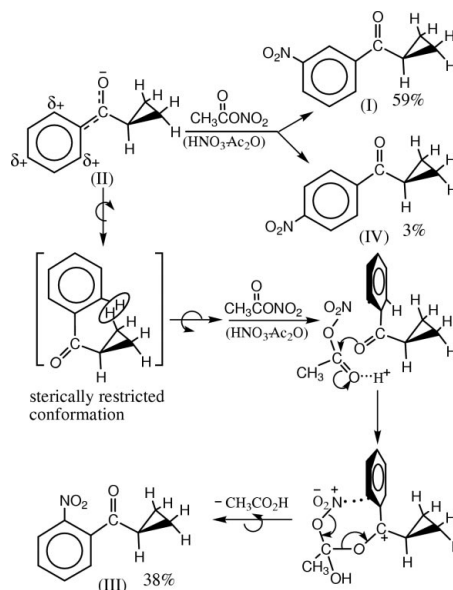
Data-to-parameter ratio = 10.1

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

The title compound, $\text{C}_{10}\text{H}_9\text{NO}_3$, exhibits near coplanarity of the phenyl ring with the $\text{C}=\text{O}$ bond and the nitro group. Through the O atoms of the carbonyl and nitro groups and the H atoms of the phenyl rings, a network of intermolecular hydrogen bonds involves each molecule with four other molecules. The result is a structure composed of discrete two-dimensional hydrogen-bonded molecular layers.

Comment

In virtually every organic chemistry textbook (*e.g.* Wade, 1999; Solomons & Fryhle, 2000), ketones are denoted as '*meta* directors' as opposed to '*ortho-para* directors' in electrophilic aromatic substitution reactions. Surprisingly, a systematic study of the nitration of aromatic ketones in this context has not apparently been reported. We have carried out the nitration of a series of alkyl phenyl ketones (alkyl is *n*-propyl, isopropyl, *tert*-butyl, cyclopropyl, cyclobutyl, and cyclohexyl) with acetyl nitrate (fuming HNO_3 -acetic anhydride; *e.g.* Kolb *et al.*, 1984), as well as with the more commonly used 'mixed acid' (concentrated HNO_3 - H_2SO_4 ; *e.g.* Nimitz, 1991; Corson & Hazen, 1930) and identified the products by NMR, supported by GC-MS. While the extent of *para* nitration was very minor (except for the *tert*-butyl compound), these ketones unexpectedly underwent a high degree of *ortho* nitration, especially with acetyl nitrate, a phenomenon we attribute to complexation of the nitrating agent with the carbonyl group (Donahue, 1999; Kolb & Donahue, 1999; Kolb *et al.*, 2002), as illustrated in the Scheme below.



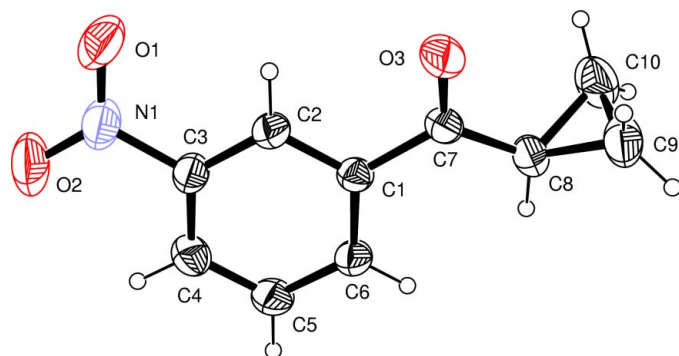


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids at the 30% probability level.

We assessed the steric and electronic interactions of the carbonyl group in our systems *via* a series of *ab initio* calculations (Kolb *et al.*, 2002). Since no literature data are available for the X-ray structures of alkyl nitrophenyl ketones, we are now obtaining the X-ray structural parameters of our nitro products to provide a check on the important parameters, *e.g.* the angle between the carbonyl group and the benzene ring. We now report the X-ray analysis of cyclopropyl *m*-nitrophenyl ketone, (I).

The structure of (I), with the atom numbering, is shown in Fig. 1. The molecule, excluding atoms C9 and C10 of the cyclopropyl group and their H atoms, is nearly planar. If all non-H atoms, except C9 and C10, are included in a least-squares-plane calculation, the atoms with the largest deviations from the plane are C8, O3, and O1, with values of 0.307 (3), -0.283 (2) and 0.192 (3) Å, respectively. When atoms C9 and C10 are included in this calculation, their deviations from the least-squares plane are -0.299 (3) and 1.097 (3) Å, respectively. The carbonyl C=O vector is at an angle of 12.31 (17)° to the benzene-ring plane, and the angle between the benzene and cyclopropyl rings is 75.1 (3)°. The molecules pack into infinite two-dimensional sheets made up of a network of C—H...O intermolecular interactions, as shown in Fig. 2. Within each sheet, each molecule is hydrogen bonded to four surrounding molecules. Three phenyl C atoms (C4, C5, and C6) act as H-donors, while the O atoms of the nitro and carbonyl groups act as acceptors. The hydrogen-bond geometry is given in Table 1. The two-dimensional planes stack normal to [001] with no bonding between the layers, as shown in Fig. 3. An examination of the structure indicates that there are no close intra- or intermolecular contacts between non-H atoms.

Experimental

The title compound, (I), was prepared according to a published procedure for the nitration of ketones with acetyl nitrate, prepared *in situ* from fuming nitric acid–acetic anhydride (*e.g.* Kolb *et al.*, 1984). Cyclopropyl phenyl ketone, (II) (Aldrich; 2.080 g, 14.2 mmol), was thus converted into 2.373 g (87.2%) of a mixture of crude nitration products (a mixture of crystals and a yellow oil), shown by ¹H NMR to be composed of *meta* (I) (59%), *ortho* (III) (38%), and *para* (IV)

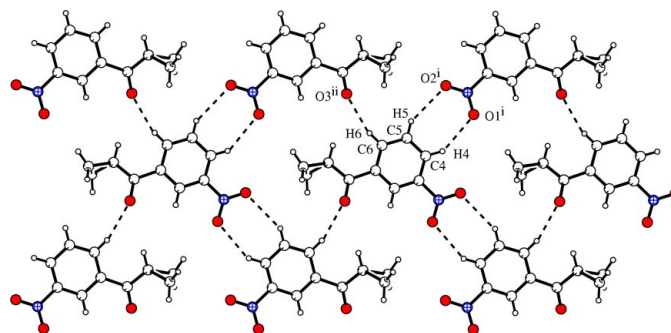


Figure 2
Hydrogen bonding in (I) and the resultant infinite two-dimensional molecular planes. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{7}{4} - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{7}{4} - z$.]

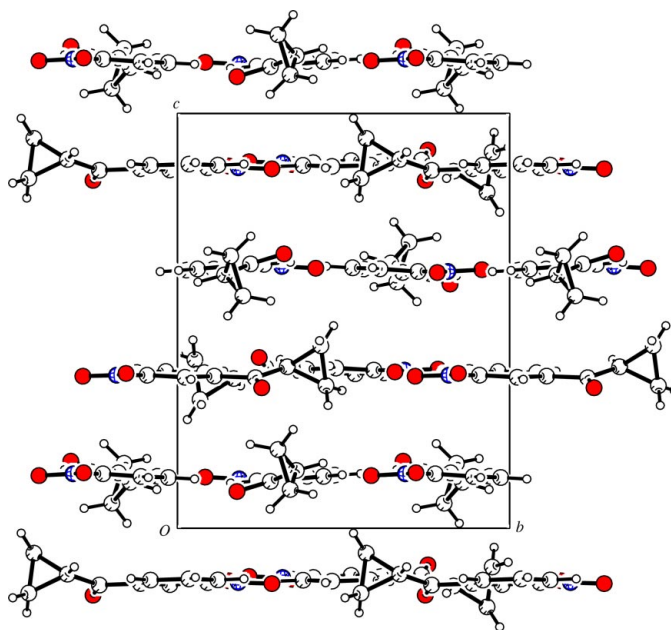


Figure 3
Packing drawing of (I), showing the stacking of the two-dimensional molecular planes.

(3%) nitro isomers. We obtained 30% *ortho* product with the 'mixed acid' (*e.g.* Nimitz, 1991; Corson & Hazen, 1930) nitrating reagent. Trituration with light petroleum ether afforded a mass of white crystals, which, upon recrystallization from absolute EtOH, provided the pure *meta* isomer (I), m.p. 346–347 K [literature m.p. 345.5–346.5 K (Newman & Kaugars, 1966); 344–346 K (Thaisrivongs *et al.*, 1995)]. The latter authors reported the IR and ¹H NMR spectra. We now report the ¹³C NMR spectrum (CDCl₃): 12.58, 17.51, 122.68, 126.99, 130.07, 133.84, 138.99, 148.30, 198.41.

Crystal data

C₁₀H₉NO₃
M_r = 191.18
 Tetragonal, *P*4₂1₂
a = 11.438 (2) Å
c = 14.284 (2) Å
V = 1868.8 (6) Å³
Z = 8
D_x = 1.359 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11.1–12.1°
 μ = 0.10 mm⁻¹
T = 296 K
 Tetragonal bipyramid, colorless
 0.43 × 0.34 × 0.33 mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 2438 measured reflections
 1296 independent reflections
 674 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 27.6^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 18$
 3 standard reflections
 every 100 reflections
 intensity decay: 6.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.105$
 $S = 0.98$
 1296 reflections
 128 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.12 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.021 (2)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C4—H4 \cdots O1 ⁱ	0.93	2.57	3.378 (4)	146
C6—H6 \cdots O3 ⁱⁱ	0.93	2.47	3.369 (3)	163
C5—H5 \cdots O2 ⁱ	0.93	2.65	3.484 (4)	149

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{7}{4} - z$; (ii) $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{7}{4} - z$.

All H atoms were refined as riding. The absolute configuration could not be determined, because of the lack of significant anomalous scattering effects. The data set contained no Friedel pairs.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to

refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON*.

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