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Cyclohexyl phenyl ketone

Paul D. Robinson,[a]* Cal Y. Meyers[b] and Vera M. Kolb[c]

[a]Department of Geology, Southern Illinois University-4324, Carbondale, IL 62901, USA, [b]Meyers Institute for Fundamental Research in Organic and Medicinal Chemistry, Department of Chemistry and Biochemistry, Southern Illinois University-4409, Carbondale, IL 62901, USA, and [c]Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000, USA

Correspondence e-mail: robinson@geo.siu.edu

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.080
Data-to-parameter ratio = 9.5

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

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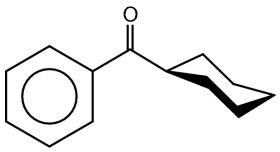
The C═O bond of the title compound, $C_{13}H_{17}O$, is essentially coplanar with the phenyl ring. The cyclohexyl ring is in the chair conformation and its least-squares plane is at an angle of 55.48 (9)° to the phenyl ring. No intermolecular hydrogen bonding is exhibited.

Comment

The designation of the carbonyl in phenyl ketones as a '*meta* director,' as opposed to an '*ortho-para* director,' in electrophilic aromatic substitution reactions, is presented in virtually every organic chemistry textbook (*e.g.* Wade, 1999; Solomons & Fryhle, 2000). Our recent work, however, has shown that, while *para* nitration of such ketones indeed is generally insignificant, *ortho* nitration is substantial (Kolb & Donahue, 1999; Kolb, Donahue, Putnam & Robinson, 2002). For example, we found that cyclopropyl phenyl ketone was 38% *ortho* nitrated, but only 3% *para* nitrated, with acetyl nitrate (*i.e.* fuming HNO_3–acetic anhydride; *e.g.* Kolb *et al.*, 1984), and 30% *ortho* nitrated, but only 6% *para* nitrated, with the more commonly used 'mixed acid' (*i.e.* concentrated HNO_3—H_2SO_4; *e.g.* Nimitz, 1991; Corson & Hazen, 1930). In both cases, the *meta*-nitro product was predominant. We recently reported its X-ray analysis (Kolb, Donahue, Putnam, Meyers & Robinson, 2002). Moreover, while *tert*-butyl phenyl ketone (pivalophenone), in which coplanarity of the phenyl ring with the C═O bond is sterically reduced, was 42% *ortho* nitrated with acetyl nitrate, it was concurrently 24% *para* nitrated, and with 'mixed acid' 25% *ortho* and 24% *para* nitration was attained. Although it was possible that the variable conformation of the cyclohexyl ring in cyclohexyl phenyl ketone, (I), might likewise interfere with the coplanarity of its phenyl ring and C═O bond, this ketone underwent 36% *ortho* nitration with acetyl nitrate and 14% with 'mixed acid', while no *para* nitration was observed in either case. In the light of these results, an X-ray analysis of (I) was undertaken.



(I)

The X-ray structure and atom numbering of (I) are shown in Fig. 1. The cyclohexyl ring is in the chair conformation and its least-squares plane is at an angle of 55.48 (9)° to the phenyl plane. The angle between the carbonyl C═O bond and the phenyl ring is 2.52 (11)°, making them essentially coplanar, a geometry thus easily attainable in solution and required for good electron withdrawal by the C═O from phenyl *via* resonance. It is suggested that the resulting enhanced anionic character of the carbonyl O atom of (I) is responsible for the high degree of *ortho* nitration, while not increasing that at the *para* position (Kolb, Donahue, Putnam, Meyers & Robinson, 2002). The carbonyl function alone in (I) is not enough to make any of the H atoms sufficiently acidic to promote hydrogen bonding, a fact which is reflected by the absence of intermolecular hydrogen bonding in the molecular packing (Fig. 2). In contrast, cyclopropyl *m*-nitrophenyl ketone, whose nitro group enhances the acidity of the H atoms of the phenyl ring, exhibits a molecular packing in which each molecule hydrogen bonds with four other molecules *via* these H atoms and the O atoms of the C═O and NO_2 groups (Kolb, Donahue, Putnam, Meyers & Robinson, 2002).

Experimental

Compound (I), purchased from the Aldrich Chemical Co., was triturated with cold absolute ethanol and recrystallized several times from petroleum ether, then hexane (m.p. 329–330 K; Aldrich catalog, m.p. 328–330 K).

Crystal data

$C_{13}H_{16}O$
$M_r = 188.26$
Orthorhombic, $P2_12_12_1$
$a = 9.3624\ (6)$ Å
$b = 9.8350\ (6)$ Å
$c = 11.5019\ (7)$ Å
$V = 1059.09\ (11)$ Å^3
$Z = 4$
$D_x = 1.181$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4618 reflections
$\theta = 2.7$–$24.5°$
$\mu = 0.07$ mm^{-1}
$T = 120\ (2)$ K
Irregular fragment, colorless
0.20 × 0.18 × 0.14 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
16430 measured reflections
1220 independent reflections

1023 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$
$\theta_{\rm max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.03$
1220 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.0878P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.015 (3)

All H atoms were treated as riding, with C—H distances in the range 0.93–0.98 Å. All equivalent data were averaged, including Friedel pairs. The absolute configuration could not be determined, because of the lack of significant anomalous scattering effects.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SIR*92 (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997) and *PLATON* (Spek, 2000); software used to prepare material for publication: *TEXSAN*, *SHELXL*97 and *PLATON*.

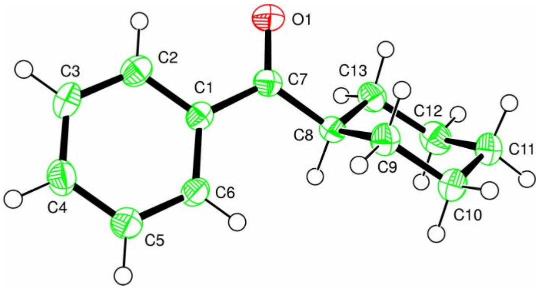


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids at the 50% probabililty level.

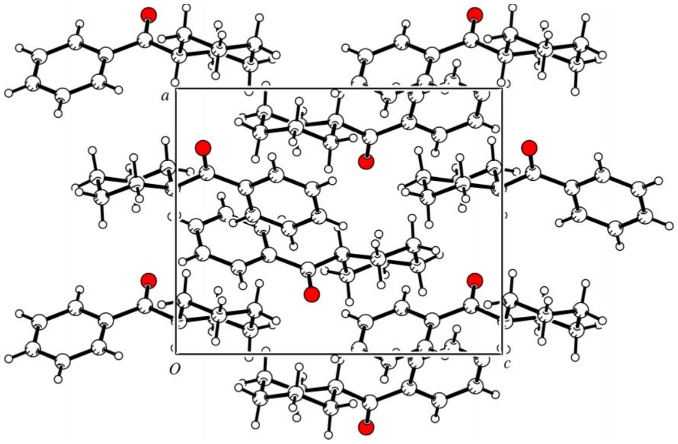


Figure 2
A *b*-axis projection of the molecular packing in (I).

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