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2-Bromo-2-propyl 2-(5-*tert*-butyl-1,3-xylyl) ketone

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.070
wR factor = 0.261
Data-to-parameter ratio = 16.2

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

The 2-bromo-2-propyl (α-bromopropyl) group in crystalline 2-bromo-2-propyl 2-(5-*tert*-butyl-1,3-xylyl) ketone, $C_{16}H_{23}BrO$, exhibits a surprisingly high degree of rotational disorder, although it is freely rotating in solution.

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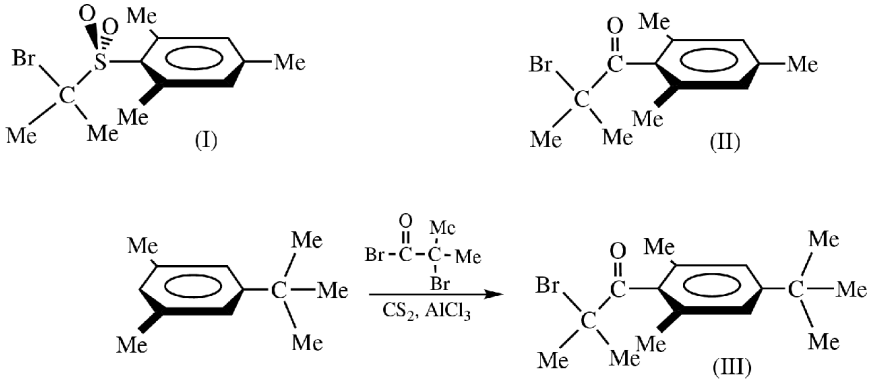
Comment

We recently observed that the α-bromoisopropyl group of 2-bromo-2-propyl mesityl sulfone (I) in solution is freely rotating (^{1}H NMR), but exhibits a significant rotational disorder in the compound's crystalline state (Chan-Yu-King *et al.*, 2001). The possibility that this phenomenon was associated with the sulfonyl group flanked by *ortho*-dimethyl groups prompted us to examine the crystal structure of the corresponding 2-bromo-2-propyl mesityl ketone (II). The latter was reported to melt near room temperature (300 K; Fisher *et al.*, 1930) or remain a viscous oil (Kolb, 1976). In our hands, the crystals formed at ice-bath temperature reverted to an oil when the bath was removed, which precluded an X-ray crystal study. To achieve a higher-melting crystalline analog whose C═O function was still flanked by *ortho*-dimethyl groups, we then prepared 2-bromo-2-propyl 2-(5-*tert*-butyl-1,3-xylyl) ketone (III) (Scheme). Fortunately, this ketone melted at a convenient temperature to allow an X-ray study. The X-ray structure of (III) with atom numbering is shown in Fig. 1.



X-ray diffraction of (III) shows a high degree of rotational disorder of the α-bromoisopropyl group, similar to that exhibited in related (I) (Chan-Yu-King *et al.*, 2001). Restrained site-occupancy refinement of the six disordered sites produced the following site-occupancy values: Br1 = 0.3369 (17), C11 = 0.6631 (17), Br2 = 0.581 (2), C12 = 0.419 (2), Br3 = 0.082 (2), and C13 = 0.918 (2). As we observed for crystalline (I), this disorder in (III) may likewise be associated with the small intra- and intermolecular non-bonding distances. For example, the intramolecular distances

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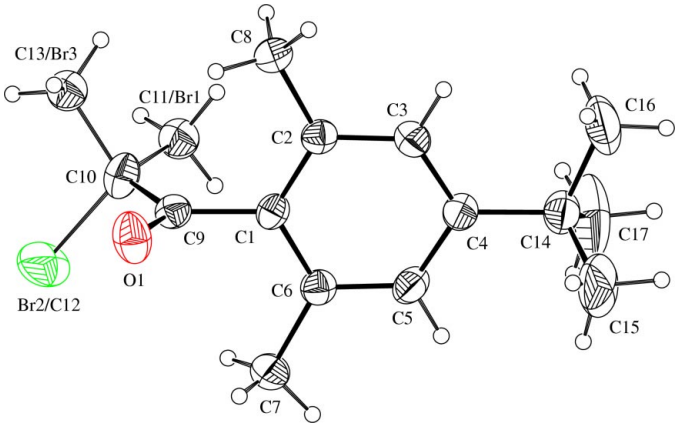

Figure 1
The molecular structure and atom-numbering scheme for (III) with displacement ellipsoids at the 30% probablilty level. Although all three rotamers of the α-bromoisopropyl group occur in the structure, this drawing shows only the most prevalent rotamer.

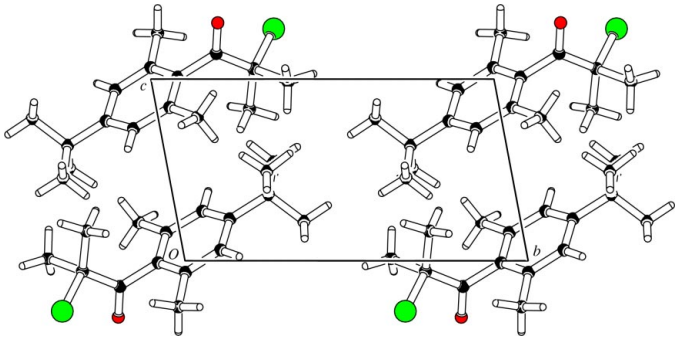

Figure 2
The molecular packing in (III). The disorder is not shown. Color code: green = Br, red = O, black = C.

Br3···O1, Br2···O1 and Br1···C6 are 0.23, 0.25, and 0.02 Å, respectively, less than the sum of their van der Waals radii, while Br3···C8, Br1···C7, and C8···C10 are larger, respectively, by only 0.02, 0.17 and 0.19 Å, and the intermolecular distances Br2···Br2, Br1···C17 and Br3···C15 are 0.09 and 0.07 and 0.04 Å, respectively, less than the sum of their van der Waals radii, while C2···C8 is larger by only 0.19 Å. Table 2 gives the actual non-bonding distances for the interactions listed above. The sharp singlet (6 H) for the isopropyl methyl groups in the ^{1}H NMR ($CDCl_3$) spectrum of (III), like that of (I), indicates a freely rotating α-bromoisopropyl group in solution.

Experimental

2–Bromo-2-propyl 2-(5-*tert*-butyl-1,3-xylyl) ketone (I) was prepared by a Friedel–Crafts reaction of 5-*tert*-butyl-1,3-xylene (Acros) with α-bromoisobutyryl bromide (Aldrich) in the presence of anh. $AlCl_3$, following the general procedure reported by Fisher *et al.* (1930) for the preparation of 2-bromo-2-propyl mesityl ketone. Slow recrystallization from absolute ethanol afforded large transparent crystals, m.p. 366–366.5 K; subsequent slow recrystallization from hexanes provided similar crystals and the same melting point. Diffraction results from single crystals isolated from both solvents were essentially identical. ^{1}H NMR ($CDCl_3$) exhibited a single sharp peak for the isopropyl methyl H atoms, δ1.97, 6 H.

Crystal data

$C_{16}H_{23}BrO$
M_r = 311.25
Triclinic, $P\overline{1}$
a = 11.669 (4) Å
b = 11.7771 (16) Å
c = 6.1750 (12) Å
α = 101.711 (14)°
β = 95.71 (3)°
γ = 75.948 (17)°
V = 804.9 (4) Å^3
Z = 2
D_x = 1.284 Mg m^{-3}
Mo Kα radiation
Cell parameters from 24 reflections
θ = 10.0–10.8°
μ = 2.54 mm^{-1}
T = 296 K
Prism, colorless
0.48 × 0.29 × 0.10 mm
Crystal source: synthesized by the authors

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.427, T_{max} = 0.776
2997 measured reflections
2842 independent reflections
1180 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25.1°
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -7 \rightarrow 7$
3 standard reflections every 100 reflections intensity decay: 11.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.261
S = 1.03
2842 reflections
175 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1280P)^2 + 0.6997P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C10	1.903 (3)	C12—C10	1.543 (3)
Br2—C10	1.897 (3)	C13—C10	1.539 (3)
Br3—C10	1.901 (3)	C9—C10	1.490 (8)
C11—C10	1.541 (3)		
C13—C10—C11	98.7 (7)	C9—C10—Br3	108.5 (5)
C9—C10—C12	110.0 (11)	C11—C10—Br3	99.8 (7)
C13—C10—C12	90.8 (11)	C12—C10—Br3	99.3 (11)
C11—C10—C12	121.6 (12)	C9—C10—Br1	115.2 (4)
C9—C10—Br2	109.6 (3)	C13—C10—Br1	117.4 (5)
C13—C10—Br2	103.0 (4)	C12—C10—Br1	99.8 (10)
C11—C10—Br2	111.5 (5)		

Table 2
Non-bonding distances (Å).

Br3···O1	3.135 (12)	C8···C10	3.593 (8)
Br2···O1	3.121 (5)	Br2···Br2^{i}	3.615 (3)
Br1···C6	3.528 (6)	Br1···C17^{ii}	3.485 (12)
Br3···C8	3.567 (12)	Br3···C15^{iii}	3.512 (16)
Br1···C7	3.718 (8)	C2···C8^{iv}	3.588 (9)

Symmetry codes: (i) $-x, 1-y, 3-z$; (ii) $-x, -y, 1-z$; (iii) $x, 1+y, z$; (iv) $1-x, -y, 2-z$.

Before final refinement the sum of the site occupancy factors for the disordered Br and C sites were restrained to values of 1.0 and 2.0, respectively. Also the total site occupancy of each disordered Br/C site was restrained to 1.0. Final site occupancy factors for the six disordered atoms were determined using isotropic displacement parameters and restraining the three disordered C-atom displacement parameters as well as the three disordered Br displacement parameters to be equal. Subsequent refinement cycles used fixed site

occupancies. The C10—Br and C10—C distances were restrained to chemically reasonable values of 1.91 and 1.54 Å. The Br atoms were refined anisotropically and a restraint was used to cause the displacement parameters of Br3 to equal those of Br2. A satisfactory anisotropic refinement of the three disordered C atoms could not be attained so they were refined isotropically with a restraint to force all of their displacement parameters to equal that of C13. The rotational orientation of the C7 and C8 methyl groups were refined by the circular Fourier method available in *SHELXL*97 (Sheldrick, 1997). All H atoms are riding. Table 1 shows that the disordered group in (III) deviates significantly from tetrahedral geometry although a nearly identical disordered group in (I) was geometrically well behaved. Attempts to force tetrahedral geometry on (III) through extensive restraints met with failure. The elongated displacement parameters of the *tert*-butyl group suggests minor rotational disorder. A linear decay correction was applied.

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: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN*, and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* in *TEXSAN* (Johnson, 1965); software used to prepare material for publication: *TEXSAN, SHELXL*97 and *PLATON* (Spek, 2000).

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