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Brendan Twamley *et al.*

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A terphenyl halide series: 2,6-Trip₂-H₃C₆X (Trip = 2,4,6-triisopropylphenyl; X = Cl, Br, I)

Brendan Twamley,^{a*} Ned J. Hardman^b and Philip P. Power^b

^aUniversity Research Office, 109 Morrill Hall, University of Idaho, Moscow, ID 83844-3010, USA, and ^bDepartment of Chemistry, University of California, Davis, CA 95616, USA

Correspondence e-mail: btwamley@uidaho.edu

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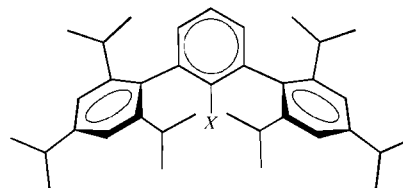
The sterically encumbered terphenyl halides 2'-chloro-2,2'',4,4'',6,6''-hexaisopropyl-1,1':3',1''-terphenyl, C₃₆H₄₉Cl, (I), 2'-bromo-2,2'',4,4'',6,6''-hexaisopropyl-1,1':3',1''-terphenyl, C₃₆H₄₉Br, (II), and 2'-iodo-2,2'',4,4'',6,6''-hexaisopropyl-1,1':3',1''-terphenyl, C₃₆H₄₉I, (III), crystallize in space group *Pnma*. They are isomorphous and isostructural with a plane of symmetry through the centre of the molecule. The C–halide bond distances are 1.745 (3), 1.910 (4) and 2.102 (6) Å for (I)–(III), respectively.

Comment

Terphenyl halides are useful starting materials for the synthesis of a wide variety of compounds with unusual coordination numbers and bonding (Twamley *et al.*, 1999). The synthesis of these materials is a relatively straightforward process (Harada *et al.*, 1985; Saednya & Hart, 1996; Frank Du *et al.*, 1986; Schiemenz & Power, 1996; Simons *et al.*, 1998) involving the addition of two equivalents of aryl Grignard reagent to 1-lithio-2,6-dichlorobenzene at 195 K and subsequent quenching with the appropriate dihalide. Using this technique, good yields (>80%) of 2,6-Trip₂-C₆H₃X (Trip = 2,4,6-triisopropylphenyl; X = Cl, Br, I) can be obtained. All are high-melting solids (m.p. > 453 K) and can be crystallized easily from hydrocarbon solvents such as hexanes, giving colourless needles.

Compounds (I)–(III) form isomorphous crystals and are isostructural. They crystallize in the orthorhombic space group *Pnma*, with very similar cell constants. Each molecule has a plane of symmetry through the halide atom and the central ring with C1, C4 and the halide atom occupying special positions. The aromatic rings show normal C–C bond lengths and C–C–C angles. The pendant aromatic C–C bond to the central ring [1.491 (5)–1.500 (3) Å] shows a slight elongation commonly observed in terphenyl groups as a result of steric

effects. The C–X distances range from 1.745 (3) Å in the chloride, (I), to 1.910 (4) Å in the bromide, (II), and 2.102 (6) Å in the iodide, (III). These bond lengths are almost identical to those found in the few structurally characterized



(I) X = Cl
(II) X = Br
(III) X = I

terphenyl halides. Previously reported C–Br bond lengths are 1.892 (5) (Haaland *et al.*, 1994), 1.887 (9) (Allman & Hellner, 1968) and 1.90 (2) Å. The latter refers to the isostructural perfluorinated terphenyl bromide 2,6-(C₆F₅)₂-C₆F₃Br (Bowen Jones & Brown, 1980). The less crowded 2,6-Mes₂C₆H₃I (Mes = 2,4,6-trimethylphenyl) has a reported C–I distance of 2.122 (4) Å (Niemeyer, 1998), and the polychlorinated terphenyl iodide ArICl₂ [Ar = 2,6-bis(3,5-dichloro-2,4,6-trimethylphenyl)benzene] has a C–I distance of 2.127 (13) Å (Protasiewicz, 1995). Although no *m*-terphenyl chlorides have been structurally characterized, the C–Cl distance falls within normal aromatic chloride distances (1.673–1.785 Å).

Experimental

Compounds (I)–(III) were synthesized according to the published method for the iodine derivative of Schiemenz & Power (1998) with quenching by the appropriate halide. This route may be illustrated by the synthesis of the bromide derivative, (II). Triisopropylphenylbromide (59.79 g, 0.211 mol) was reacted with Mg (5.20 g, 0.220 mol) in tetrahydrofuran (THF) to form the Grignard reagent. A solution of *n*-BuLi in hexanes (56.1 ml of a 1.6 M) was added to 1,3-dichlorobenzene (13.20 g, 0.090 mol) in THF at 195 K. This solution was stirred for 30 min and the above Grignard reagent added dropwise *via* cannula. The reaction mixture was gradually warmed to room temperature overnight. Br₂ (6.62 ml, 0.130 mol) was added *via* syringe at 273 K. The mixture was stirred (2 h) and then washed with 200 ml of a saturated Na₂CO₃ solution. The organic phase was separated and the aqueous phase extracted with 150 ml of diethyl ether. The combined organic phase was dried over MgSO₄, filtered and the solvent removed. The yellow solid was distilled at 0.1 mm Hg and 383 K to remove side products (TripBr). The solid was refluxed in ethanol for 3 h. The product was filtered and washed with 50 ml of cold acetone and recrystallized from hexanes. [Yield 36.45 g (72.3%); m.p. 484–486 K.] (I): ¹H NMR (C₆D₆, 300 MHz) δ 1.20 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.24 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.35 [*d*, 12H, *p*-CH(CH₃)₂, ³J_{HH} = 6.6 Hz], 2.85 (*sept*, 3H, *o,p*-CH, ³J_{HH} = 6.9 Hz), 6.97 (*t*, 1H, *p*-C₆H₃, ³J_{HH} = 6.6 Hz), 7.07, (*d*, 2H, *m*-C₆H₃, ³J_{HH} = 7.35 Hz), 7.23 (*s*, 4H, *m*-Trip). ¹³C [¹H] NMR (C₆D₆, 75 MHz) δ 24.3, 24.5, 24.9, 31.6, 34.9, 121.1 (*m*-Trip), 126.4 (*p*-C₆H₃), 130.5 (*m*-C₆H₃), 135.1 (*o*-C₆H₃), 135.7 (*ipso*-C₆H₃), 140.8 (*i*-Trip), 146.6 (*o*-Trip), 148.9 (*p*-Trip). (II): ¹H NMR (CDCl₃, 300 MHz) δ 1.12 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.18 [*d*, 12H, *o*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 1.33 [*d*, 12H, *p*-CH(CH₃)₂, ³J_{HH} = 6.9 Hz], 2.58 (*sept*, 2H, *o*-CH, ³J_{HH} = 6.9 Hz), 2.97 (*sept*, 1H, *p*-CH, ³J_{HH} = 6.9 Hz), 7.08 (*s*, 4H,

m-Trip), 7.19 (*d*, 2H, *m*-C₆H₃, ³J_{HH} = 7.5 Hz), 7.38 (*t*, 1H, *p*-C₆H₃, ³J_{HH} = 6.9 Hz). ¹³C {¹H} NMR (CDCl₃, 75 MHz) δ 23.6, 24.1, 24.7, 30.9, 34.2, 120.6 (*m*-Trip), 126.4 (*p*-C₆H₃), 128.3 (*ipso*-C₆H₃), 129.6 (*m*-C₆H₃), 136.4 (*o*-C₆H₃), 142.2 (*i*-Trip), 145.8 (*o*-Trip), 148.1 (*p*-Trip).

Compound (I)

Crystal data

C₃₆H₄₉Cl
M_r = 517.20
Orthorhombic, *Pnma*
a = 8.2186 (5) Å
b = 25.4368 (16) Å
c = 15.6604 (10) Å
V = 3273.9 (4) Å³
Z = 4
D_x = 1.049 Mg m⁻³

Mo Kα radiation
Cell parameters from 4302 reflections
θ = 2.60–31.42°
μ = 0.137 mm⁻¹
T = 93 (2) K
Needle, colourless
0.32 × 0.15 × 0.04 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick 1999)
T_{min} = 0.957, T_{max} = 0.995
47 039 measured reflections
3852 independent reflections
2275 reflections with I > 2σ(I)

R_{int} = 0.134
θ_{max} = 27.49°
h = 0 → 10
k = 0 → 33
l = 0 → 20
50 frames remeasured standard reflections beginning and end reflections intensity decay: <0.01%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.047
wR(F²) = 0.128
S = 0.912
3852 reflections
172 parameters

H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0660P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.55 e Å⁻³
Δρ_{min} = -0.42 e Å⁻³

Compound (II)

Crystal data

C₃₆H₄₉Br
M_r = 561.66
Orthorhombic, *Pnma*
a = 8.2823 (14) Å
b = 25.831 (4) Å
c = 15.856 (3) Å
V = 3392.2 (10) Å³
Z = 4
D_x = 1.100 Mg m⁻³

Mo Kα radiation
Cell parameters from 934 reflections
θ = 2.88–24.64°
μ = 1.232 mm⁻¹
T = 293 (2) K
Needle, colourless
0.78 × 0.30 × 0.20 mm

Data collection

Siemens SMART 1000 diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1999)
T_{min} = 0.447, T_{max} = 0.791
23 472 measured reflections
3054 independent reflections
2418 reflections with I > 2σ(I)

R_{int} = 0.033
θ_{max} = 25.00°
h = -9 → 9
k = -25 → 30
l = -18 → 18
50 frames remeasured standard reflections beginning and end reflections intensity decay: <0.01%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.044
wR(F²) = 0.114
S = 1.023
3054 reflections
178 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.0522P)² + 2.2426P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.26 e Å⁻³
Δρ_{min} = -0.40 e Å⁻³

Compound (III)

Crystal data

C₃₆H₄₉I
M_r = 608.65
Orthorhombic, *Pnma*
a = 8.1100 (13) Å
b = 25.549 (6) Å
c = 15.978 (6) Å
V = 3310.7 (16) Å³
Z = 4
D_x = 1.221 Mg m⁻³

Mo Kα radiation
Cell parameters from 50 reflections
θ = 4.73–14.73°
μ = 0.988 mm⁻¹
T = 130 (2) K
Parallelepiped, colourless
0.76 × 0.36 × 0.30 mm

Data collection

Siemens R3 diffractometer
ω scans
Absorption correction: empirical (*XABS2*; Parkin *et al.*, 1995)
T_{min} = 0.521, T_{max} = 0.756
8539 measured reflections
3891 independent reflections
3185 reflections with I > 2σ(I)

R_{int} = 0.0452
θ_{max} = 27.5°
h = 0 → 10
k = 0 → 33
l = 0 → 20
2 standard reflections every 198 reflections intensity decay: 1%

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.059
wR(F²) = 0.186
S = 1.044
3891 reflections
172 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.1110P)² + 10.4168P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.97 e Å⁻³
Δρ_{min} = -0.94 e Å⁻³

For compounds (I) and (II), data collection and cell refinement: *SMART* (Bruker, 1998); data reduction: *SHELXTL* (Sheldrick, 1998). For compound (III), data collection and cell refinement: *P3* (Siemens, 1991); data reduction: *XDISK* (Siemens, 1991). For all compounds, program(s) used to solve and refine structure, and prepare material for publication: *SHELXTL*.

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