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Key indicators

Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
Disorder in main residue
 R factor = 0.053
 wR factor = 0.161
Data-to-parameter ratio = 14.9

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

2,2',5,5'-Tetrakis(trifluoromethyl)biphenyl

The title compound, $\text{C}_{16}\text{H}_6\text{F}_{12}$, has been obtained as a by-product of the reaction between 2,5-bis(trifluoromethyl)phenyllithium and zinc(II) chloride. The asymmetric unit contains two independent molecules with a similar almost perpendicular conformation of the biphenyl fragments.

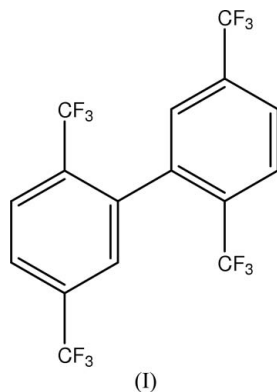
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Comment

As a part of our ongoing studies into the reactions between lithiated trifluoromethyl-substituted aromatic compounds and main group halides (Batsanov *et al.*, 2001; Batsanov *et al.*, 2002; Batsanov *et al.*, 2003; Cornet *et al.*, 2003; Cornet *et al.*, 2005), we have reacted lithiated 1,4-bis(trifluoromethyl)benzene (ArLi) with zinc(II) chloride in diethyl ether solution. A few crystals were isolated from the reaction mixture and X-ray analysis proved them to be a by-product of the reaction, 2,5,2',5'-tetrakis(trifluoromethyl)biphenyl (I), probably formed *via* a radical reaction.



The structures of the two molecules in the asymmetric unit of (I) are shown in Fig. 1, while selected bond distances and

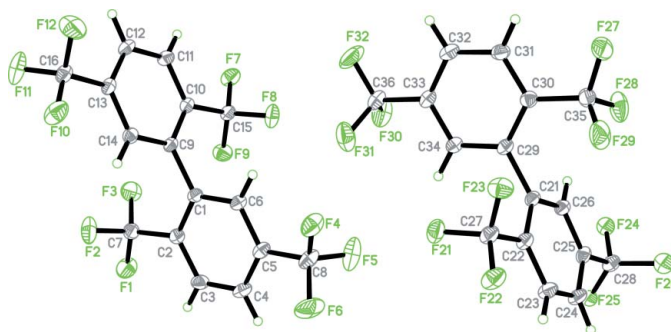


Figure 1

The two independent molecules of (I), with the minor component of the disordered F atoms omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

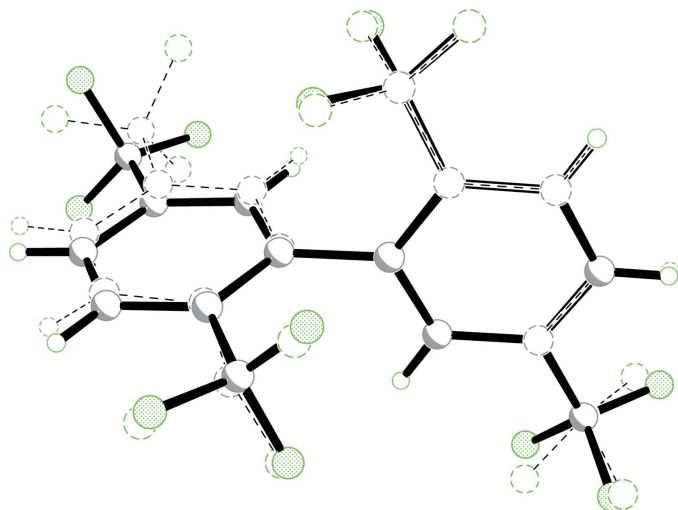


Figure 2
Least-squares fit of the two independent molecules. The minor components of the disordered F atoms are omitted for clarity.

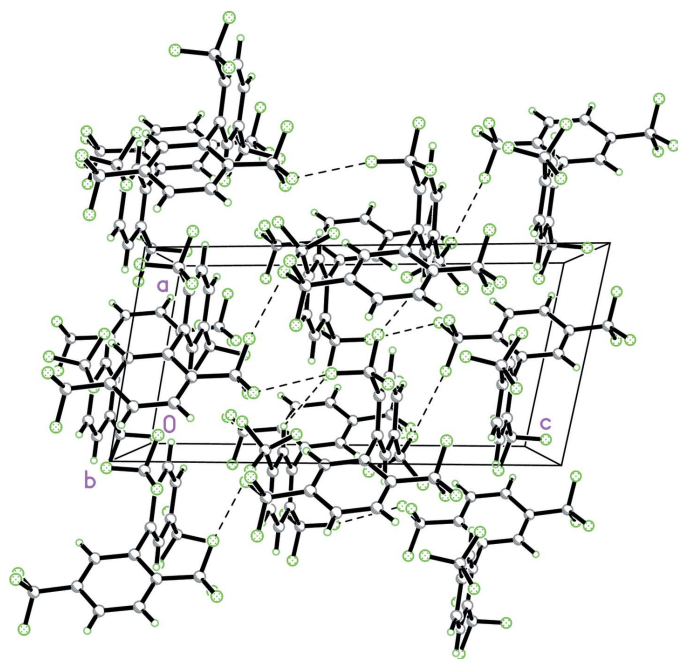


Figure 3
Packing of the molecules of (I) in the crystal structure, viewed along the *b* axis. Dashed lines correspond to short H...F and F...F intermolecular contacts.

angles are listed in Table 1. The asymmetric unit contains two crystallographically independent molecules, both of them adopting a similar perpendicular conformation of the biphenyl fragment and differing slightly in the orientation of CF₃ groups (Fig. 2). The perpendicular conformation, with an absolute value of the torsion angle around the central C–C bond close to 90°, is typical for 2,2′-substituted biphenyls [see, for example, Leser & Rabinovich (1978), and references therein] and Nieger *et al.* (1998)]. The lengths of the central C–C bonds in (I) [1.498 (2) and 1.499 (2) Å] are well within the range of the central bond lengths in substituted biphenyls

(Bahl *et al.*, 1996; Shimada *et al.*, 2003). The geometrical parameters of the CF₃ groups are also entirely comparable with those described in the literature for other CF₃-substituted benzene derivatives (Lynch *et al.*, 1992; Couldwell & Penfold, 1976; Baenziger *et al.*, 1995).

The packing of the molecules of (I) in the crystal structure is determined by a number of short C–H...F and F...F interactions, which link molecules in a three-dimensional network (Fig. 3). The role of such interactions in crystal engineering has been discussed recently by Reichenbacher *et al.* (2005). The shortest contacts of each type are H34...F27(1 + *x*, *y*, *z*) 2.52 (2) and F24...F32(−*x*, 1 − *y*, 1 − *z*) 2.788 (2) Å.

Experimental

A solution of ZnCl₂ (3.07 g, 22.5 mmol) in diethyl ether was added *via* a cannula, with stirring, to a solution of ArLi (22.5 mmol) in diethyl ether at 195 K. ArLi was prepared *in situ* from ArH (5.3 g, 24.8 mmol) and *n*-BuLi (22.5 mmol from a 1.6 M solution in hexane) in diethyl ether at 195 K. The mixture was allowed to warm to room temperature, and most of the solvent was removed *in vacuo*. A liquid layer above an oily layer was produced. The liquid layer was separated, and left in a tube at room temperature to see whether crystals would form. Crystals of (I) were observed on the following day and were isolated. The title compound, (I), was also characterized by ¹⁹F NMR spectroscopy, giving the expected two singlets in a 1:1 ratio at −59.2 and −63.9 p.p.m., assigned to the CF₃ groups *ortho* and *meta* to the ring junction, respectively, and by elemental analysis (Found, C, 43.7, H, 1.38%; C₁₆H₆F₁₂ requires C, 45.1, H, 1.42%). All manipulations of air- and/or moisture-sensitive compounds were performed either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk and cannula techniques, or in a nitrogen-filled glovebox. ¹⁹F NMR spectra were recorded on a Varian Unity 300 Fourier-transform spectrometer at 282.2 MHz; chemical shifts were measured relative to external CFCl₃.

Crystal data

C₁₆H₆F₁₂
M_r = 426.21
 Triclinic, *P* $\bar{1}$
a = 7.4296 (2) Å
b = 14.3048 (4) Å
c = 15.1315 (4) Å
 α = 79.73 (1)°
 β = 77.21 (1)°
 γ = 76.39 (1)°
V = 1510.6 (1) Å³

Z = 4
D_x = 1.874 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 6646 reflections
 θ = 2.2–31.0°
 μ = 0.21 mm^{−1}
T = 120 (2) K
 Block, colourless
 0.36 × 0.32 × 0.24 mm

Data collection

Bruker SMART 6000 CCD diffractometer
 ω scans
 Absorption correction: none
 14596 measured reflections
 8297 independent reflections

6387 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.033
 θ_{\max} = 29.5°
h = −10 → 10
k = −19 → 19
l = −20 → 20

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.161
S = 1.05
 8297 reflections
 558 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 0.6P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.86 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.49 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C1–C9	1.498 (2)	C21–C29	1.499 (2)
C6–C1–C2	118.26 (13)	C26–C21–C22	118.54 (13)
C6–C1–C9	117.08 (13)	C26–C21–C29	117.99 (13)
C2–C1–C9	124.53 (13)	C22–C21–C29	123.17 (13)
C14–C9–C10	118.70 (13)	C34–C29–C30	118.16 (14)
C14–C9–C1	117.35 (13)	C34–C29–C21	116.95 (13)
C10–C9–C1	123.69 (13)	C30–C29–C21	124.79 (13)
C2–C1–C9–C14	85.42 (18)	C22–C21–C29–C34	–79.54 (19)

One of the CF₃ groups (F24–F26) is severely disordered and has been modelled by several sets of F atoms with partial occupancy (site-occupancy factors 0.4:0.3:0.3). These atoms were refined isotropically. H atom parameters were refined freely [C–H = 0.91 (3)–0.97 (2) Å].

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1998); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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