Supplemental Material

CSD searches were performed using the November 2005 of the Cambridge Structural Database. Hits were restricted to only organic entries with 3-D coordinates, with R<7.5%, no disorder, no ions, no errors, not polymeric and no powder structures. Several structures contained multiple examples with all present used.

CSD codes for biphenyls

No ortho-substitution:

BPPFBP, MALFBO, ASAKIO, BUHSIG, FIDKIN, WUNLEW, XABPOG

CSD codes ortho-F-biphenyls

Mono-ortho-substitution:

DAMWOE, FLUBIP, NAFTAP, NEBHOR, ETOMAB

1,2-di-ortho-substituition:

ACORAL, SIKREJ10, TFBIPH, PFBIPH01

1,3-di-ortho-substitution:

BAWPUK, PUGPIQ

1,2,3-tri-substitution:

none

1,2,3,4-tetra-ortho-substitution:

ATOZOY, BPPFBP, CEKYUM, DECFDP01, DILDIL, HAKYOI, HUBVUV, OKICEQ, PEYVFB10, WOVYIP

CSD codes for ortho-Cl-biphenyls:

Mono-ortho-substitution:

ABESIK, FAMWIZ, FIMNOE, GUQYOG, POGNUU, ITNXON

1,2-di-ortho-substitution:

DAWSAV

1,3-di-ortho-substitution:

DUXRAP, GEKWUO, DCLBIP, EYIVIR

1,2,3-tri-ortho-substitution:

GEKWOI

1,2,3,4-tetra-substitution:

DCLBPH, DAWRUO

CSD codes for ortho-Me-biphenyls

Mono-ortho-substitution:

MIQWUE, PARKUO, YASGAB

1,2-di-ortho-substitution:

NEJQEY02, VINVUJ, VINWEU

1,3-di-ortho-substitution:

EYFVOX

1,2,3-tri-ortho-substitution:

none

1,2,3,4-tetra-ortho-substitution:

NIYROC, VINVUJ, ZZZMBSO1

CSD codes for ortho-Br,I-biphenyls

Mono-ortho-Br-substitution:

SUNSOJ

Mono-ortho-I-substitution:

ARUTUC, HITDUJ

CSD codes for aromatic vicinal Cl, F search:

ETIJEW, EVINIG, FARRUM, FAXZAG, FOMCUG, FULQOS, IQONUX, IQULAH, IQULEL, KUMTER, MEYHED, MOPXUK, REMYOX, UGIGIA, VUHVUP, XERPOZ, XUWTOY

Disorder refinement details:

3-2’F

Late refinement difference maps suggested a minor disorder of 180° rotation about the >C1 - C1'< bond of the C1' - C6' phenyl ring. The relative occupancy refined to 0.9763(15):0.0237(15) with the sum constrained to 1.0. Also, Uiso(F2) = 1.2*Uiso,eq(C2') and the C2'' - F2 bond was constrained to be the same as C2' - F1 bond. Only the F and H atoms were disordered. Partial C atoms were constrained to have the same coordinates and displacement parameters.

3-3’F

The molecule was disordered (180° rotation about the >C1-C1'< bond of the C1' - C6' ring. Two molecules (occupancies refined to 0.874(3):0.126(3)) were used to model the disorder and were restrained to have the same conformation. The Cl atoms were constrained to have the same coordinates and displacement parameters. The minor orientation is indicated by * and '' suffixes on the atom labels. Partial atoms in close proximity (<0.5 Å) were constrained to have the same displacement parameters. The phenyl rings of the minor component were restrained to be flat.

3-4’-F

Both molecules in the structure are disordered in the same amount. The second orientation for each molecule (labels with * and '' suffix) can be approximated by inversion through the molecular center of the main component. The conformations of the second orientations were restrained to be the same as the first orientations. The relative occupancies refined to 0.841(3):0.159(3) and were constrained to sum to 1.0. Displacement parameters for atoms in close proximity were (e.g. C1 and C1*) were constrained to be the same. Cl1 and F1* were constrained the have the same coordinates as were Cl2 and F2*, F1 and Cl1* and F2 and Cl2*. The phenyl rings of the minor components were restrained to be flat.