2,2′:6′,2″-TERPYRIDINE AS MONODENTATE LIGAND: HALOGEN BONDING DRIVEN FORMATION OF DISCRETE 2 : 1 AGGREGATES WITH 1,2,4,5-TETRAFLUORO-3,6-DIIODOBENZENE+

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2,2′:6′,2″-Terpyridine (**1**) is a well-known electron donor module in metal coordination chemistry and typically works as a tridentate ligand. Here it is shown that **1** can also work as electron donor towards iodoperfluorocarbons both in solution and in the solid phase. Halogen-bonded supramolecular systems are thus obtained. Specifically, terpyridine **1** self-assembles with 1,2,4,5-tetrafluoro-3,6-diiodobenzene (**2**) and affords the trimeric adduct **3**, which is stable and crystalline in the air at room temperature. Single crystal X-ray analysis shows how in adduct **3** both iodine atoms of one molecule of **2** are halogen-bonded to the nitrogen atoms of external pyridine rings of two molecules of **1** that act as monodentate electron donors.

Keywords: Halogen bonding; Donor-acceptor interactions; Supramolecular chemistry; Perfluorocarbon compounds; Co-crystals; Pyridines; Crystal structure; X-Ray diffraction.

Hydrogen bonding[2] and metal coordination[3] are the non-covalent interactions most frequently used to drive supramolecular self-assembly[4], *i.e.* the spontaneous association of molecular modules, usually referred to as supramolecular synthons[5] or tectons[6], into ordered aggregates. 2,2′:6′,2″-Terpyridines (terpys) are well-established tectons for the construction of

+ Perfluorocarbon–Hydrocarbon Self-Assembly: Part 18. For Part 17, see ref.[1]

organometallic supramolecular architectures[7], and they typically act as tridentate meridionally coordinating ligands of transition metals. In few cases, usually when some of the coordination sites at the metal are occupied by particularly strong ligands, terpys act as bidentate electron donors[8], and, to the best of our knowledge, only one example has been described where they act as monodentate ligand[9].

In this paper we describe the formation of a supramolecular architecture having the trimer **3** as the key structural unit. In these trimers two molecules of 2,2′:6′,2″-terpyridine (**1**) and one molecule of 1,2,4,5-tetrafluoro-3,6-diiodobenzene (**2**) are associated. Single-crystal X-ray analysis of **3** shows some peculiarities of the self-assembly process. First, terpy **1** works as a monodentate, rather than tri- or bidentate ligand; second, the non-covalent interaction driving the single module association is not the metal coordination but the N···I halogen bonding[10], the coordinated atom being an iodine atom rather than a metal ion.

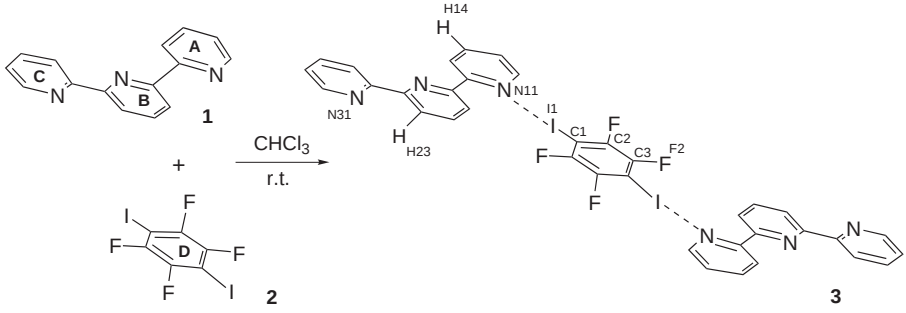
RESULTS AND DISCUSSION

The halogen bonding is the attractive interaction originated from an electron donation from a lone pair possessing atom, either neutral or anionic, to a halogen atom. Nitrogen, oxygen, and sulfur atoms or halide anions[11] have been extensively used as electron donor modules (Lewis bases) and halogen molecules (mainly I_2 and Br_2, but also Cl_2 and interhalogens[12] or pseudohalogens[12j,13]) have been the most commonly employed electron acceptor modules (Lewis acids). Polyhalogenated carbon derivatives have also been frequently involved in the halogen-bonding-driven formation of supramolecular architectures. Triiodo- and tribromomethane as well as analogous tetrahalomethanes have been employed since the early sixties while, more recently, particular attention has been paid to diiodobenzene[14] and iodoacetylene[11b,15] derivatives. The excellent donor-acceptor properties of fluorinated monomers have been put to use also in fluorinated copolymers[16].

Considering that fluorine atoms and perfluorinated residues are strongly electronegative, we reasoned that the electron-acceptor ability of halogen atoms in perfluorocarbon (PFC) halides is definitely higher than in corresponding hydrocarbon (HC) halides. Indeed, the halogen bonding between PFC iodides or bromides and heteroatom substituted HC can be successfully employed as a general protocol[10a,17] to overcome, both in the solid and in the liquid, the low affinity[18] existing between PFCs and HCs and to drive the formation of PFC–HC non-covalent adducts. When telechelic[19] PFC

diiodides and dinitrogen or dioxygen HCs are used as electron acceptor and donor modules, respectively, the halogen bonding reiterates at either ends of the PFC and HC modules and one-dimensional (1D) infinite chains are formed where the acid and basic modules alternate.

Slow evaporation of an equimolar solution of terpyridine **1** and tetrafluorodiiodobenzene **2** in chloroform affords a crystalline white solid **3** (Scheme 1). $^{19}F/^{1}H$ NMR in the presence of $(CF_3CH_2)_2O$ as internal standard showed that the **1** to **2** ratio in the co-crystal **3** is 2 : 1. The same ratio was obtained starting from different **1** to **2** stoichiometric ratios in solution (ranging from 2 : 1 to 1 : 3).



SCHEME 1

Quantum-mechanical calculations[20] predict that the N···I halogen bonding is a quite strong non-covalent interaction (25–30 kJ mol^{-1}). Consistently with these calculations, halogen bonded co-crystals obtained from PFC diiodides and dinitrogen-HCs typically exhibit melting points higher than the single starting materials[10,17]. Co-crystals can thus be easily distinguished from solid starting materials by measuring the melting point of the air-dried crystalline product. The modules **1** and **2** melt at 90 and 109 °C, respectively, while the isolated solid **3** melts at 119 °C. The formation of well-defined molecular aggregates rather than disordered mixtures is thus revealed.

^{1}H and ^{19}F NMR spectra of highly dilute chloroform solutions of **3** are identical to those of single pure HC and PFC modules **1** and **2**, respectively. Unchanged starting adduct **3** is obtained on evaporation of these dilute solutions proving the non-covalent and reversible nature of the interaction driving the self-assembly of modules **1** and **2** into solid co-crystal **3**. The ^{19}F signal of concentrated solutions of **3** is shifted to higher fields compared to pure **2**. By increasing the concentration of co-crystal **3** or by adding a molar excess of electron donor module **1**, larger high-field shifts were observed

[$\Delta\delta_F$ = (δ_F of pure **2**) – (δ_F of **2** in the presence of **1**), here $\Delta\delta_F < 0.1$]. In solution, the recognition between the PFC and HC modules is clearly driven by an N···I intermolecular interaction as high-field shifts in ^{19}F NMR spectra of PFC iodides in the presence of electron donor species has been unequivocally associated with halogen bonding formation[21]. No signal broadening has ever been observed revealing that the association equilibrium between **1** and **2** in solution is rapid at room temperature on the NMR time scale.

IR spectrum (KBr pellets) of adduct **3** roughly corresponds to the sum of the spectra of starting modules **1** and **2**. Some minor frequency shifts and intensity changes are present, consistent with the involvement of only some of the acid and basic modules atoms in interactions weaker than covalent and ionic bonds. These changes are typical of halogen-bonded PFC–HC supramolecular architectures formed by pyridine derivatives and perfluoroaryl and perfluoroalkyl iodides[22]. For instance, a blue-shift and intensity decrease are observed for some of the ν_{C-H} stretching modes of pure HC modules **1** (3 100–3 000 cm^{-1} region). These changes are consistent with an n → σ* electron donation from nitrogen to iodine atoms[23], and may be

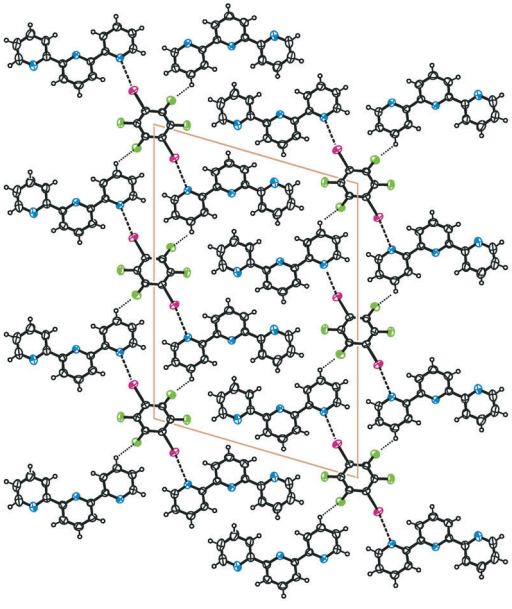


FIG. 1
Crystal packing of **3** viewed down the *b*-axis. Strong halogen bondings are dashed, weak hydrogen bondings are dotted. Colours are as follows: violet, I; blue, N; green, F; black, C and H

correlated with a higher positive charge on some hydrogen atoms in adduct **3**, which are more acidic than in pure precursor **1**.

The molecular parameters and the lattice organisation of the halogen-bonded supramolecular architecture were established through single-crystal X-ray analyses (Fig. 1). The key structural unit in the packing is the terpy···I–C_6F_4–I···terpy trimer **3**, where the two iodine atoms of one tetrafluorodiiodobenzene molecule **2** are halogen-bonded to the nitrogen atoms of external pyridine rings of two terpy molecules **1**. The N···I distance is 299.8(2) pm, significantly shorter than the sum of van der Waals radii[24] (353 pm), but longer than the average covalent N–I bond[25] (207 pm). The N···I–C angle is 170.57(5)°, a value typical of an N···I halogen bonding[26] and consistent with the $n \rightarrow \sigma^*$ character of the interaction[23] (which requires that the N···I non-covalent interaction is colinear to the C–I bond). The halogen-bonded benzene and pyridine rings are tilted, exhibiting a dihedral angle of 53.3(1)° between the least square planes of the rings A and D (Fig. 2).

Several co-crystals, where the halogen bonding has self-assembled PFC diiodides and dinitrogen-HCs into 1D infinite networks, have been described[10a,17,26]. A single crystalline structure of a trimeric adduct formed through the halogen-bonding-driven self-assembly of a monoacceptor PFC and a didonor HC has been reported[27]. The X-ray structure described in this paper is the first case where a trimer is formed starting from a diacceptor PFC and a monodonor HC. Clearly, the N···I non-covalent interaction has a general ability to drive the co-crystallisation of PFC and HC derivatives not only when polymeric but also discrete adducts are formed.

In the solid state and in solution[28], the three pyridine rings of 2,2′:6′,2″-terpyridine[29] (**1**) and of various derivatives[30] are close to a co-planar arrangement and adopt the most stable 2,2′-*s*-*trans*,6′,2″-*s*-*trans*

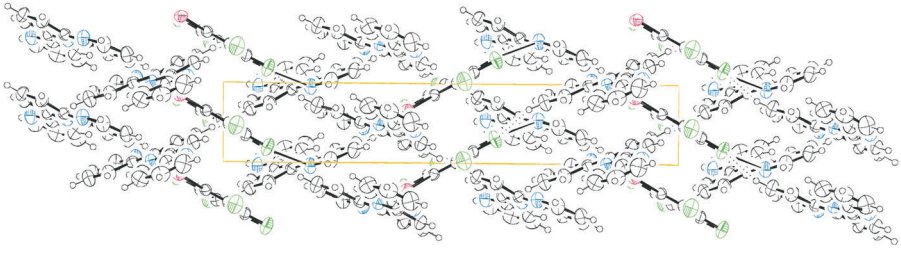
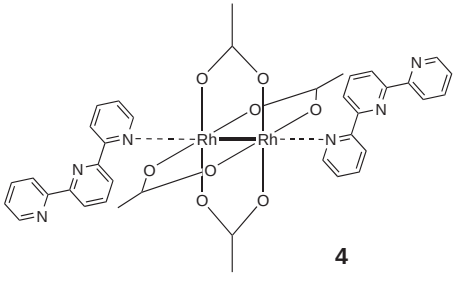


Fig. 2
Crystal packing of **3** viewed down the *a*-axis. Colours are as follows: violet, I; blue, N; green, F; black, C

conformation. The module **1** in the co-crystal **3** also adopts the *s-trans*,*s-trans* conformation where all the three aromatic rings are in the planes expected for the non-aggregated module (dihedral angles between least square planes of A/B, B/C, and A/C pyridine rings are 4.86(7), 4.17(7), and 3.24(7)°, respectively). In contrast, whenever terpys have self-assembled with a complementary metal module, they have to adopt a partner-induced conformation. In most cases, complexation reshaped the whole conformation of terpys from the most stable 2,2′-*s-trans*,6′,2″-*s-trans* to the less stable 2,2′-*s-cis*,6′,2″-*s-cis* arrangement so that terpys can act as tridentate donors to a single cationic centre[7]. Exceptionally, only a partial reshaping of the terpy conformation to the 2,2′-*s-cis*,6′,2″-*s-trans* arrangement is induced and terpy acts as bidentate donor to a single cationic centre by employing 1,1′-nitrogen atoms[8]. To the best of our knowledge, the $[Rh_2(OAc)_4(terpy)_2]$ complex (**4**), where the nitrogen atoms of two distinct terpy molecules occupy one octahedral position at each of the acetate-bridged rhodium atoms, is the only case reported so far where **1** acts as a monodentate ligand[9].



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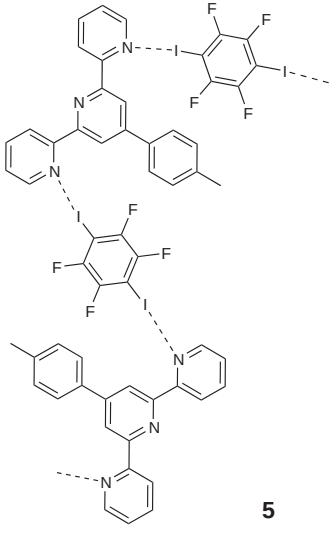

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Interestingly, the terpy **1** in complex **4** adopts a conformation close to the 2,2′-*s-trans*,6′,2″-*s-trans* arrangement preferred in the pure form. The terpy module assumes an *s-trans*,*s-trans* conformation also in the herringbone infinite network **5** that 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine forms when acts as a bidentate donor towards the diiodide **2** [8f]. This is the

only other case described so far of halogen-bonded supramolecular architecture involving terpy as an electron donor module. Clearly, the halogen-bonding-driven self-assembly of terpys with diiodide **2** prefers to maintain the ground state conformation of the HC module in the PFC–HC system.

While the N···I interaction is largely responsible for keeping terpy **1** and diiodoarene **2** in place in the well defined terpy···I–C_6F_4–I···terpy unit, weak H···F interactions[27] play a role in determining the packing of these units in the co-crystal and are preferred to H···H and F···F interactions[31]. Specifically, the F2–H14 distance is 260(2) pm, with the H14 being a particularly acidic hydrogen *para* positioned to the halogen-bonded nitrogen atom. Any tetrafluorodiiodobenzene unit **2** is thus involved in two halogen bondings and two hydrogen bondings (Fig. 1). The N···I interactions give rise to the trimeric units, the H···F interactions form a loosely connected three-dimensional network of trimers.

In summary, the supramolecular aggregate described here encompasses typical features of halogen-bonded adducts (interaction length and geometry) and provides the second case where a terpy module preserves the *s-trans,s-trans* conformation in a complex. This may occur through optimization of the geometry of the halogen bonding, the inherent conformational preferences of single modules, and the space-filling requirements in the co-crystal packing.

EXPERIMENTAL

Commercial HPLC-grade solvents were used without further purification. Starting materials **1** and **2** were purchased from Sigma–Aldrich and Apollo Scientific, respectively. NMR spectra were recorded with a Bruker AV 500 spectrometer. Chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. For ^{1}H and ^{13}C NMR spectra, $CDCl_3$ was used as both solvent and internal standard. ^{19}F NMR spectra were recorded in $CDCl_3$ with $CFCl_3$ as external standard. IR spectra (wavenumbers in cm^{-1}) were obtained using KBr pellets in a Perkin– Elmer 2000 FT-IR spectrometer. The values were rounded up to 1 cm^{-1} upon automatic assignment. Selected IR data of starting modules are reported to show the changes occurring on co-crystal formation. The X-ray crystal structure was determined using a Bruker Smart Apex diffractometer. Melting points were established with a Reichert instrument by observing the melting and crystallising process in a microscope using polarised light.

Synthesis of Co-crystal **3** from 2,2′:6′,2″-terpyridine (**1**) and 1,2,4,5-Tetrafluoro-3,6-diiodobenzene (**2**)

The liquid-liquid diffusion technique was used for the crystallisation. A 1 M solution of terpy **1** (189 mg, 1.2 mmol) in chloroform and a 1 M solution of **2** in the same solvent (240 mg, 0.6 mmol) were mixed in a clear borosilicate vial. The opened vial was placed in a closed cylindrical wide-mouth bottle containing pentane and solvents were allowed to diffuse at room

temperature until needle-like crystals were formed. The crystals were filtered off the mother liquor (from which two more co-crystal fractions can be obtained in the same manner), washed with pentane and rapidly dried in air at room temperature. M.p. 119 °C. IR (KBr, selected bands): pure terpy **1**: 3 050, 3 012; pure diiodide **2**: 1 467, 943, 760; aggregate **3**: 3 062, 3 016, 2 926, 1 583, 1 562, 1 463, 1 422, 1 214, 1 103, 1 079, 991, 945, 763. ^{1}H NMR: 7.28 (ddd, J = 7.8, 4.8, 1.1, 2 H, H-5,5″); 7.80 (ddd, J = 7.8, 7.8, 1.9, 2 H, H-4,4″); 7.93 (t, J = 7.8, 1 H, H-4′); 8.44 (d, J = 7.8, 2 H, H-3′,5′); 8.58 (d, J = 7.8, 2 H, H-3,3″); 8.68 (ddd, J = 7.8, 4.8, 2 H, H-6,6″). ^{13}C NMR: 73.00 (m, C-I); 120.83, 120.95, 123.56, 136.64, 137.68, 146.29 (m, $^1J_{CF}$ = 253, C-F); 148.91, 155.02, 155.91. ^{19}F NMR: δ_2: –118.30, $\Delta\delta = \delta_2 - \delta_3$ (0.1 M solution): 0.1, $\Delta\delta$ = 0.04, 0.08, 0.11 for 0.1 M solutions of **1** and where the **1** : **2** molar ratio was 1, 2 and 5, respectively. In another experiment, ^{1}H and ^{19}F NMR spectra were recorded in the presence of bis(2,2,2-trifluoroethyl) ether as an internal standard[32]. On calibrating integration parameters so that in the ^{1}H NMR spectrum the CH_2O quartet of bis(2,2,2-trifluoroethyl) ether was corresponding to four and in the ^{19}F NMR spectrum the CF_3 triplet of bis(2,2,2-trifluoroethyl) ether was corresponding to six, the ratio of the –CF=CI signal area (derived from **2**) and the H-6,6″ signal area (at 8.68, derived from **1**) is 1 : 1 thus revealing that the **1** : **2** ratio in **3** is 2 : 1.

X-Ray Crystal Structure Analysis of Co-crystal **3**

Crystal data: colourless elongated rhombic prism 0.36 × 0.12 × 0.10 mm^3, monoclinic, a = 17.3876(16), b = 4.0213(4), c = 24.098(2) Å, β = 106.245(2)°, U = 1 617.7(3) Å^3, T = 291 K, space group: $P21/c$, Z = 2, μ(MoKα) = 2.004, $\rho_{X\text{-}ray}$ = 1.783 g cm^{-3}. Data were collected on a Bruker Smart Apex CCD diffractometer: 28 899 reflections measured, 5 374 independent (R_{ave} = 0.0212), 4 324 with $I > 2\sigma(I)$. Empirical multiscan absorption correction (SADABS)[33], min/max transmission factor = 0.867637. The structure was solved by direct methods (SIR-92)[34] and refined by full-matrix least-squares (SHELX97)[35]; non-H atoms anisotropic; isotropic, "riding" H atoms were refined with soft constraints (SADI parameters of SHELX97) by imposing similar C–H distances. Final results on all 5 374 data: R = 0.0321, wR = 0.0645, goodness-of-fit 0.943, maximum residue 0.88 e Å^{-3} near the iodine atom. CCDC 179405 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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REFERENCES AND NOTES

1. Metrangolo P., Panzeri W., Recupero F., Resnati G.: *J. Fluorine Chem.* **2002**, *114*, 27.
2. a) Jeffrey G. A.: *An Introduction to Hydrogen Bonding*. Oxford University Press, Oxford 1997; b) Ermer O., Eling A.: *J. Chem. Soc., Perkin Trans. 2* **1994**, 925; c) Aakeröy C. B., Seddon K. R.: *Chem. Soc. Rev.* **1993**, *22*, 397.
3. Sauvage J.-P. (Ed.): *Transition Metals in Supramolecular Chemistry*. Wiley, Chichester 1999.
4. Lehn J.-M.: *Supramolecular Chemistry: Concepts and Perspectives*. VCH, Weinheim 1995.

5. a) Desiraju G. R.: *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311; b) Desiraju G. R.: *Chem. Commun.* **1997**, 1475.
6. a) Simard M., Su D., Wuest J. D.: *J. Am. Chem. Soc.* **1991**, *113*, 4696; b) Su D., Wang X., Simard M., Wuest J. D.: *Supramol. Chem.* **1995**, *6*, 171.
7. Piguet C., Bernardinelli G., Hopfgarten G.: *Chem. Rev. (Washington, D. C.)* **1997**, *97*, 2005.
8. a) Deacon G. B., Patrick J. M., Skelton B. W., Thomas N. C., White A. H.: *Aust. J. Chem.* **1984**, *37*, 929; b) Ferretti V., Gilli P., Bertolasi V., Marangoni G., Pitteri B., Chessa G.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 814; c) Civitello E. R., Dragovich P. S., Karpishin T. B., Novick S. G., Bierach G., O'Connell J. F., Westmoreland T. D.: *Inorg. Chem.* **1993**, *32*, 237; d) Ramdeehul S., Barloy L., Osborn J. A., DeCian A., Fischer J.: *Organometallics* **1996**, *15*, 5442; e) Anderson P. A., Keene F. R., Horn E., Tiekink E. R. T.: *Appl. Organomet. Chem.* **1990**, *4*, 523; f) Messina M. T., Metrangolo P., Resnati G., Quici S., Manfredi A., Pilati T.: *Supramol. Chem.* **2000**, *12*, 405.
9. Pruchnik F. P., Robert F., Jeannin Y., Jeannin S.: *Inorg. Chem.* **1996**, *35*, 4261.
10. a) Metrangolo P., Resnati G.: *Chem. Eur. J.* **2001**, *7*, 2511; b) Hassel O.: *Science* **1970**, *170*, 497; c) Dumas J. M., Gomel L., Guerin M.: *The Chemistry of Functional Groups, Suppl. D* (S. Patai and Z. Rappoport, Eds), p. 985. John Wiley and Sons, New York 1983; d) Bent H. A.: *Chem. Rev. (Washington, D. C.)* **1968**, *68*, 587; e) Legon A. C.: *Chem. Eur. J.* **1998**, *4*, 1890; f) Legon A. C.: *Angew. Chem., Int. Ed.* **1999**, *38*, 2687.
11. a) Farina A., Meille S. V., Messina M. T., Metrangolo P., Resnati G., Vecchio G.: *Angew. Chem., Int. Ed.* **1999**, *38*, 2433; b) Weiss R., Rechinger M., Hampel F., Wolski A.: *Angew. Chem., Int. Ed.* **1995**, *34*, 441.
12. a) Bloemink H. I., Legon A. C.: *Chem. Eur. J.* **1996**, *2*, 265; b) Soled S., Carpenter G. B.: *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *30*, 910; c) Okishi Y., Imai Y., Aida K.: *J. Inorg. Nucl. Chem.* **1973**, *35*, 101; d) Yarwood J., Person W. B.: *J. Am. Chem. Soc.* **1968**, *90*, 3930; e) Yagi Y., Popov A. I.: *J. Am. Chem. Soc.* **1965**, 87, 3577; f) Whitaker R. D., Ambrose J. R., Hickam C. W.: *J. Inorg. Nucl. Chem.* **1961**, *17*, 254; g) Wynter C. I., Hill J., Bledsoe W.: *J. Chem. Phys.* **1969**, *50*, 3872; h) Yagi Y., Popov A. I.: *J. Phys. Chem.* **1967**, *71*, 2439; i) Popov A. I., Marshall J. C., Stute F. B., Person W. B.: *J. Am. Chem. Soc.* **1961**, *83*, 3586; j) Jander J., Maurer A.: *Z. Naturforsch. B* **1978**, *33*, 1446.
13. Tebbe K. F., Graefe-Kavoosian A.: *Z. Naturforsch. B* **1996**, *51*, 1007.
14. a) Ranganathan A., Pedireddi V. R.: *Tetrahedron Lett.* **1998**, *39*, 1803; b) Masciocchi N., Bergamo M., Sironi A.: *Chem. Commun.* **1998**, 1347; c) Sarma J. A. R. P., Allen F. H., Hoy V. J., Howard J. A. K., Thaimattam R., Biradha K., Desiraju G. R.: *Chem. Commun.* **1997**, 101; d) Weiss R., Schwab O., Hampel F.: *Chem. Eur. J.* **1999**, *5*, 968.
15. Ghassemzadeh M., Harms K., Dehnicke K.: *Z. Naturforsch. B* **1997**, *52*, 772.
16. Takakura T. in: *Modern Fluoropolymers* (J. Scheirs, Ed.), Chap. 29, p. 557. Wiley, New York 1997.
17. a) Cardillo P., Corradi E., Lunghi A., Meille S. V., Messina M. T., Metrangolo P., Resnati G.: *Tetrahedron* **2000**, *56*, 5535; b) Grebe J., Geiseler G., Harms K., Neumüller B., Dehnicke K.: *Angew. Chem., Int. Ed.* **1999**, *38*, 222.
18. a) Smart B. E. in: *Organofluorine Chemistry: Principles and Commercial Applications* (R. E. Banks, B. E. Smart and J. C. Tatlow, Eds). Plenum Press, New York 1994; b) Hildebrand J. H., Cochran D. R. F.: *J. Am. Chem. Soc.* **1949**, *71*, 22; c) Dorset D. L.: *Macromolecules* **1990**, *23*, 894.
19. Améduri B., Boutevin B.: *J. Fluorine Chem.* **1999**, *100*, 97.

20. a) Valerio G., Raos G., Meille S. V., Metrangolo P., Resnati G.: *J. Phys. Chem. A* **2000**, *104*, 1617; b) Walsh R. B., Padgett C. W., Metrangolo P., Resnati G., Hanks T. W., Pennington W. T.: *Cryst. Growth Des.* **2001**, *1*, 165.
21. Messina M. T., Metrangolo P., Panzeri W., Ragg E., Resnati G.: *Tetrahedron Lett.* **1998**, *39*, 9069.
22. Messina M. T., Metrangolo P., Navarrini W., Radice S., Resnati G., Zerbi G.: *J. Mol. Struct.* **2000**, *524*, 87.
23. Foster R.: *Organic Charge-Transfer Complexes*, p. 100. Academic Press, London 1969.
24. a) Bondi A.: *J. Phys. Chem.* **1964**, *68*, 441; b) Pauling L.: *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press, Ithaca 1960.
25. Padmanabhan K., Paul I. C., Curtin D. Y.: *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 88.
26. a) Messina M. T., Metrangolo P., Panzeri W., Pilati T., Resnati G.: *Tetrahedron* **2001**, *57*, 8543; b) Corradi E., Meille S. V., Messina M. T., Metrangolo P., Resnati G.: *Tetrahedron Lett.* **1999**, *40*, 7519; c) Amico V., Meille S. V., Corradi E., Messina M. T., Resnati G.: *J. Am. Chem. Soc.* **1998**, *120*, 8261; d) Navarrini W., Metrangolo P., Pilati T., Resnati G.: *New J. Chem.* **2000**, *24*, 777.
27. Fontana F., Forni A., Metrangolo P., Panzeri W., Pilati T., Resnati G.: *Supramol. Chem.* **2002**, *14*, 47.
28. a) Thummel R. P., Jahng Y.: *J. Org. Chem.* **1985**, *50*, 2407; b) Elsbernd H., Beattie J. K.: *J. Inorg. Nucl. Chem.* **1972**, *34*, 771; c) Elytle F., Petrosky L. M., Carlson L. R.: *Anal. Chim. Acta* **1971**, *57*, 239; d) Fielding P. E., Le Fevre R. J. W.: *J. Chem. Soc.* **1951**, 1811.
29. Bessel C. A., See R. F., Jameson D. L., Churchill M. R., Takeuchi K. J.: *J. Chem. Soc., Dalton Trans.* **1992**, 3223.
30. a) Armspach D., Constable E. C., Housecroft C. E., Neuburger M., Zehnder M.: *New J. Chem.* **1996**, *20*, 331; b) Constable E. C., Thompson A. M. W. C., Tocher D. A., Daniels M. A. M.: *New J. Chem.* **1992**, *16*, 855; c) Constable E. C., Khan F. K., Marquez V. E., Raithby P. R.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 932.
31. Thalladi V. R., Weiss H. C., Bläser D., Boese R., Nangia A., Desiraju G. R.: *J. Am. Chem. Soc.* **1998**, *120*, 8702.
32. **CAUTION**: Bis(2,2,2-trifluoroethyl) ether is a highly toxic and volatile substance. It is known to act as a CNS stimulant (Merck Index, 11th ed., p. 657).
33. *SADABS*. Bruker AXS Inc., Madison (WI) 1999.
34. Altomare A., Cascarano G., Giacovazzo G., Guagliardi A.: *J. Appl. Crystallogr.* **1994**, *27*, 43535.
35. Sheldrick G. M.: *SHELX97. Program for the Refinement of Crystal Structures*. University of Göttingen, Göttingen 1997.