Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 47 (2006) 1249–1252

Tetrahedron Letters

Self-assembly of nitroxide radicals via halogen bonding—directional NO$^\bullet\cdots$I interactions

Kamal Boubekeur,[a] Jean-Laurent Syssa-Magalé,[b,†] Pierre Palvadeau[c] and Bernd Schöllhorn[b,*]

[a]*Université Pierre et Marie Curie, UMR CNRS 7071—Laboratoire de Chimie Inorganique et Matériaux Moleculaires, 4 place Jussieu, 75252 Paris Cedex 5, France*
[b]*Ecole Normale Supérieure, Département de Chimie, UMR CNRS 8640—PASTEUR, 24 rue Lhomond, 75231 Paris Cedex 05, France*
[c]*Institut des Matériaux Jean Rouxel, UMR CNRS 6502—Laboratoire de Chimie des Solides, 2, rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

Received 2 November 2005; revised 12 December 2005; accepted 16 December 2005

Abstract—Novel supramolecular self-assemblies of nitroxide free radicals via noncovalent halogen bonding are synthesised. A directional NO$^\bullet\cdots$I interaction is observed in a one-dimensional coordination polymer consisting of alternating electron donor and acceptor molecules.

An area of still growing interest is the construction of novel organic spin systems aiming at new molecular magnetic materials.[1] Light weight, optical transparency and solubility in organic solvents are some of their potential advantages. Nitroxide free radicals are widely used as building blocks in this field. The first organic ferromagnetic material, *p*-nitrophenyl nitronyl nitroxide, has been reported in 1991.[2] In order to realise specific relative spin orientations, different strategies have been adopted to control the molecular arrangement of open shell molecules in crystals. The construction of such solids requires that the structural subunits exhibit noncovalent interactions which can be controlled in a predictable way. Hydrogen bonding and transition-metal ligation have already been successfully employed.[3]

It has been shown that the construction of one-dimensional molecular arrays can be achieved by noncovalent halogen bonding,[4] a particularly predictable supramolecular tool in crystal engineering. Organic halides (I, Br and Cl) can act as electron acceptors (A), able to complex electron donors (D) containing electronegative atoms with lone pairs, such as nitrogen, oxygen or sulfur. Perfluorocarbon iodides form particularly strong halogen bonds owing to the electron withdrawing fluor atoms.[5] In fact, the high energy (comparable to strong H-bonding[6]) and the strong directionality of the interactions with amines enable the controlling of the relative orientation of the molecules. For example, 1,4-diiodo-tetrafluorobenzene (TFDIB) co-crystallises with a variety of donors, forming infinite chains of alternating D and A modules.[5,7,8] We report herein, a preliminary study on the structural aspects of novel supramolecular self-assemblies of stable nitroxide radicals and TFDIB via halogen bonding.

The slow evaporation of equimolar chloroform solutions of TFDIB and, respectively, *4-phenyl-2,2,5,5-tetramethyl-3-imidazolin-1-yloxyl radical* (PTIO) or *4-amino-2,2,6,6-tetramethyl(piperidin-1-yloxyl) radical* (ATEMPO) at room temperature afford the air stable, yellow/orange co-crystals **1a**, **1b** and **2** (Scheme 1). IR spectroscopy demonstrates that some of the stretching modes of TFDIB (1468, 944 cm^{-1}) shift to lower

---

Keywords: Supramolecular chemistry; Self-assembly; Nitroxide radicals; Halogen bonding.

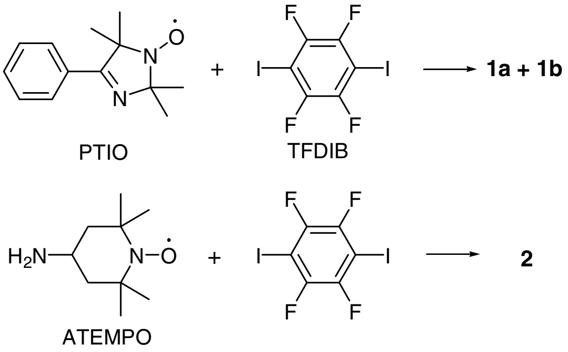
[*] Corresponding author. Tel.: +33 1 44323263; fax: +33 1 44322402; e-mail: bernd.schollhorn@ens.fr

[†] Permanent address: Université de Bangui, Faculté des Sciences, BP 908, Bangui, Central African Republic.

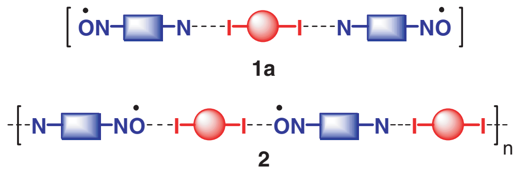
0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.12.088

wave-numbers in all studied compounds,[‡] which is consistent with the spectral changes in analogous aggregates based on N···I halogen bonding.[5]

In the preparation of compound **1** two different products were formed. The transparent monoclinic crystals (**1a**) were easily separated from a white powder (**1b**). The crystal structure of **1a**[§] reveals an assembly of termolecular [D···A···D] complexes (Scheme 2, Fig. 1). The imino nitrogen of PTIO is involved in the halogen bonding between D and A. The N···I distance of 3.209(3) Å is longer than in comparable assemblies involving imines (2.89 Å)[9] indicating a relatively weak interaction. However it is still significantly shorter than the sum of the van der Waals radii of nitrogen and iodine (3.68 Å).[10] Also the nearly linear arrangement of N···I–C (176.75(9)°) is consistent with the common parameters of halogen bonding[4] reflecting the anisotropic electron density distribution of the iodine atom.[10] We have recently described similar [D···A···D] assemblies involving heterocycles containing two nitrogen atoms.[11]



Scheme 1. Self-assembly of TFDIB with the nitroxides PTIO and ATEMPO.



Scheme 2. Coordination of donors (blue) and acceptors (red) via halogen bonding in compounds **1a** and **2**.

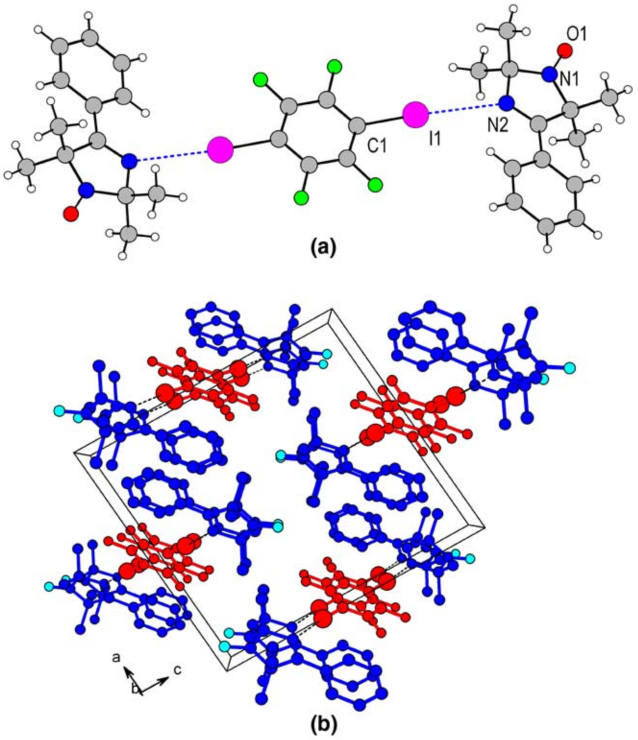


Figure 1. (a) [D···A···D] complex in **1a** with all cycles being approximately in the same plane. (b) Crystal packing, view on the a,c plane, acceptors (red), donors (blue), oxygen (cyan), hydrogen atoms are omitted. TFDIB molecules are lying on inversion centres.

Elemental analysis of compound **1b** reveals a 1:1 D/A ratio.[‡] Several attempts to obtain suitable single-crystals for X-ray structure analysis were unsuccessful. The product probably consists of a homogeneous phase, since the melting point (72–74 °C) is higher than for **1a**

[‡] The co-crystals were obtained by slow evaporation of a solution of 1,4-diiodotetrafluorobenzene (TFDIB) (0.10 mmol) and nitroxide (0.10 mmol) in chloroform (2 mL). All reagents were purchased from Sigma–Aldrich (France). Compound **1a**: IR ν/cm^{-1} 1462 (s), 942 (s). Compound **1b**: IR ν/cm^{-1} 1458 (s), 940 (s). Found: C, 37.35; H, 2.94; N, 4.88. Calcd for $C_{19}H_{17}F_4I_2N_2O$: C, 36.86; H, 2.77; N, 4.52. Compound **2**: IR ν/cm^{-1} 1453 (s), 938 (s).

[§] Single crystal X-ray analysis: Intensity data were collected on an NONIUS Kappa-CCD four-circle diffractometer at room temperature by using a graphite monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods with SHELXS-86, refined by full least-squares on F^2 and completed with SHELXL-97 (G. M. Sheldrick, SHELXL-97, Computer program for structure refinement, University of Gottingen, Germany, 1997; G. M. Sheldrick, SHELXS-86, Computer program for structure solution, University of Gottingen, Germany, 1986). Graphics were carried out with DIAMOND (Crystal Impact GbR). All non-H atoms were refined with anisotropic displacement parameters and H atoms were simply introduced at calculated positions (riding model with isotropic temperature factors fixed at 1.2-times that of the parent atom). Crystallographic data for compound **1a**: $C_{32}H_{34}F_4I_2N_4O_2$, $M = 836.44$, monoclinic, space group $P2_1/n$, $a = 13.4840(4)$, $b = 8.6420(2)$, $c = 14.9012(3)$ Å, $\beta = 95.8070(10)°$, $U = 1727.51(7)$ Å^3, $Z = 2$, $D_{calcd} = 1.608$ g cm^{-3}, μ (Mo-K$_\alpha$) = 1.875 mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 824$, $T = 293(2)$ K, crystal size = 0.40 × 0.14 × 0.13 mm^3, 28,452 reflections measured, 4159 unique ($R_{int} = 0.0525$) which were used in all calculations. The final reliability factors are $R = 0.0366$ (3104 reflections with $F_0 > 4\sigma(F_0)$) and $wR(F^2) = 0.1085$ (all data). Compound **2**: $C_{15}H_{19}F_4I_2N_2O$, $M = 573.13$, monoclinic, space group $P121/c\,1$, $a = 7.4220(7)$, $b = 23.404(3)$, $c = 12.5493(14)$ Å, $\beta = 113.799(7)°$, $U = 1994.5(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.909$ g cm^{-3}, μ (Mo-K$_\alpha$) = 3.193 mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 824$, $T = 293(2)$ K, crystal size = 0.39 × 0.12 × 0.12 mm^3, 9383 reflections measured, 4131 unique ($R_{int} = 0.0584$) which were used in all calculations. The final reliability factors are $R = 0.0725$ (1897 reflections with $F_0 > 4\sigma(F_0)$) and $wR(F^2) = 0.1568$ (all data). Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 284962 (for compound **1a**), 284,963 (for compound **2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

(54–56 °C). It is possible that the crystal structure of **1b** consists of polymeric chains involving both donor sites of PTIO.

Since we had no proof for any NO$^{\bullet}\cdots$I interactions, we co-crystallised TFDIB and ATEMPO. The resulting compound **2** possesses a D/A stoichiometry of 1:1. Its melting point (85–87 °C), being significantly higher than for pure ATEMPO (35–36 °C), indicates a relatively strong assembly. Crystal structure analysis of **2**[§] shows infinite one-dimensional $[\mathrm{D}\cdots\mathrm{A}\cdots]_n$ chains with directing N···I and O···I interactions (Figs. 2 and 3). The

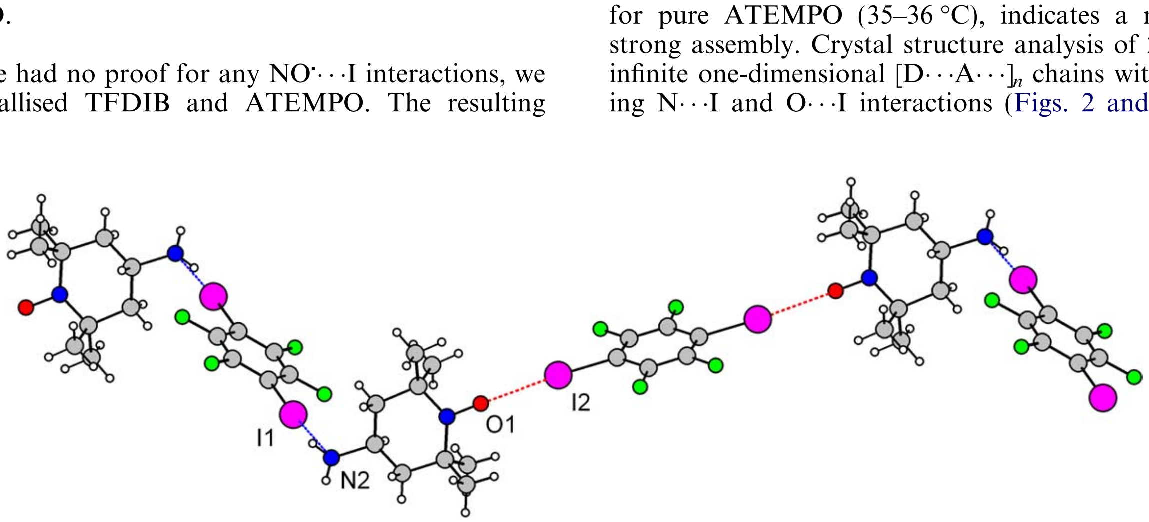
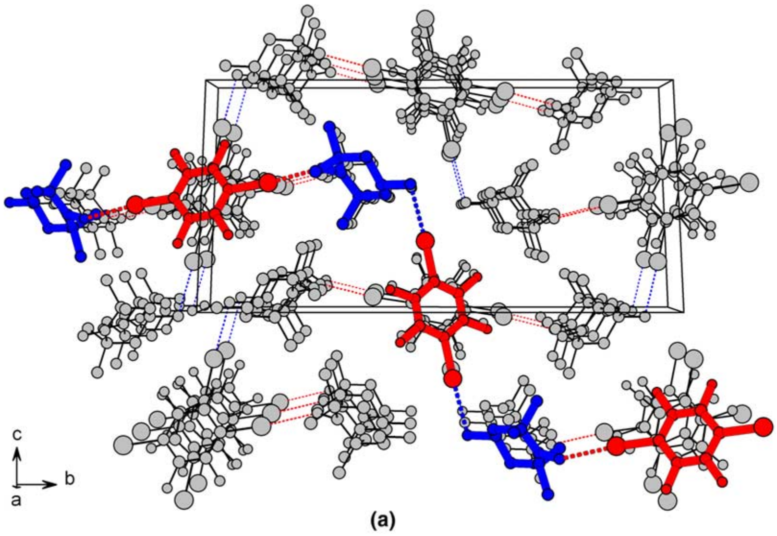


Figure 2. One-dimensional chain fragment in compound **2** with alternating donor and acceptor molecules.



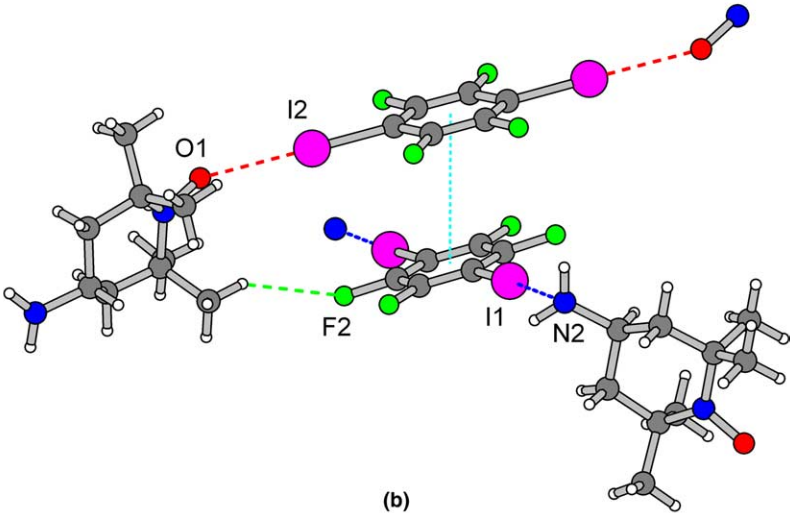
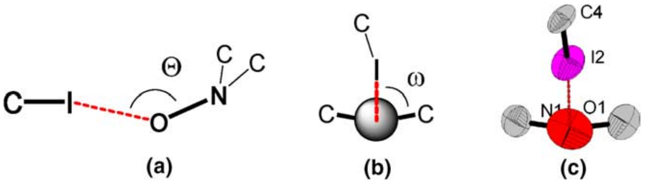


Figure 3. (a) Crystal packing in **2** (view on the b, c plane), a polymeric chain with alternating donors (blue) and acceptors (red) is highlighted (hydrogen atoms are omitted). (b) Relative orientation of two one-dimensional chain fragments, crosslinked via π···π and CH···F interactions. TFDIB molecules are lying on inversion centres.



Scheme 3. Schematic representation of the NO···I halogen bond in compound **2** indicating the corresponding angles. (a) Projection on the plane of the C–I···O bond; (b) Newman projection viewed down the O–N bond; (c) thermal ellipsoid plot of the corresponding fragment.

N···I contact is remarkably shorter (2.906(11) Å) than in **1a**. The NO$^\bullet$···I interaction is characterised by an O···I distance of 2.827(9) Å (sum of the van der Waals radii of O and I, 3.48 Å),[10] indicating a surprisingly strong[5] interaction compared to other oxygenated donors assembled with TFDIB (O···I contacts for: N-oxide 2.75 Å;[7] aldehyde 2.95 Å;[8] ketone 3.10 Å[8]). This observation is not in agreement with the in general poor donor properties of nitroxides in metal complexes and accounts for the probably important electrostatic contribution to the halogen bonding. Both D···I–C bonds are approximately linear (175–176°). The N–O···I angle Θ of 145.0° and the dihedral angle ω of 80.1° (Scheme 3) are suggesting that the halogen bond forms along the lone-pair directions of the oxygen, tending to the π-type arrangement,[12] established for hydrogen bridging in nitroxides. The polymeric structure of **2** can be rationalised as an alignment of [D···A···] units, the donor molecules being in alternating orientations, as shown in Scheme 2. This particular arrangement leads to a certain proximity of the radical centres bridged by a TFDIB unit, necessary for any potential spin transfer. The halogen bonded chains are crosslinked in the third dimension by π···π interactions (centroid–centroid distance 3.71 Å) and CH···F hydrogen bonds (H···F, 2.57 Å; C···F, 3.41 Å; angle C–H···F, 146.90°) as shown in Figure 3.

In conclusion, we have shown the promising use of halogen bonding as a tool for the construction of novel nitroxide assemblies with potentially interesting magnetic properties. A structure determining NO$^\bullet$···I intermolecular interaction is identified suggesting how important it is to understand and to take into account this type of noncovalent interactions not only in the solid state but also in solution. The characteristics of this particular interaction are of general interest, concerning all research domains in which intermolecular interactions with nitroxides can play an important role, such as in medicinal and biological chemistry[13] or materials science.[1,3] The preparation of further co-crystals as well as the investigation of the magnetic properties of this new class of materials are in progress.

References and notes

1. Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, 392–398; Gatteschi, D. *Adv. Mater.* **1991**, *6/9*, 635–645; *Molecular Magnetism—New Magnetic Materials*; Itho, K., Kinoshita, M., Eds.; Kodansha: Tokyo, 2000, and references cited therein.
2. Turek, P.; Nozawa, K.; Shiomi, D.; Awage, K.; Inabe, T.; Maruyama, Y.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *180*, 327–331.
3. See for recent examples: Sugawara, T.; Matsushita, M. M.; Izuoka, A.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1723–1724; Matsushita, M. M.; Izuoka, A.; Sugawara, I.; Kobayashy, T.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 4369–4379; Pontillon, Y.; Akita, T.; Grand, A.; Kobayashi, K.; Lelievre-Berna, E.; Pécaut, J.; Ressouche, E.; Schweizer, J. *J. Am. Chem. Soc.* **1999**, *121*, 10126–10133; Vostrikova, K. E.; Luneau, D.; Wernsdorfer, W.; Rey, P.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 718–719; Maspoch, D.; Catala, L.; Gerbier, P.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Rovira, C.; Veciana, J. *Chem. Eur. J.* **2002**, *8/16*, 3635–3645; Lemaire, M. T. *Pure Appl. Chem.* **2004**, *76/2*, 277–293.
4. Bent, H. A. *Chem. Rev.* **1968**, *68*, 587–648; Lommerse, J. P. M.; Stone, A. J.; Taylor, R.; Allen, F. H. *J. Am. Chem. Soc.* **1996**, *118*, 3108–3116; Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G. *Acc. Chem. Res.* **2005**, *38*, 386–395, and references cited therein.
5. Chen, Q. Y.; Qiu, Z. M. *J. Fluorine Chem.* **1987**, *35/1*, 79; Metrangolo, P.; Resnati, G. *Chem. Eur. J.* **2001**, *7*, 2511–2519; Walsh, R. B.; Padgett, C. W.; Metrangolo, P.; Resnati, G.; Hanks, T. W.; Pennington, W. T. *Cryst. Growth Des.* **2001**, *1/2*, 165–175.
6. Aacheröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397–407.
7. Messina, M. T.; Metrangolo, P.; Panzeri, W.; Pilati, T.; Resnati, G. *Tetrahedron* **2001**, *57/40*, 8543–8550.
8. Leroy, J.; Schöllhorn, B.; Syssa-Magalé, J.-L.; Boubekeur, K.; Palvadeau, P. *J. Fluorine Chem.* **2004**, *125/9*, 1379–1382; Syssa-Magalé, J.-L.; Boubekeur, K.; Schöllhorn, B. *J. Mol. Struct.* **2004**, *737*, 21–25.
9. Syssa-Magalé, J-L.; Boubekeur, K.; Palvadeau, P.; Meerschaut, A.; Schöllhorn, B. *J. Mol. Struct.* **2004**, *691*, 79–84.
10. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451; Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274–279.
11. Syssa-Magalé, J-L.; Boubekeur, K.; Palvadeau, P.; Meerschaut, A.; Schöllhorn, B. *Cryst. Eng. Commun.* **2005**, *50/7*, 302–308.
12. Otsuka, T.; Motozaki, W.; Nishikawa, K.; Endo, K. *J. Mol. Struct.* **2002**, *615*, 147–151.
13. Swartz, H. M. *Pure Appl. Chem.* **1990**, *62/2*, 235–239; Auffinger, P.; Hays, F. A.; Westhof, E.; Ho, P. S. *PNAS* **2004**, *101/48*, 16789–16794.