[2 + 2]Photocyclization in a single-crystal-to-single-crystal transformation of a TTF-amido-pyridine

Thomas Devic, Patrick Batail* and Narcis Avarvari*

Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers, UMR 6200, Université d'Angers, UFR Sciences, Bât. K, 2 Bd. Lavoisier, 49045 Angers Cedex, France. E-mail: patrick.batail@univ-angers.fr; narcis.avarvari@univ-angers.fr; Fax: (33) 24173 5405; Tel: (33) 24173 5084

The redox active ligand EDT-TTF-CONH-3-pyridine undergoes a [2 + 2] cycloaddition upon irradiation with polychromatic light, an unprecedented single-crystal-to-single-crystal transformation for a TTF derivative.

Among the organic reactions which take place in the solid state, the [2 + 2] cycloaddition between two alkenes upon photoactivation is certainly one of the most studied,[1] and sometimes occurs *via* a single-crystal-to-single-crystal conversion.[2] Contrary to the solution behaviour, where regio- and stereochemistry are governed by HOMO–HOMO and LUMO–LUMO orbital overlapping and mixtures of compounds are often obtained in the case when several reactive sites are present, reactions occurring in the solid state impose the formation of one isomer only, as the result of the structural arrangement of the reactants. This solid state reactivity is currently not just an exotic feature, but, combined with crystal engineering, emerges as a powerful method to synthesize new ligands like tetrakis(4-pyridyl)cyclobutane[3] or unusual objects like ladderanes,[4] hardly available by other synthetic pathways. The convenient arrangement of the reactants in the crystalline state prior to photoactivation, is often dictated by intermolecular interactions combined with the crystal packing. Intermolecular interactions such as hydrogen bonding, π–π stacking or donor–acceptor interactions, the favourite tools of the crystal engineers, play also an important role in the solid state arrangement of functionalized tetrathiafulvalenes (TTF), a class of compounds widely studied in the search of molecular conductors and superconductors.[5] Thus, many chemical modifications have been performed on the TTF core, with the aim of modifying the solid state arrangement of these molecules, and thereby the properties of their radical cation salts.[6,7] Despite the presence of electron rich double bonds in the TTF structure, only few examples of their intrinsic reactivity have been reported to date,[8,9] and only one related to a solid state [2 + 2] photodimerization.[10] Indeed, Neilands and co-workers have noticed a color change from red to yellow, upon irradiation in the solid state, for a series of mono-, di- and tetra-carbamoyl-TTFs. Their proposition of a [2 + 2] cycloaddition was confirmed later by a single crystal X-ray study on one of the TTFs derivatives, though no structural evidence for the cycloaddition product was obtained.[11] Recently we synthesized a series of TTF-amidopyridines and -2,2′-bipyridines as redox active ligands and studied in depth their arrangement in the solid state at a supramolecular level, as resulting from the balance of the different intermolecular interactions and the crystal packing.[12] One of these compounds, formulated as EDT-TTF-CONH-3-pyridine, crystallized as a MeCN solvate with the molecules arranged in hydrogen-bonded ribbons. The same type of arrangement is observed in a second isomorphic phase, including this time as solvate a THF molecule, disordered on the inversion center. In between two ribbons of molecules, the donors arrange in centrosymmetric pairs, very likely stabilized by donor–acceptor interactions. Indeed, within such a pair, the electron poor amidopyridine group of one donor stacks over the electron rich TTF core of the second donor (Fig. 1).†

This peculiar arrangement leads to an eclipsed conformation of the peripheral C(1)=C(2) double bonds, with a very short distance (3.543(7) Å) in between. These characteristics[13] prompted us to investigate the reactivity of this compound in the crystalline state upon lighting. Thus, polychromatic irradiation of single crystals of EDT-TTF-CONH-3-Py·0.5THF induced a color change from red to yellow; remarkably, the crystallinity is retained in spite of the inclusion solvent in the structure (Scheme 1)‡.

As expected, the [2 + 2] cycloaddition product **2** is obtained, as confirmed by the ^{1}H NMR spectroscopy and especially by a single crystal X-ray diffraction study. In the ^{1}H NMR spectrum, measured in DMSO-d6 at 60 °C because of the sparing solubility of **2**, the two protons of the new cyclobutane ring resonate as a singlet at 5.25 ppm, whereas the ethylenedithio bridge protons are now different unlike within the starting compound and resonate as two distinct multiplets. The color change associated with the photoaddition reaction was also evidenced by UV spectroscopy, since a hypsochrome shift of the absorption band in the visible region, corresponding to a π–π* transition, is observed. Indeed, the maximum of this band locates at 416 nm for **1** and at 400 nm for **2**, which demonstrates a larger HOMO–LUMO gap in the latter, a consequence of a lower degree of conjugation. The ultimate proof for the solid state photodimerization process was afforded by a single crystal X-ray analysis. The compound **2** is isostructural with the donor **1**, but the motif now consists in a functionalized cyclobutane ring located on an inversion centre, with the substituents arranged *trans* each other (Fig. 2).†

As evidenced also by the color change, a loss of conjugation within the TTF core accompanied the formation of the cyclobutane ring: the former C(1)–C(2) double bond became single and the former C(1)···C(2′) intermolecular contact became a single bond. Moreover, the whole geometry of the dithiafulvalene ring fused with the cyclobutane is modified, since the C(1)–S(1) and C(2)–S(2) distances increased and the cycle became highly folded along the S(1)···S(2) hinge, with a dihedral angle of 35.49(10)° which is to be compared with a value of 9.11(34)° in **1**. On the contrary, the other part of the molecule remained essentially unaffected. The cycloaddition product is thermally stable, since no detectable retro
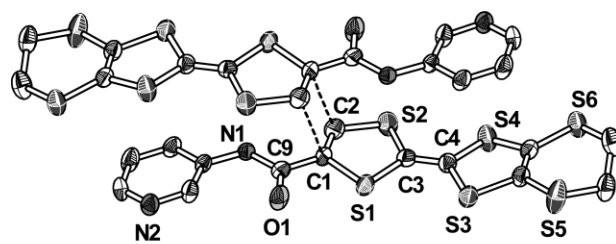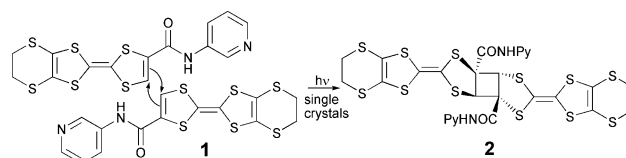

Fig. 1 Centrosymmetric pair of donors, with an emphasis on the short intermolecular distance (3.543(7) Å, dotted lines) between the C(1)=C(2) double bonds, in the crystalline structure of EDT-TTF-CONH-3-Py·0.5THF (thermal ellipsoids set at 50% probability, H atoms omitted). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.334(7), S(1)–C(1) 1.758(5), S(2)–C(2) 1.718(5); C(9)–C(1)–S(1) 112.0(4).

Scheme 1 [2 + 2] Photodimerization of EDT-TTF-CONH-3-Py·0.5THF (**1**) in single-crystal-to-single-crystal conversion.
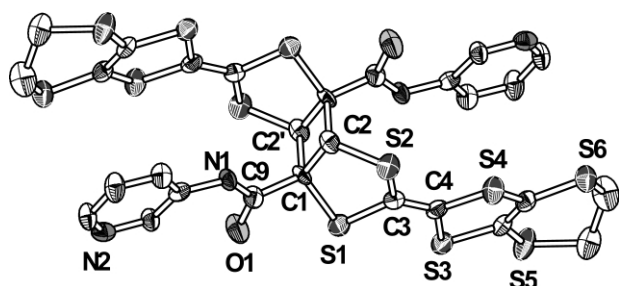
Fig. 2 ORTEP view of the [2 + 2] cycloaddition product **2** (thermal ellipsoids set at 50% probability, H atoms omitted). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.545(8), C(1)–C(2′) 1.591(8), S(1)–C(1) 1.809(6), S(2)–C(2) 1.803(6); C(9)–C(1)–S(1) 105.6(4).

[2 + 2] cyclization occurred upon heating, either in the solid state (110 °C) or in a DMSO solution. Cyclic voltammetry measurement on compound **2** (ref. Ag/AgCl, 0.1 M TBAPF$_6$ in DMSO, 0.1 V s^{-1}) shows an irreversible oxidation peak at 0.80 V, a normal behaviour for such a 1,4-dithiafulvene system.[14]

It is clear, with regard to the mutual arrangement of the donors in the solid state, that the photochemical process has occurred with an exo stereochemistry, which, in principle, is not the most favourable one. In order to check this supposition, a DMSO solution of **1** was irradiated, but only an intractable mixture of compounds was obtained after 48 h of lighting, with no indication for the formation of cyclobutane **2**. This proves once again that crystal engineering provides an invaluable tool for a highly selective reactivity in the solid state, which can be hardly paralleled by that in solution, especially when several reactive sites are present, as is the case with the donor **1**. The results disclosed herein open the way towards the solid state synthesis of a multitude of functionalized sulfur rich redox active compounds, since many TTF functional derivatives may organize in the solid state in such a manner to allow the occurrence of photochemical processes.

Notes and references

† Crystal data for **1**: C$_{16}$H$_{14}$N$_2$O$_{1.5}$S$_6$, M = 450.65, orthorhombic, space group *Pbca*, a = 13.3412(15), b = 11.6686(15), c = 24.183(3) Å, U = 3764.6(8) Å^3, Z = 8, T = 293(2) K, μ = 0.738 mm^{-1}, D$_c$ = 1.590 g cm^{-3}, 42389 refl. measured, 2141 refl. with I > 2σ(I), R = 0.059, R$_W$ = 0.128. For **2**: C$_{32}$H$_{28}$N$_4$O$_3$S$_{12}$, M = 901.39, orthorhombic, space group *Pbca*, a = 14.3756(13), b = 11.1605(7), c = 22.9236(19) Å, U = 3677.8(5) Å^3, Z = 4, T = 293(2) K, μ = 0.755 mm^{-1}, D$_c$ = 1.628 g cm^{-3}, 23684 refl. measured, 1083 refl. with I > 2σ(I), R = 0.047, R$_W$ = 0.090. Hydrogen atoms for the solvent molecules in both structures were not located. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-square on F^2 (SHELXL-97). CCDC 235419 for **1**, CCDC 235420 for **2**. See http://www.rsc.org/suppdata/cc/b4/b404482g/ for crystallographic data in .cif or other electronic format.

‡ Compound **1** was prepared as previously described.[12] Recrystallization in THF afforded red, air-stable, single crystals which were placed in an ice bath under polychromatic light (Oriel Xe lamp, 80 mW cm^{-2}). Within a few hours a complete color change from red to yellow occurred.

Spectroscopic data for **2**: ^{1}H NMR (500.04 MHz, DMSO-d$_6$) δ 3.29–3.33 (m, 2H, S(CH$_2$)$_2$S), 3.37–3.42 (m, 2H, S(CH$_2$)$_2$S), 5.25 (s, 2H, CH$_{cyclobut.}$), 7.35 (dd, ^3J = 4.7 Hz, ^3J = 8.2 Hz, 2H, Py), 7.96–7.98 (m, 2H, Py), 8.32 (dd, , ^4J = 1.3 Hz, ^3J = 4.7 Hz, 2H, Py), 8.73 (d, ^4J = 2.4 Hz, 2H, Py), 10.31 (s, 2H, NH).

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