Extended Analogues of Tetrathiafulvalene (TTF): 1,2-Bis, 1,4-Bis and 1,2,4,5-Tetrakis(1,4-Dithiafulven-6-yl) Benzenes; Synthesis and π -Donor Abilities.

Marc SALLE,^a Ahmed BELYASMINE,^a Alain GORGUES,^{a*} Michel JUBAULT^{a*} and Noël SOYER^b

a) Laboratoire de Synthèse Organique et d'Electrochimie, Université d'Angers, 2 bd Lavoisier, 49045 Angers, France

b) Laboratoire de Chimie Organique, ENSCR, Avenue des Buttes de Coesmes, 35043 Rennes, France.

Key Words: Dithiafulvenylbenzenes; Electron Donors; Organic Conductors; Charge-Transfer Complexes; Wittig (-Horner) Reactions.

Abstract: The title compounds are prepared by Wittig or Wittig-Horner reactions between the corresponding benzenes di- and tetracarbaldehydes and the P-reagents W or P bearing the 1,3-dithiol-2-ylidene moiety; among them, the tetrakis(dithiafulvenyl)benzene 3c is shown by cyclic voltammetry to possess the best π -donor character and, also, is chemically or electrochemically oxidized.

Since the discovery of the properties of tetrathiafulvalene (TTF) in the early 1970s,¹ much effort has been devoted to designing new analogues of this π -donor in order to improve the electroconductive properties of the corresponding salts;^{2,3} thanks to subtle chemical modifications, the first organic superconductors have been obtained, and their Tc has been gradually raised⁴ (up to 11.6 K at ambient pressure, to date⁵). One of the present trends consists in separating two or more 1,3-dithiol-2-ylidene moieties by extending and conjugating blocks such as mono or polyolefinic,⁶⁻⁸ cumulenic,^{6,9} acetylenic,¹⁰



quinonic¹¹ and carbo^{14,15} or heteroaromatic¹⁶ π -systems. Such modifications are expected to decrease the on-site coulombic repulsion thanks to a greater separation of charges in the oxidized states of the donor. Moreover, when more than two S-heterocyclic moieties are connected in this way, an enhancement of the dimensionality in the related materials may result, since the greater the number of S atoms, the greater the number of S....S intra- and inter-chains contacts.

As there are only a few examples of benzenic analogues of TTF,^{14,15} we decided to study the synthesis and π -donor properties of 1, 2 and in particular 3 which was held to be a suitable precursor of "organic metals" because of its large space expansion and its four conjugated S-heterocycles.

As previously shown in the case of 1a,¹⁴ a straight access to the target molecules involves the Wittig or Wittig-Horner olefinations of the corresponding benzenic di- or tetra-¹⁷ aldehydes with the P-ylids **Wa** $c^{14,18}$ or the phosphonate anion **Pb**.^{11a,19}

All the reactions applied hereafter were run by *quantitative* deprotonation (BuⁿLi, THF, below -70°C) of the corresponding phosphonium tetrafluoroborates (for **Wa**,**b**) and hexafluorophosphate (for **Wc**) or of the phosphonate (for **Pb**), and then adding the aldehydes (tetrahydrofuran (THF) soln) dropwise; however, the *equilibrated* deprotonation procedure (Et₃N, CH₃CN or CH₂Cl₂, r. t.) was also used in the case of **Wa** (90% yield of **1a** according to¹⁴). So, when *ortho*- and terephtalaldehydes were reacted with the fairly stabilized P-reagents **Wa** and **Pb**, we isolated the expected compounds: **1b**(*) (75%, yellow solid, recrystallized from chloroform-hexane, m.p. 175°C), **2a** (83%, red needles from dichloromethane, m.p. 234-235°C), and **2b**²⁰ (40%, yellow powder, washed with THF, m.p. 291°C with decomp.).

The syntheses of **3a-c** through four-fold Wittig reactions of benzene-1,2,4,5-tetracarboxaldehyde with **Wa-c** occured happily thanks to its previous conversion into 1,2,4,5- tetravinylbenzene with $Ph_3P=CH_2$.²¹ Thus, when the tetraaldehyde (previously dried for 8 hrs at 130°C) was reacted with the phosphoranes **Wa-c** (10% excess), the corresponding **3a-c**^(**) precipitated as brightly-coloured powders and these were respectively isolated in 50, 90 and 59% yields after subsequent washings with methanol, acetonitrile and diethyl ether.



As they strongly depend on the nature of the solvents used, cyclic voltammograms of 1-3 were recorded in N,N-dimethylformamide (DMF) and in 1,1,2-trichloroethane (TCE) (see table). With the

exception of **3b**, the Epa₁ values are lower in DMF than in TCE, in agreement with the solvent effect.²² As expected, the π -donating abilities are dependent upon the electronic effect of the R substituents and the best case does correspond to the derivative **3c**, its reducing character being slightly lower than that of TTF (Epa₁= 0.38 V.SCE in DMF). Compounds 1-3 generally exhibit two irreversible anodic peaks, the second often being poorly defined, with the exception of **3c** in TCE for which two reversible systems are observed. In this case, the difference between Epa₁ and Epc₁ of the fully reversible first system is about 0.06 V (see table) in agreement with a one-electron transfer;²³ the difference between Epa₂ and Epc₂ (0.12 V) shows the second one-electron system to be quasi-reversible. Finally, the slight difference between the two anodic peaks (Epa₂ - Epa₁= 0.15 V) suggests a weak coulombic repulsion in the dicationic states of **3c** which should allow it to be a suitable precursor of conducting salts.

Thus, when a 1,2-dichloroethane solution of 3c and tetracyanoquinodimethane (TCNQ) was refluxed, a 1:1 molar ratio²⁴ complex was precipitated as black shiny needles, m. p. 308°C, with $\sigma = 10^{-3}$ S.cm⁻¹(measured on compressed pellet by the two-probe technique). Moreover, generating cation-radicals salts by anodic oxidation in the presence of Buⁿ₄N+X⁻ (X = ClO₄, BF₄, I₃) proved to be feasible, but conducting powders which are unfortunately only microcrystalline were produced, and attempts to grow single crystals are still under way.

	1a	1b	2a	2 b	3a	3b	3c
<u> </u>			· · · · · · · · · · · · · · · · · · ·	DMF			
Epa ₁	1.04	0.85	0.88	0.72	0.85	0.68	0.46
Epa ₂	a	0.95 ^b	1.08	0.86 ^b	0.99	_a	_a
				TCE			
Epa ₁	1.20	0.93	1.03	d	0.96	0.68	0.57
Epa ₂	a	1.05	a,c	b	1.15	0.96	0.72

Table. Oxidation peaks potentials (V.SCE) determined by cyclic voltammetry: Pt electrode, 20°C, under nitrogen, $Bu^n_4NClO_4$ 0.1 mol.l⁻¹ in DMF or TCE, scan rate 0.2 V.s⁻¹.

a no well-defined peak appears at more anodic potential

b two other poorly-defined anodic peaks are present at more anodic potential

c existence of a cathodic peak

d sparingly soluble

e reversible processes: cathodic peak potentials, $Epc_1 = 0.50$, $Epc_2 = 0.60$.

We thank the Agence Nationale de Valorisation de la Recherche (ANVAR) and the Centre National d'Etudes des Télécommunications (CNET) for financial support, and the CNRS and the Région des Pays de la Loire for a grant (to M. S.).

REFERENCES AND NOTES

- a) F. Wudl, G.M. Smith and E.J. Hufnagel, J. Chem. Soc., Chem. Commun., 1970, 1453; b) F. 1 Wudl, D.Wobshall and E.J. Hufnagel, J. Am. Chem. Soc., 1972, 94, 670; c) J. Ferraris, D.O. Cowan, V.V. Walatka and J.H. Perlstein, J. Am. Chem. Soc., 1973, 95, 948.
- For general reviews see a) M. R. Bryce, Aldrichim. Acta, 1985, 18, 73; b) M. R. Bryce and L. C. 2 Murphy, Nature, 1984, 309, 119; c) J. H. Perlstein, Angew. Chem., Int. Ed. Engl., 1977, 16, 519; d) D. J. Sandman and G. P. Ceasar, Isr. J. Chem., 1986, 27, 293.
- For reviews about TTF chemistry see a) A. Krief, Tetrahedron, 1986, 42, 1209; b) M. Narita and C. 3 U. Pittman, Synthesis, 1976, 489.
- H. Inokuchi, Angew. Chem., Int. Ed. Engl., 1988, 27, 1747. 4
- A. M. Kini, V. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwock, K. G. 5 Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung and M. Whangbo, Inorg. Chem., 1990, 29, 2555.
- Z. I. Yoshida and T. Sugimoto, Angew. Chem., Int. Ed. Engl., 1988, 27, 1573. 6
- a) T. Sugimoto, H. Awaji, I. Sugimoto, I. Misaki, T. Kawase, S. Yoneda and Z.I. Yoshida, Chem. Materials, 1989, 1, 535; b) M. Sato, N. C. Gonnella and M. P. Cava, J. Org. Chem., 1979, 44, 7 930; c) A. Belyasmine, Thesis, Rennes, July 5, 1990. I. Misaki, Y. Matsumura, T. Sugimoto and Z. I. Yoshida, *Tetrahedron Lett.*, 1989, **30**, 5289.
- H. Awaji, T. Sugimoto and Z. I. Yoshida, J. Phys. Org. Chem., 1988, 1, 47. 10
- a) A. Khanous, A. Gorgues and F. Texier, Tetrahedron Lett., 1990, 31, 7307; b) A. Khanous, A. Gorgues and M. Jubault, Tetrahedron Lett., 1990, 31, 7311.
- a) M. R. Bryce, A. J. Moore, D. Lorcy, A. S. Dhindsa and A. Robert, J. Chem. Soc., Chem. 11 Commun., 1990, 470; b) M. R. Bryce and A. J. Moore, Synth. Metals, 1988, 25, 203; c) idem, 27, 557; d) idem, Tetrahedron Lett., 1988, 29, 1975; e) Y. Yamashita, Y. Kobayashi and T. Miyashi, Angew. Chem., Int. Ed. Engl., 1989, 28, 1052; f) Y. Yamashita and T. Miyashi, Chem. Lett., 1988, 664; g) Y. Yamashita, T. Suzuki and T. Miyashi, idem, 1989, 1607; see also 20.
- K. Takahashi and T. Nikira, Tetrahedron Lett., 1989, 30, 5903 and ref. cited. 12
- W. Frank and R. Gompper, Tetrahedron Lett., 1987, 28, 3083. 13
- 14
- 15
- M. V. Lakshmikantham, M.P. Cava and P. J. Caroll, J. Org. Chem., 1984, 49, 726. M. G. Miles, J. S. Wager, J. D. Wilson and A. R. Siedle, J. Org. Chem., 1975, 40, 2577. R. R. Shumaker, S. Rajeswari, M. V. Joshi, M. P. Cava, M. A. Takassi and R. M. Metzger, J. Am. Chem. Soc., 1989, 111, 308. 16
- 17 N. Soyer, M. Kerfanto and D. Raphalen, Bull. Soc. Chim. Fr., 1975, 2121.
- a) E. A. Manhal, Thesis, Montpellier, Oct. 17, 1985; b) L. Giral, J. M. Fabre and A. Gouasmia, 18 Tetrahedron Lett., 1986, 27, 315; c) J. M. Fabre, L. Giral, A. Gouasmia, H. J. Cristau and Y Ribeill, Bull. Soc. Chim. Fr., 1987, 823.
- K. Akiba, K. Ishikawa and N. Inamoto, Bull. Chem. Soc. Jpn, 1978, 51, 2674 and ref. cited. 19
- 20 Another route to compound 2b has recently been described: M. R. Bryce, E. Fleckenstein and S. Hünig, J. Chem.Soc. Perkin Trans 2, 1990, 1777.
- T. Schrievers and U. H. Brinker, Synthesis, 1988, 331. 21
- 22 D.L. Lichtenberger, R.L. Johnston, K Hinkelmann, T. Suzuki and F. Wudl, J. Am. Chem. Soc, 1990, 112, 3302.
- 23 Electrooxydation in Organic Chemistry; the Role of Cation Radicals as Synthetic Intermediates, ed. by K. Yoshida, J. Wiley, New York, 1984, chapter I.
- 24 Determined from elementary analysis.
- Under acidic conditions (SiO₂, or by standing of its CHCl₃ soln.), this compound undergoes a cyclisation into an isomeric derivative whose structure elucidation is in progress. For a preliminary report, see7c. Similar conversion, with R=H or Me, has also been observed by I. Johannssen et al. (personal communication).
- All new compounds gave satisfactory elemental analyses and spectral data. Compound **3a**: bright orange powder; m.p. 221-226°C (THF); ¹H n.m.r. [(²H₆)-Dimethylsulphoxyde (DMSO)] 3.77 (s, 12H), 3.81 (s, 12H), 6.70 (s, 4H), 7.06 (s, 2H); i.r.(nujol) 1730 cm.-1 Compound 3b: bright yellow powder; m.p.>260°C (chlorobenzene); ¹H n.m.r. ((²H₆)-DMSO) 6.86 (s, 4H), 7.17-7.56 (m, 16H), 7.61(s,2H).

Compound 3c: orange powder; m.p.159°C (decomp.) (chlorobenzene); ¹H n.m.r. ((²H₆)-DMSO) 6.65 (d, 4H), 6.66 (s, 4H), 6.77 (d, 4H), 7.41 (s, 2H); ¹³C n.m.r. ((²H₆)-DMSO) 109.32 (d), 117.99 (d), 118.59 (d), 121.58 (d), 131.75 (s), 138.36 (s); m.s. thermal decomp.

(Received in France 20 February 1991)