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A New Building Block for Diels–Alder Reactions in π-Extended Tetrathiafulvalenes: Synthesis of a Novel Electroactive C_{60}-Based Dyad

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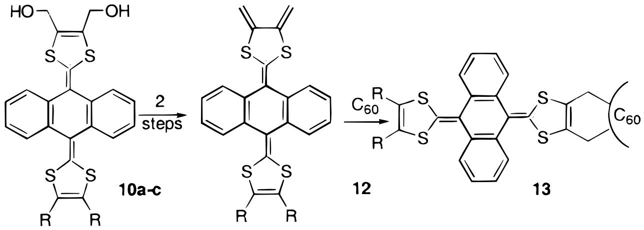
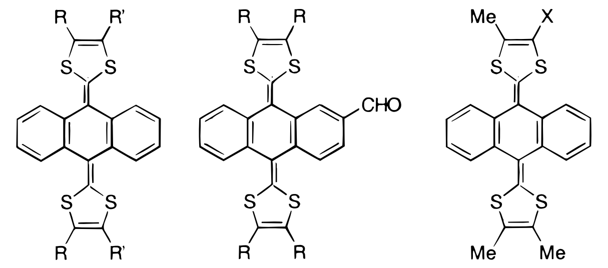
ABSTRACT



The synthesis of quinonoid π-extended tetrathiafulvalene (TTF) derivatives bearing two hydroxymethyl groups on one 1,3-dithiole ring (10) have been prepared in seven steps from commercially available ethylene trithiocarbonate. From these compounds, the transient 4,5-dimethylene intermediate (12) has been favorably generated and trapped in situ by the reactive dienophile C_{60} to form the first Diels–Alder cycloaduct of a π-extended TTF (13).

Tetrathiafulvalene (TTF) derivatives with extended π-conjugation are an important class of electron-donor systems which present remarkable differences with the parent TTF in terms of oxidation potential values, geometry, and charge delocalization.[1−3] In particular, *p*-quinodimethane analogues of TTF such as **1** and **2** (Figure 1) show a saddle-shaped structure, due to the steric hindrance caused by benzoannulation of the quinonoid moiety,[4] which is in contrast to the almost planar structure of the TTF molecule.[5]



1a: R = R' =H
1b: R = R' = Me
1c: R =SMe, R' = Me

2a: R = H
2b: R = SMe
2c: R = $(SCH_2)_2$

3: X = Li; CHO; C(S)NHMe; CO_2Me; SC(O)Ph; SMe; $S(CH_2)_6OH$

Figure 1.

Despite the highly distorted geometry, compound **1** forms electrically conducting charge-transfer complexes with tetracyano-*p*-quinodimethane.[3] Other properties such as nonlinear optics[6] or photovoltaics,[7] when the compounds are covalently linked to an electron-acceptor unit, have been also reported. However, a chemical functionalization is still required for the systematic study of the properties shown by these quinonoid π-extended TTFs. Although some derivatives

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[4] Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268−1279 and references therein.
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[6] Herranz, M. A.; Martín, N.; Sánchez, L.; Garín, J.; Orduna, J.; Alcalá, R.; Villacampa, B.; Sánchez, C. *Tetrahedron* **1998**, *54*, 11651−11658.
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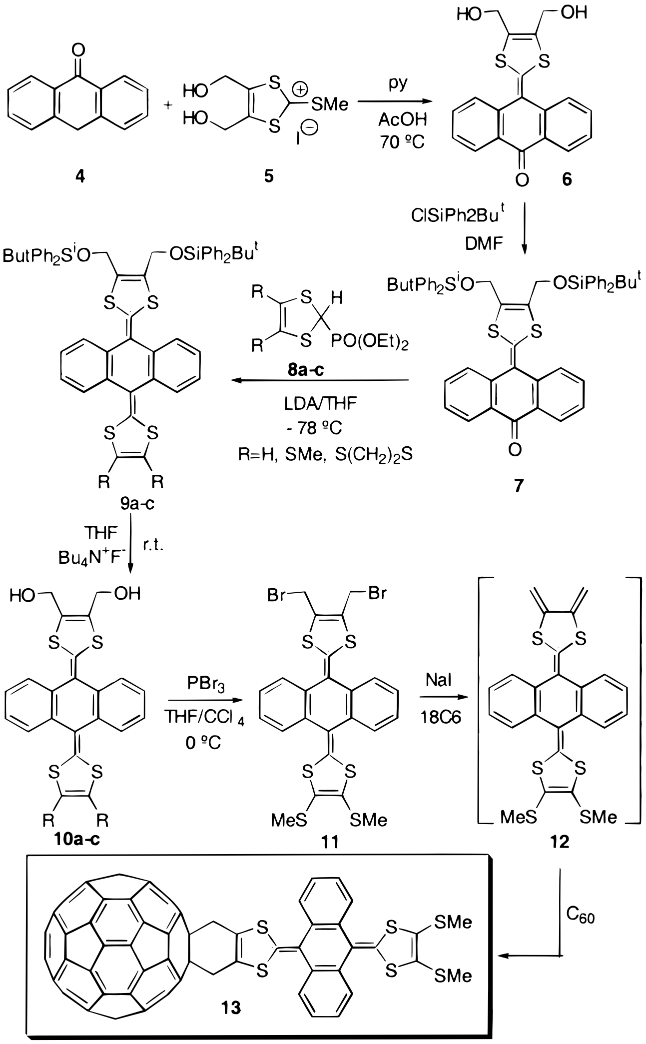
bearing a functional group on the central hydrocarbon skeleton (**2**) are known,[8] the synthesis of appropriately monofunctionalized quinonoid π-extended derivatives **3** has been only recently reported.[9]

In this Letter we report on the preparation of novel 4′,5′-functionalized 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives **10** and **11** as precursors of the elusive intermediate 4′,5′-dimethylene derivative **12**. This *o*-quinodimethane analogue[10] of the 1,3-dithiol-2-ylidene moiety **12** undergoes a rapid [4 + 2] cycloaddition reaction with [60]-fullerene as the dienophile to form a novel C_{60}-based donor−acceptor dyad (**13**).

This first example of a Diels−Alder reaction involving a quinonoid π-extended TTF derivative facilitates the use of cycloadditions as a useful tool for the preparation of other more sophisticated π-extended TTF derivatives. In this regard, our present approach complements the recently reported [4 + 2] cycloadditions of the parent 2,3-dimethylene-TTF to C_{60}.[11]

The synthesis of the novel diols **10a**−**c** is shown in Scheme 1. Thus, reaction of the anion of anthrone **4** with the dithiolium salt **5**, prepared in a three-step synthetic procedure by following the method reported in the literature,[12] affords compound **6** in 54% yield. Introduction of the second 1,3-dithiol unit in **6** requires the previous protection of hydroxyl groups, which was carried out with *tert*-butyldiphenylsilyl chloride ($ClSiPh_2{}^tBu$) in 81% yield. Olefination reaction of bis-protected diol **7** with the anion of the phosphonate esters **8a**−**c**[13] generated in the basic medium led to the protected quinonoid π-extended TTFs **9a**−**c** in good yields. Further deprotection of **9a**−**c** was carried out by using tetrabutylammonium fluoride to give diols **10a**−**c**,[14] which were further purified by flash chromatography using hexane:ethyl acetate (1:1) as eluant.

Scheme 1



9-(4,5-Dihydroxymethyl-1,3-dithiol-2-ylidene)-10-(1,3-dithiol-2-ylidene)-9,10-dihydroanthracenes **10** are interesting electron donors for the preparation of salts and charge-transfer complexes since, in addition to their strong electron-donor character, they present two -OH groups which are able to form a net of hydrogen bonds, thus increasing the dimensionality in the solid state. Bryce has recently reviewed the importance of TTF systems endowed with hydroxy substituents in order to gain control of crystal architectures.[15] In this regard, the strength, directionality, and selectivity of the hydrogen bond make it an excellent candidate to increase the dimensionality and hence the conductivity in π-extended TTF derivatives.

Diols **10** react with phosphorus tribromide in THF/CCl_4 at 0 °C to form dibromomethyl derivatives **11**. Thus, when compound **10b** was treated with PBr_3 under these conditions, **11** was obtained in 71% yield as an orange solid which could be stored in the refrigerator for a few days without decomposition.

Among the different methods reported in the literature for the generation of *o*-quinodimethanes and related heteroanalogues,[10] iodide-induced 1,4-dehydrohalogenation has played a very important role. By using this method, in the presence of 18-crown-6 ether, the transient 4,5-dimethylene

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(14) Selected spectroscopic data for **10b**: 79% yield; FTIR (KBr disk) v (cm^{-1}) 2922, 2853, 1528, 1499, 1445, 1385, 1283, 1171, 1049, 999, 947, 858, 779, 756, 675, 644, 625; ^1H NMR (DMSO-d_6, 300 MHz) δ 7.61−7.58 (2H, m), 7.51−7.48 (2H, m), 7.40−7.36 (4H, m), 5.43 (2H, t, J = 5.8, -OH), 4.27 (2H, dd, J_1 = 13.7, J_2 = 5.8), 4.19 (2H, dd, J_1 = 13.7, J_2 = 5.8), 2.4 (6H, s); ^{13}C NMR (DMSO-d_6, 50 MHz) δ 134.4, 134.1, 133.6, 129.6, 129.4, 126.7, 126.2, 125.3, 125.0, 124.8, 123.6, 120.8, 56.0 ($-CH_2OH$), 18.4 ($-SCH_3$); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) nm 242 (4.52), 266 (4.21), 364 (4.15), 430 (4.40); MS (*m*/*z*) 532 (M$^+$, 100%), 514 (M − 18, 68%).

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intermediate **12** was generated in situ and reacted with a good dienophile such as C_{60} to form the Diels−Alder cycloaduct as a yellow-brown solid in 25% yield (37% yield based on recovered C_{60}).[16]

The UV−vis spectrum of **13** shows absorption bands at 424 (4.33) and 442 (4.39) nm which are assigned to the π-extended donor moiety (**10b**: 420 and 430 nm), thus hiding the characteristic weak absorption band at $\lambda = 430$ nm of dihydrofullerenes. The ^{13}C NMR spectrum shows a peak observed at 77.4 ppm, characteristic of those quaternary sp^3-hybridized carbons of attachment to the substituent, thus confirming the linkage of the organic addend on a [6,6] ring junction of the C_{60} core. Confirmation of the structure was carried out by MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometry which showed the molecular ion at *m*/*z* 1219.

The solution redox properties of the new compounds have been investigated by cyclic voltammetry. 4,5-Dihydroxymethyl π-extended TTF derivatives **10** showed the presence of a quasireversible oxidation wave involving a two-electron process to form the dication. This fact had been previously confirmed by Coulometric analysis of other related π-extended derivatives (Table 1).[17]

Table 1. Cyclic Voltammetry Data at Room Temperature for π-Extended TTFs (**10**) and C_{60}−TTF Dyad (**13**)[a]

compound	E^1_{ox}	E^1_{red}	E^2_{red}	E^3_{red}	E^4_{red}
C_{60}		−0.60	−1.00	−1.52	−2.04
13	0.75 (2e$^-$)	−0.72	−1.17	−1.75	−2.30
10a	0.53 (2e$^-$)				
10b	0.60 (2e$^-$)				
1a[b]	0.44 (2e$^-$)				

[a] Experimental conditions: toluene:MeCN (4:1), V vs SCE, GCE as working electrode, $Bu_4N^+ClO_4^-$ as supporting electrolite; 200 mV s^{-1}. [b] Measured in CH_2Cl_2.

Substitution on the 1,3-dithiole ring in **10** results in a shift of the oxidation potential to more positive values. The electrochemical redox behavior of **10b** was studied at different temperatures. The oxidation potentials are anodically shifted as the temperature decreases [E_{ox}(40 °C) = 0.55 V; E_{ox}(rt) = 0.60 V; E_{ox}(0 °C) = 0.67 V; E_{ox}(−78 °C) = 0.89 V], which indicates a greater difficulty in the formation of the dication species. A much more remarkable effect is observed in the wave associated with the process donor^{2+} → donor°, which undergoes a drastic cathodic shift when the temperature is decreased [E_{red}(40 °C) = 0.17 V; E_{red}(rt) = 0.10 V; E_{red}(0 °C) = 0.01 V, E_{red}(−78 °C) = −0.27 V]. This behavior has been interpreted as an indication of the high stability of the former dications.[17]

C_{60}-Based dyad **13** shows, in addition to the oxidation wave of the donor fragment to form the dication, the presence of four quasireversible reduction waves, similar to those observed for the parent C_{60}. These reduction potentials are slightly shifted to more negative values than those of C_{60} due to the saturation of a double bond which raises the LUMO energy of the molecule (Table 1).[18] It is important to note that the redox values are remarkably shifted in comparison with both donor and acceptor independent units which suggests a kind of electronic interaction between them.

In conclusion, we have reported the synthesis of dihydroxymethyl quinonoid π-extended TTF derivatives **10** which are appealing systems for the preparation of salts and CT complexes with higher dimensionality. These compounds (**10**) have been used as starting materials for obtaining the respective dibromides (**11**) which can favorably generate the first heteroanalogue *o*-QDM of a π-extended TTF. The facile generation of these reactive intermediates paves the way for use of cycloadditions for the design and synthesis of more elaborate π-extended TTF derivatives. As a practical application, we have prepared the first C_{60}-based donor−acceptor dyad by Diels−Alder reaction of C_{60} and a π-extended TTF derivative, which has been spectroscopically and electrochemically characterized. These dyads bearing π-extended TTFs connected to the C_{60} core through a rigid spacer are excellent candidates for photovoltaic devices.[19] Photophysical studies on these novel systems (**13**) as well as preparation of CT complexes by mixing donors **10** with strong electron acceptors are currently in progress.

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[16] Selected spectroscopic data for **13**: 25% yield (37% based on recovered C_{60}); FTIR (KBr disk) υ (cm^{-1}) 2915, 1522, 1496, 1443, 1426, 1281, 1182, 968, 766, 752, 696, 674, 642, 623, 575, 553, 526; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.84−7.79 (2H, m), 7.57−7.54 (2H, m), 7.38−7.29 (4H, m), 4.38 (2H, d, J = 14.7), 4.31 (2H, d, J = 14.7), 2.43 (6H, s); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) nm 260 (4.99), 316 (4.52), 424 (4.33), 442 (4.39), MALDI-TOF *m*/*z* 1219 (M$^+$ 82%), 498 (diene, 100%).

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