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Base-catalyzed condensation of cyclopentadiene derivatives. Synthesis of fulvalene analogues: strong proaromatic electron acceptors

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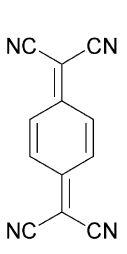
Abstract—A series of proaromatic electron acceptors derived from fulvenes were synthesized from tetrachlorocyclopentadiene and previously unknown 1,4-dicyano- and 1,4-dialkoxycarbonyl-2,3-dimethoxy cyclopentadienes. Two reversible one-electron reductions steps observed for fulvalenes coalesce into one two-electron reduction step upon increasing the length of the conjugating bridge.

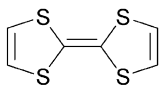
1. Introduction

Recent theoretical[1] and synthetic[2] studies on fulvalene (1,1′-bi(cyclopenta-2,4-dien-1-ylidene)) derivatives demonstrated renewed interest to this class of cross-conjugated polyenes. In particular, these derivatives should possess properties of proaromatic electron acceptors, i.e. afford the aromatic dianions upon two-electron reduction.[3] A majority of strong organic electron acceptors employed in the synthesis of donor–acceptor charge transfer complexes is based on the *p*-benzoquinone parent system,[4] of which tetracyanoquinodimethane (**1**) is the most popular example. Employing proaromatic acceptors based on fulvalenes in combination with popular proaromatic electron donors based on tetrathiafulvalenes (TTF, **2**) could give a promising series of organic conductors.[5] Unfortunately, very limited data on the accepting properties of pentafulvalenes are available and from the synthetic point of view these compounds still present a challenge. Whereas the parent compound is unstable, the perchloro derivative is a stable compound widely used as a diene or alkene component in the Diels–Alder type of cycloaddition reactions[6] and is capable of charge transfer complex formation with electron donors.[7] The tetraamino substituted fulvalenes were shown to undergo both reversible reduction and oxidation processes.[8] Recently, a series of fulvalenes and their vinylogs was studied by the CV technique. In particular, perchlorofulvalene (**3**) was shown to undergo two-step one-electron reduction, affording the aromatic anion.[9]

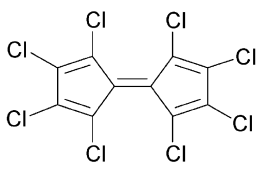
Here we report on synthesis and properties of a series of new fulvalene vinylogs.



TCNQ, **1**



TTF, **2**



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2. Results and discussion

All fulvalenes described in this study were prepared starting from the corresponding substituted cyclopentadiene derivatives **4**, **7a**, **7b** and **7c**.

Tetrachlorocyclopentadiene (**4**) was prepared according to known procedure.[10] The synthesis of cyclopentadiene derivatives **7a**–**7c** was achieved starting from the corresponding dihydroxycyclopentadienes **6a**–**6c** (Scheme 1).

Keywords: condensation; electron acceptors; fulvalene.
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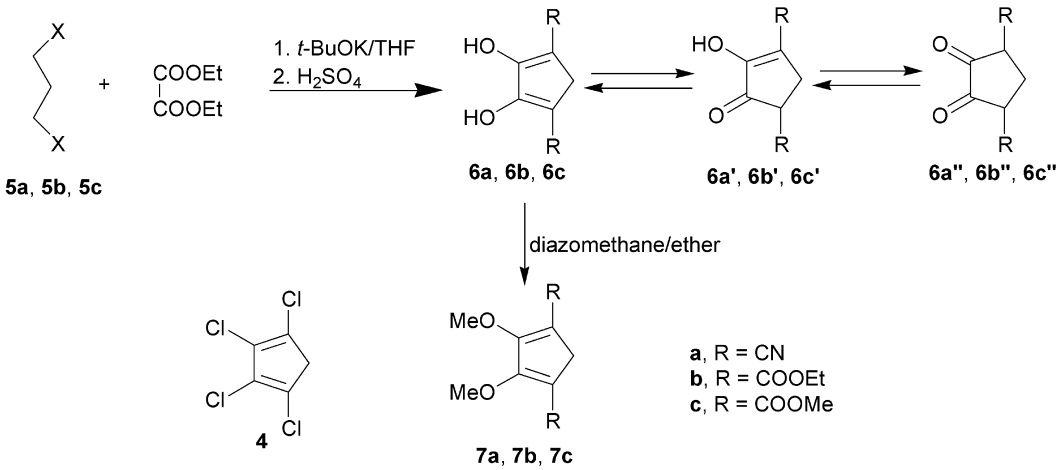


Scheme 1.

The cyclocondensation of glutaronitrile and diethyl oxalate was first reported by Dieckmann in 1894.[11]

In attempts to reproduce the synthesis, Friedrich reported that the 1,4-dicyano-2,3-dihydroxycyclopentadiene is formed as a by-product with yield which did not exceeded 20%.[12] More recently, an improved approach to **6a** using *t*-BuOK/THF was published, but the experimental details were not reported. The dipotassium salt of **6a** was employed for further derivatization[8] and, to the best of our knowledge, the chemical properties of **6a** have never been described.

The dipotassium salt of **6a** was obtained using *t*-BuOK in THF in a quantitative yield. The corresponding neutral compound precipitated from water solution of the salt upon acidification only at low temperatures. Under the same experimental conditions, known cyclopentadiene derivatives **6b** and **6c** were obtained in high yields starting from diethyl and dimethyl glutarate (**5b** and **5c**), respectively. According to the solid state IR spectrum of **6a** and its ^{1}H NMR spectrum in DMSO, this compound exists as a dienolic form both in solid and in solution. The diesters **6b** and **6c**, according to the X-ray structure determined for **6b** (Fig. 1), exist also as dienols in solid state (The atoms H1–H4 were located from Fourier difference synthesis and refined isotropically, the remaining H atoms in all the crystal were located without affinement). Noteworthy, strong intramolecular hydrogen bonds were observed for **6b** between H01 and O3 (δ=2.214(32) Å, O1–H01–O3 133.6°) and between H02 and O5 (δ=2.102(29) Å, O2–H02–O5 133.1°).

In chloroform, the ^{1}H NMR spectrum indicated the existence of both the dienolic form **6b** (60%) as well as the monoketo form **6b′** (40%). In DMSO solution, the presence of about 35% of dienolic form **6b** and 65% of monoketo form **6b′** was observed. The similar ^{1}H NMR spectral features were observed for compound **6c**. Interestingly, the diketo forms **6a″**–**6c″** were not observed.

Both hydroxyl groups in **6a** can be smoothly methylated using an excess of diazomethane and the corresponding 1,4-dicyano-2,3-dimethoxycyclopentadiene **7a** was obtained in a high yield. The molecular structure of **7a** is shown in Figure 2. The same method can be applied for methylation of **6b** and **6c** and 1,4-dialkoxycarbonyl-2,3-dimethoxycyclopentadiene derivatives **7b** and **7c** were prepared in high yields (Scheme 1).

Condensation of cyclopentadiene derivatives **7a**, **7b** and **4** with terephthaldicarboxaldehyde or 2,5-thiophenedicarbaldehyde afforded bis-fulvenes (fulvalene vinylogs) **8**–**13** (Scheme 2). The optimal yields were obtained when piperidine was used as a base in acetic acid solution. Our initial experiments on condensation of **4** and terephthaldicarboxaldehyde made in methanol in presence

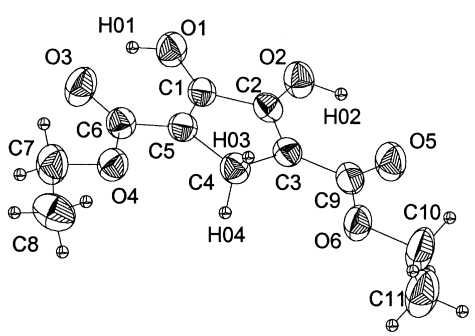


Figure 1. X-Ray crystal structure of **6b**. Selected bond length: 1.472(3) Å (C1–C2), 1.351(4) Å (C2–C3), 1.491(4) Å (C3–C4), 1.496(4) Å (C4–C5), 1.350(4) Å (C1–C5), 1.331(3) Å (C1–O1), 1.338(3) Å (C2–O2), 0.88(3) Å (O1–H01), 0.94(3) Å (O2–H02).

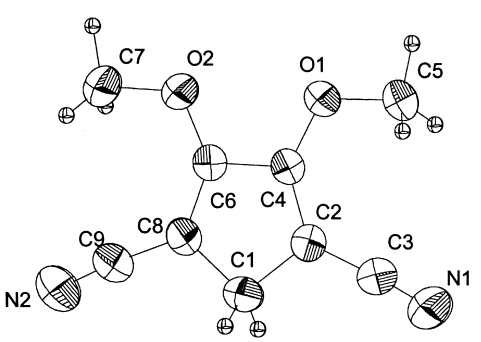
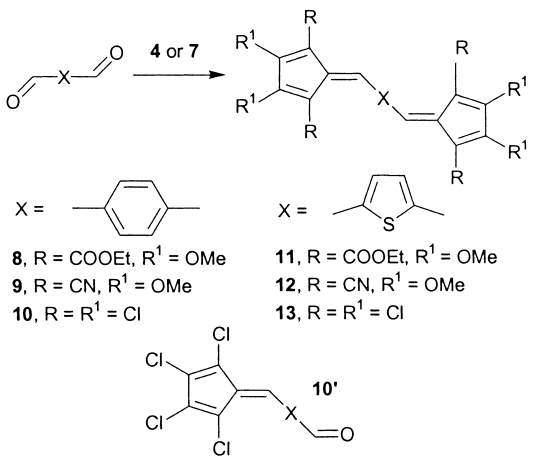


Figure 2. X-Ray crystal structure of **7a**. Selected geometric parameters: 1.507(2) Å (C1–C2), 1.502(3) Å (C1–C8), 1.360(2) Å (C2–C4), 1.470(3) Å (C4–C6), 1.360(2) Å (C6–C8).



Scheme 2.

of pyrrolidine afforded monofunctionalised derivative **10′** as small blue monocrystals suitable for X-ray structure determination. As shown in Figure 3, this derivative is not planar owing to the steric hindrance between the Cl atoms and aromatic periplanar protons.

We found that the same reaction conditions are effective for the synthesis of other π-extended derivatives. Thus, vinylogs **14**–**16** were prepared in good yields starting from glyoxal ethylenediacetal **4**, **7c** and **7a′**, respectively

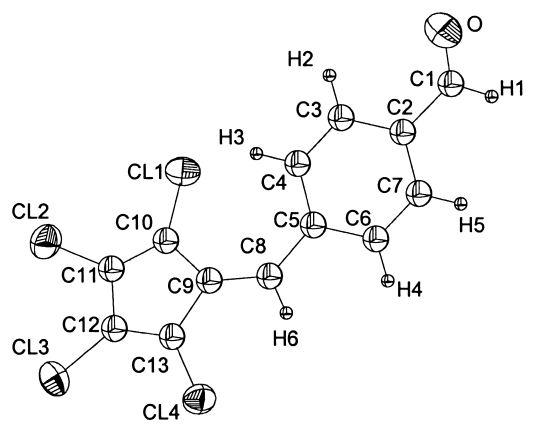
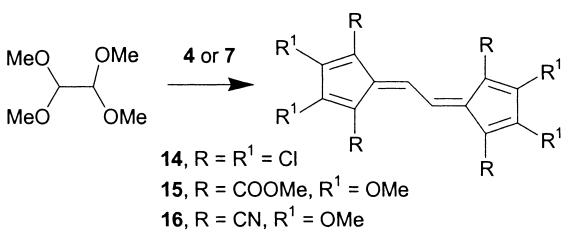


Figure 3. X-Ray crystal structure of **10′**. Selected geometric parameters: 1.474(9) Å (C1–C2), 1.394(8) Å (C2–C3), 1.369(8) Å (C3–C4), 1.393(8) Å (C4–C5), 1.401(8) Å (C5–C6), 1.384(8) Å (C2–C7), 1.359(9) Å (C6–C7), 1.459(8) Å (C5–C8), 1.348(8) Å (C8–C9), 1.473(8) Å (C9–C10), 1.328(8) Å (C10–C11), 1.449(8) Å (C11–C12), 1.342(8) Å (C12–C13), 1.483(8) Å (C9–C13), torsion angle C4–C5–C8–C9=39.5°.



Scheme 3.

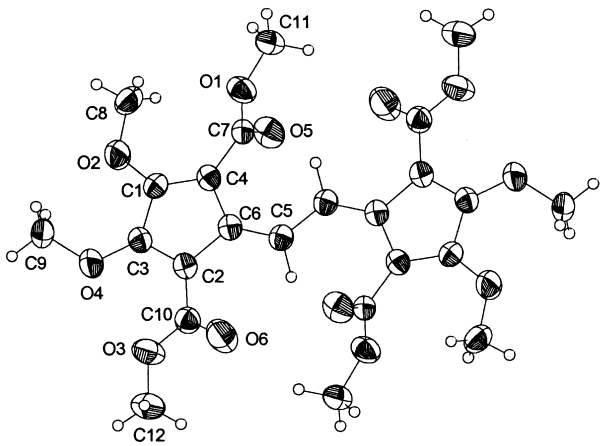
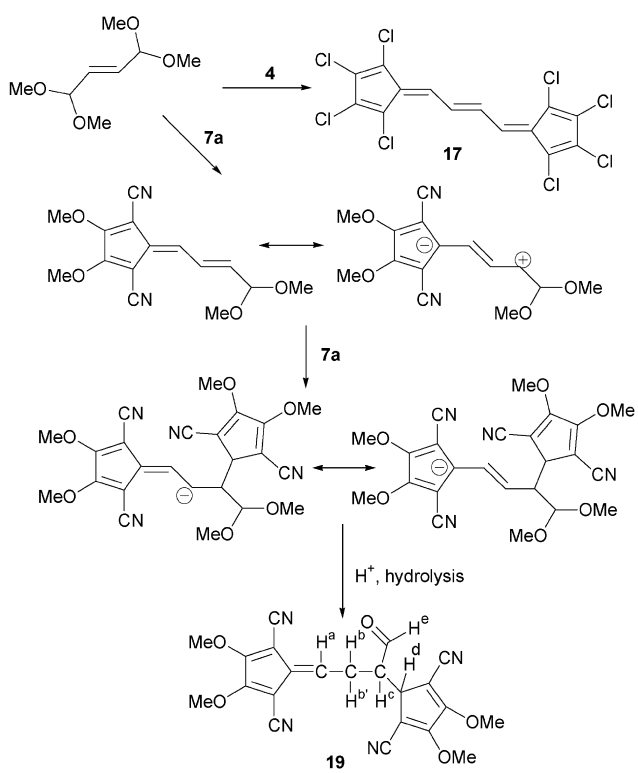


Figure 4. X-Ray crystal structure of **15**. Selected geometric parameters: 1.460(6) Å (C1–C3), 1.382(5) Å (C2–C3), 1.466(6) Å (C2–C6), 1.474(5) Å (C4–C6), 1.355(6) Å (C1–C4), 1.372(5) Å (C5–C6), 1.420(6) Å (C5–C5′), torsion angle C5′–C5–C6–C4 1.76(70); C5′–C5–C6–C2 179.77(78)°.

(Scheme 3). The structure of derivative **15** was determined by the single crystal X-ray diffraction experiment (Fig. 4).

Interestingly, the bis-cyclopentadieneylidene ethane moiety is planar, which indicates efficient conjugation. Surprisingly, although derivative **17** was prepared by the same method starting from **4** and 1,1,4,4-tetramethoxy-2-butene in a good yield, the attempted synthesis of **18** under the same conditions afforded, a product, spectroscopic properties of which corresponded to the structure **19** (80% yield) (Scheme 4). The structure of **19** was confirmed by the single crystal X-ray analysis (Fig. 5). The presence of two oxygen



Scheme 4.

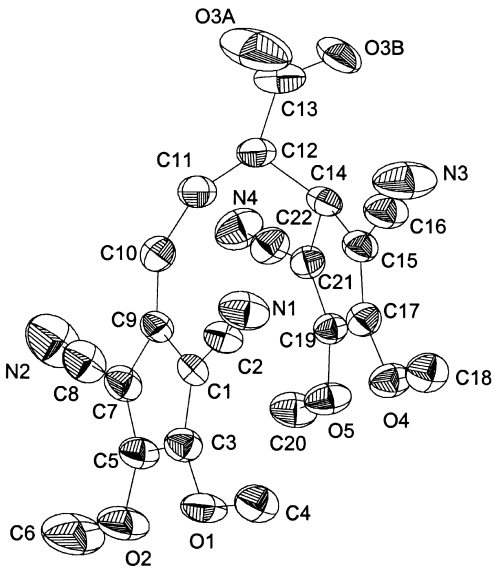
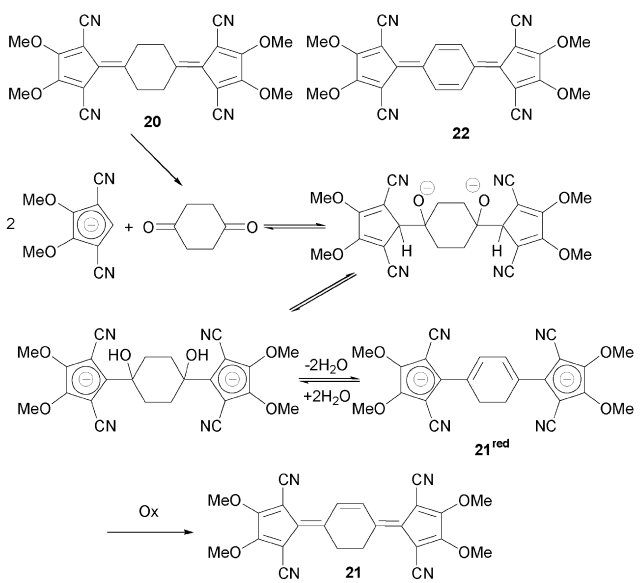


Figure 5. X-Ray crystal structure of **19**. Selected geometric parameters: 1.416(8) Å (C1–C2), 1.368(7) Å (C1–C3), 1.481(7) Å (C1–C9), 1.456(7) Å (C3–C5), 1.358(8) Å (C5–C7), 1.411(8) Å (C7–C8), 1.466(7) Å (C7–C9), 1.324(7) Å (C9–C10), 1.499(7) Å (C10–C11), 1.542(8) Å (C11–C12), 1.507(9) Å (C12–C13), 1.542(7) Å (C12–C14), 1.532(7) Å (C14–C15), 1.508(7) Å (C14–C21), 1.411(8) Å (C15–C16), 1.354(7) Å (C15–C17), 1.452(7) Å (C17–C19), 1.336(7) Å (C19–C21), 1.421(8) Å (C21–C22).

atoms at C13 is attributed to the positional disorder in the crystal.

Condensation of **7a** with 1,4-cyclohexanedione was also studied. Our initial attempts using a previously published procedure[13,14] involving excess of pyrrolidine and methanol failed and the starting materials were invariably recovered after the work-up. We found that the reaction outcome depended not only on solvent and a basic catalyst, but on the presence of air in the reaction mixture. Thus, using DMF and a slight excess of piperidine as a base in the presence of air, derivative **21** was isolated as the only product in 71% yield after stirring the reaction mixture at room temperature for 30 min, followed by addition of water and acidification. Derivative **20** was never detected in the reaction mixture and when the reaction was carried out under inert atmosphere, only the starting materials were isolated. A possible explanation of the above finding involves the possibility that the reduced form of **21**, i.e. **21**^{red}, formed *reversibly* as shown at Scheme 5. The reduction potential of **21** in methylene chloride is as low as −0.40 V (vs SCE) and as soon as **21**^{red} forms in the reaction mixture it can be irreversibly oxidized by oxygen. This assumption is indirectly corroborated by the observation that reversible two-electron reduction of **21** becomes irreversible in the presence of water.



Scheme 5.

Oxidation of **21** to the corresponding *p*-quinoid derivative **22** was attempted under a variety of reaction conditions. No reaction was observed with DDQ in toluene and only the starting material was recovered after refluxing for 24 h. Bromination of **21** using bromine or NBS also failed. Further attempts of oxidation of **21** are currently under way.

Condensation of tetrachlorocyclopentadiene (**4**) with 1,4-cyclohexanedione under the same conditions led to formation of a black polymeric precipitate within a few minutes. Noteworthy, polymerization was also observed during attempts to prepare bis-fulvenes derived from cyclopentadiene.[14]

Although no general synthetic approaches to pentafulvalenes are known, oxidative coupling of the cyclopentadiene anion can be synthetically the simplest and use of copper(II) chloride for the purpose is documented.[15] This method applied to **7a** gave only a complicated mixture of decomposition products. However, we found that silver nitrate smoothly reacted with potassium salt of **7a** in water and black insoluble silver cyclopentadienide **23** precipitated from the solution. Refluxing thoroughly dried **23** in toluene afforded 1,1′-bi(cyclopenta-2,4-dien-1-ylidene)-2,2′,5,5′-tetracarbonitrile **24** in 64% yield. The molecular structure of **24** was determined by X-ray single crystal measurements and was described previously.[9] In contrast, the reaction of **7b** with silver nitrate leads to formation of *colorless* precipitate, insoluble in water and organic solvents. This salt appeared to be very stable and did not decompose even during prolonged reflux in *o*-dichlorobenzene.

The above experiments clearly demonstrate the considerable difference in reactivity within a series of derivatives **4**, **7a** and **7b**. Quantum mechanical calculations were performed for these compounds and their corresponding anions to get deeper understanding of their behavior. All structures were optimized at the semiempirical AM1 level. Using calculated heats of formation and the experimental value (367.2 kcal m^{-1}) for H^+ enthalpy of formation,

Table 1. Proton affinities of cyclopentadiene derivatives (AM1//AM1)

Anion of	Charge on C1	E_{HOMO} (eV)	Proton affinity (kcal m^{-1})
CP	−0.268	−2.3	355.3
4	−0.209	−3.63	325.8
7a	−0.108	−4.26	319.4
7b	−0.050	−4.26	320.0

proton affinities of cyclopentadiene, **4**, **7a** and **7b** were derived (Table 1).

Interestingly, although both **7a** and **7b** are the strongest acids in the series and stabilization of the charge in the corresponding anion is similar, the Mullican charges on the C1 atoms of anions of both derivatives differ drastically accounting for the lack of reactivity of the latter. Derivative **4** is somewhat weaker acid and retains many features of the parent hydrocarbon.

3. Electrochemical properties and electronic absorption spectra

The electrochemical properties of the fulvalene derivatives were studied by cyclic voltammetry and the results are summarized in Table 2. As previously reported, octachorofulvalene (**3**) exhibits strong electron accepting properties.[7] The first reduction potential of **3** is at 0.21 V, somewhat lower than that of TCNQ (0.27 V at the same experimental conditions). It can be pointed out that Coulombic repulsion is expected to be larger for fulvalene deriviative than for TCNQ due to proximity of 5-member rings. However, the difference of potential between the first and second redox potential is much smaller in the case of fulvalene than for TCNQ (ΔV=0.47 V and ΔV=0.60 V respectively). Such behavior indicates the gain in stability of $\mathbf{3}^{2-}$ owing to aromatization of the second fulvene moiety.

Expectedly, increasing the π-conjugated link between the two cyclopentadiene moieties such as in vinylog **14** and derivative **17** brings about considerable decrease in the accepting ability and to a diminished difference between the first and second reduction steps (Fig. 6). Thus, while the observed difference ΔE amounts 0.17 V for **14**, coalescence of the two one-electron reduction processes into one two-electron process was observed for **17**, indicating decrease in Coulombic repulsion owing to increase in size of the molecule. A similar trend was observed for the vinylogues of TTF and BEDT-TTF with respect to the parent donor.[16] A moderate electron accepting abilities were observed for octachloro derivatives **10** and **13** incorporating aromatic spacers. Similarly to the analog **17**, derivatives **10** and **13** undergo one two-electron reduction step. The reduced intermediates derived from the chlorinated derivatives **3**, **10**, **13**, **14** and **17** are stable in degassed solutions.

Fulvalenes derived from cyclopentadienes **7a**–**7c** exhibit rather moderate electron accepting abilities owing to the presence of the electron donating methoxy substituents. Thus, while the first reduction of **24** occurs at −0.24 V, it involves two one-electron reduction steps with ΔE=0.09 V. Similarly to the trend observed for chlorinated derivatives, extension of the conjugated link (derivatives **15**, **16** and **21**) brings about further decrease in the electron accepting ability and coalescence of the two one-electron reduction processes into one two-electron process. Furthermore, derivatives **8**, **9**, **11** and **12**, incorporating the aromatic spacers, exhibit one irreversible reduction step. In those derivatives, as proven by the X-ray structure of **10′** which bears less sterically demanding chlorine atoms at the

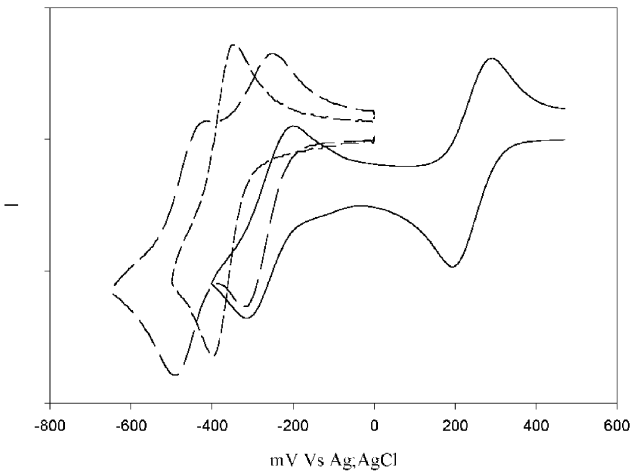


Figure 6. Cyclic voltammetry of fulvalenes **3** (line), **14** (long dashes), **17** (short dashes).

cyclopentadiene moieties, steric hindrance between the cyano or carboethoxy groups and the periplanar aromatic hydrogens prevents coplanarity. Such structure may prevent delocalization of charge along the conjugated skeleton and leads to less stable anion radicals. This assumption is corroborated by the electrochemical study of the weakest acceptor of the series [1,4-bis(cyclopentadien-1-ylidene)-methyl]benzene, which was synthesized using the known procedure.[13] This compound involves less encumbering hydrogen atoms on the cyclopentadiene rings and exhibits a perfectly reversible two-electron redox wave at −1.2 V.

Electronic absorption spectra of all fulvalene derivatives were also studied (Table 2). Bathochromic shifts of the absorption maxima were observed upon increasing the length of the spacer and the polarity of the solvent (for example perchlorofulvalene **3**: in toluene λ_{max}=379 nm; dichlorormethane λ_{max}=392 nm; benzonitrile λ_{max}=396 nm). Appearance of a fine structure in long-wave absorption bands was observed upon increasing the conjugation length

Table 2. Electrochemical data of fulvalene derivatives, CH_2Cl_2, nBu$_4$PF$_6$ (0.1 M), sweep rate 400 mV s^{-1}, 10^{-3} M, vs Ag, AgCl, UV–visible spectroscopic date 10^{-5} mol L^{-1} in dichlorormethane

Compound	E_{red} (V)	λ_{max} (nm)
3	0.21, −0.26	392
8	−1.13[a,b]	381
9	−0.86[a,b]	390
10	−0.39[a,c]	376[d]
11	−0.84[a,b]	449
12	−0.60[a,b]	469
13	−0.26[a,c]	497[d]
14	−0.32, −0.49	398
15	−0.60[a]	416
16	−0.47[a]	425
17	−0.39[a]	437
21	−0.40[a]	471
24	−0.24, −0.33	420
TCNQ	0.27, −0.33	309

[a] 2-Electron process.
[b] Non-reversible.
[c] In DMF (derivatives insoluble in CH_2Cl_2).
[d] In benzonitrile.

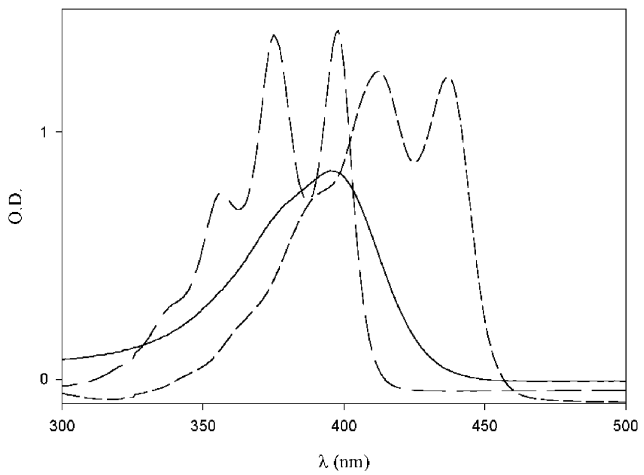


Figure 7. UV–Vis absorption spectra of **3** (line), **14** (long dashes), **17** (short dashes).

for derivatives **3**, **14** to **17** (Fig. 7) and **14** to **16**. Derivative **13** exhibits a fine structured band indicating a rigid conjugated structure. Interestingly, the absence of fine resolved structure for derivatives **8**, **9**, **11** and **12**, which bear an aromatic spacer may indicate, in accordance with the electrochemical observations, a decrease in conjugation.

Expectedly, only the strongest acceptor, the octachlororfulvalene **3**, interacts with the TTF derivatives in solution. Indeed, the absorption spectrum of **3** in benzonitrile features bands at 396 nm (strong) and 560 nm (weak). Reduction of octachlororfulvalene in the same solvent using tetrabutylammonium iodide leads to formation of the corresponding anion radical, which features an intense absorption band at 587 nm and a broad weak band at about 1200 nm (Fig. 8). Anion radical is stable in absence of moisture and disappears rapidly by addition of few drops of water. The same behavior is observed in cyclic voltammetry: addition of water to the cell destroys the reversibility of the redox processes and leads to elimination of the chlorine anion. The absorption spectrum of a benzonitrile solution of the equivalent amounts of TTF or BEDT-TTF and **3**, exhibits both the features of the anion radicals of **3** and those of the cation radicals of TTF.[17]

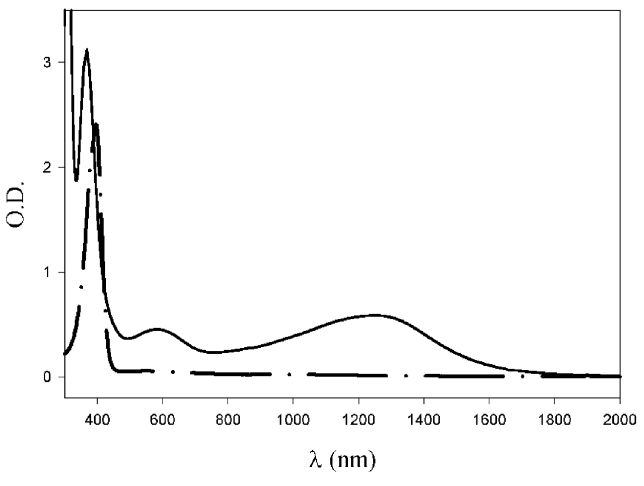


Figure 8. UV–Vis spectra for **3** (dashed dotted line) and **3′** (line) generated in presence of TBAI.

Formation of ion radical salts was also observed in solid state, when TTF and BEDTTTF were grinded with **3** in a mortar. Both salts are semiconductors with the rt conductivity around 1 S cm^{-1}.

In conclusion, syntheses and electron accepting properties of the proaromatic electron acceptors derived from pentafulvalene were studied. The new derivatives can be used for verification of importance of the proaromaticity concept for obtaining electro-conducting materials. Attempts of electro- and chemical reduction of the new acceptors at low temperatures are now in progress.

4. Experimental

4.1. General

Electrochemical studies were performed in a standard three-electrode configuration under the argon blanket. The working electrode was a 1 mm Pt disk sealed in glass, the reference electrode was Ag/AgCl 0.1 M, the potential scans were performed with an EG&G 273 potentiostat. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (Fluka puriss, used as received). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI or FAB mode on a VG-Autospec mass spectrometer, under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer or under positive electrospray (ESI+) on a JMS-700 JEOL mass spectrometer of reversed geometry. UV–visible optical data were recorded with a Perkin–Elmer lambda 19 spectrophotometer. IR spectra were recorded on a Perkin–Elmer model 841 spectrophotometer, samples being embedded in KBr discs or thin films between NaCl plates. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Column chromatography purifications were carried out on Merck silica gel Si 60 (40–63 μm). Conductivity measurements were carried out on a pressed pellet using Keithley 236 MSU instrument (four-probe method).

4.2. 1,4-Dicyano-2,3-dihydroxycyclopentadiene 6a

A solution of 7.0 g (74.4 mmol) of glutaronitrile in 70 mL of dry THF was added dropwise during 20 min to a stirred under nitrogen solution of 10.8 g (74.0 mmol) of diethyl oxalate and 16.7 g (149 mmol) of *t*-BuOK in 280 mL of dry THF. The mixture was stirred for additional 30 min at room temperature. The precipitated dipotassium salt of **6a** was filtered off, washed with ether and dried. Yield 14.5 g (87%) Mp >250°C. IR (KBr): $\tilde{\nu}$=2165 cm^{-1} (CN). ^{1}H NMR (D_2O): δ=2.65 (s, 2H).

The dipotassium salt (10 g, 44.6 mmol) was added in portions to 50 mL of 20% H_2SO_4 under stirring at −5°C. The colorless precipitate of **6a** was filtered off, washed with cold water and dried. Crystallization from water gave 5.6 g (85%) of colorless microcrystals. Mp 224°C. IR (KBr): $\tilde{\nu}$=3051 (OH), 2221 (CN), 1538 (C=C–C=C) cm^{-1}. ^{1}H

Compound	**6b**	**7a**	**10′**	**15**	**19**
Formula	$C_{11}H_{14}O_6$	$C_9H_8N_2O_2$	$C_{13}H_6C_{l4}O$	$C_{12}H_{13}O_6$	$C_{22}H_{18}N_4O_5$
Molecular weight	242.23	176.17	320.00	253.23	418.40
Temperature (K)	294	298	294	294	293
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12$	P_1	$P2_12_12$	P_12_1/n_1	P_1
a (Å)	14.965(2)	4.120(1)	3.945(2)	8.601(2)	8.111(3)
b (Å)	14.328(3)	8.193(2)	15.155(3)	6.750(5)	9.828(3)
c (Å)	5.489(3)	13.702(3)	21.250(5)	20.375(3)	13.359(4)
α (deg.)	90	100.562(5)	90	90	73.393(6)
β (deg.)	90	96.509(5)	90	101.31(1)	85.822(7)
γ (deg.)	90	100.713(5)	90	90	88.213(6)
V (Å^3)	1176(1)	441.5(2)	1270(1)	1166(1)	1017.6(6)
Z	4	2	4	4	2
Crystal colour	Colorless	Colorless	Red	Red	Orange
Crystal size (mm^3)	0.65×0.25×0.20	0.30×0.30×0.10	1.03×0.14×0.03	1.00×0.14×0.08	0.50×0.20×0.20
Dc (g cm^{-3})	1.37	1.33	1.66	1.44	1.36
F(000)	512	184	640	532	436
μ (mm^{-1})	0.112	0.096	0.908	0.117	0.099
Transmission (min/max)	–	0.45/1.00	0.63/1.00	0.49/1.00	0.71/1.00
θ (min/max)	2.5/30	2.6/26.4	2.5/29	2.15/30	2.16/22
Scan mode	ω/2θ	ϕ/ω	ω	ω/2θ	ϕ/ω
hkl limits	−7,0/0,20/0,21	−5,5/−10,10/−16,17	−5,0/−20,0/−29,0	−12,12/0,9/0,28	−8,8/−10,10/−14/14
Data measured	2009	3318	2128	3756	5477
Data observed, $I>3\sigma(I)$	1098	1267	1001	1321	1764
No. of variables	170	151	98	163	291
R	0.039	0.054	0.042	0.071	0.074
Rw	0.053	0.147	0.054	0.094	0.205
GOF	1.086	0.773	0.954	1.688	1.025
Largest peak in final: difference (eA^{-3})	0.190	0.222	0.361	0.429	0.454
CCDC deposition numbers	196,236	196,234	197,495	197,496	196,235

NMR (DMSO-d_6): δ=3.25 (s, 2H), 12.6 (s, 2H, 2OH). ^{13}C NMR (DMSO-d_6): δ=32.89, 83.90, 115.86, 161.99. HRMS for $C_7H_4N_2O_2$: calcd 148.0273; found 148.0269.

4.3. 2,3-Dihydroxycyclopentadiene 6b and 6c (a general procedure)

Diethyl or dimethyl glutarate (44.5 mmol) was added dropwise during 15 min to a refluxing and stirred under nitrogen solution of 6.5 g (44.5 mmol) of diethyl oxalate and 10 g of *t*-BuOK (89.2 mmol) in 180 mL of dry THF. The reaction mixture was stirred for additional 30 min at the same temperature. After cooling to the room temperature, the dipotassium salt was filtered off, washed with ether and dried. The salt was added in portions to a solution of 5 g of concentrated H_2SO_4 and 30 mL of water at 0°C. The precipitate was filtered off, washed with water and dried.

4.3.1. 1,4-Dicarboethoxy-2,3-dihydroxycyclopentadiene 6b. Crystallization from ethanol afforded 9.3 g of **6b** (86%) as colorless crystals. Mp 129°C. IR (KBr): $\tilde{\nu}$=3312, 1690, 1470, 1415, 1378, 1227 cm^{-1}. ^{1}H NMR ($CDCl_3$): **6b** (60%): δ=1.35 (t, 6H, *J*=7.1 Hz), 3.23 (s, 2H), 4.3 (q, 4H, *J*=7.1 Hz) **6b′** (40%): 1.28 (t, 3H, *J*=7.11 Hz), 1.38 (t, 3H, *J*=7.1 Hz), 2.88 (d*d, 1H, *J*=7.04, *J′*=17.10 Hz), 3.0 (d*d, 1H, *J*=17.1, *J′*=1.93 Hz), 3.47 (d*d, 1H, *J*=6.90, *J′*=1.96 Hz), 4.22 (q, 2H, *J*=7.10 Hz), 4.37 (q, 2H, *J*=7.10 Hz). HRMS for $C_{11}H_{14}0_6$: calcd 242.0790; found 242.0786.

4.3.2. 1,4-Dicarbomethoxy-2,3-dihydroxycyclopentadiene 6c. Mp 122–123°C. IR (KBr): $\tilde{\nu}$=3327, 1671, 1586, 1449, 1229 cm^{-1}. ^{1}H NMR ($CDCl_3$): **6c** (77%) 3.21 (s, 2H), 3.83 (s, 6H), 9.68 (s, 2H) **6c′** (23%) 2.88 (d*d, *J*=17.12, *J′*=7.05 Hz, 1H), 3.02 (d*d, *J*=17.12, *J″*=2.48 Hz, 1H), 3.51 (d*d, *J′*=7.1, *J″*=2.45, 1H), 3.78 (s, 3H), 3.91 (s, 3H), 9.04 (s, 1H) $C_9H_{10}0_6$: calcd 214.0477; found 214.0460.

4.4. 2,3-Dimethoxycyclopentadienes 7a–c (a general procedure)

An etherial solution of diazomethane (2 equiv.) was added to a stirred suspension of **6a–c** in ether at room temperature. Gas evolved immediately. After stirring for 30 min, a few drops of acetic acid were added to destroy any unreacted diazomethane. Ether was evaporated and the residue dissolved in dichloromethane and passed through a short silica gel column.

4.4.1. 7a. (1,4-dicyano-2,3-dimethoxycyclopentadiene, starting from **6a** 2 g, 13.5 mmol). Evaporation of dichromethane and recrystallization from acetic acid gave pure **7a** as colorless crystals (2.1 g, 88%). Mp 184°C. IR (KBr): $\tilde{\nu}$=2209, 1640, 1539 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.35 (s, 2H, CH_2), 4.30 (s, 6H, 2OCH_3). HRMS for $C_9H_8N_2O_2$ Calcd 176.0586; found 176.0587.

4.4.2. 1,4-Dicarboethoxy-2,3-dimethoxycyclopentadiene 7b. (starting from **6b** 2 g, 8.26 mmol). Evaporation of dichloromethane and crystallization from ethanol gave **7b** as colorless microcrystals (1.89 g, 84%). Mp 66°C. IR (KBr): $\tilde{\nu}$=1720, 1581, 1466, 1378, 1231 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=1.35 (t, 6H, *J*=7.11 Hz, 2CH_3), 3.35 (s, 2H, CH_2), 4.10 (s, 6H, 2OCH_3), 4.25 (q, 4H, *J*=7.11 Hz, 2CH_2). ^{13}C NMR: δ=163.0, 160.7, 111.8, 61.4, 60.17, 34.3, 14.3. HRMS for $C_{13}H_{18}O_6$: Calcd 270.1103; found 270.1108.

4.4.3. 1,4-Dicarbomethoxy-2,3-dimethoxycyclopentadiene 7c. (starting from **6c** 1 g, 4.67 mmol). After chromatography on silica gel (petroleum ether/diethyl ether 95:5 derivative **7c** is isolated in 80% yield) as a white powder. Mp 72–73°C. IR (KBr): $\tilde{\nu}$=1707, 1596, 1448, 1260 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.36 (s, 2H), 3.73 (s, 6H), 4.12 (s, 6H). ^{13}C NMR: δ=34.3, 51.4, 61.5, 111.3, 160.8, 163.5. HRMS for $C_{11}H_{14}O_6$: Calcd 242.0790; found 242.0789.

4.5. Derivatives 8–13

(A general procedure). Piperidine (0.5 equiv. for **8–9** and 0.15 equiv. for **10–13**) was added to a solution of dialdehyde (terephthaldialdehyde or thiophene-3,4-dicarboxaldehyde) in 5 mL acetic acid at 70–80°C. 2 equiv. of cyclopentadiene derivative (**4**, **7a** or **7b**) were added and the mixture was stirred at the same temperature for 45 min. Ethanol (10 mL) was added after cooling to room temperature. The resulting precipitate was filtered off, washed with ethanol and dried.

4.5.1. 1,4-Bis[(2,5-dicarboethyloxy-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene)methyl] benzene 8. (from terephtaldialdehyde 0.30 g, 2.24 mmol, **7b** 1.24 g, 4.60 mmol) Crystalization from acetic acid gave yellow microcrystals of **8** (1.22 g, 85%). Mp 162°C. IR (KBr): $\tilde{\nu}$=1649, 1606, 1561, 1447, 1399, 1380, 1357 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=0.85 (t, 6H, *J*=7.06 Hz, *cis*-CH_3), 1.45 (t, 6H, *J*=7.04 Hz, *trans*-CH_3), 3.55 (q, 4H, *J*=7.02 Hz, *cis*-CH_2), 4.10 (s, 6H, 2OMe), 4.20 (s, 6H, 2OMe), 4.35 (q, 4H, *J*=7.01 Hz, *trans*-CH_2), 7.28 (s, 4H, Ar), 7.97 (s, 2H,=CH–Ar). ^{13}C NMR: δ=13.6, 14.3, 60.4, 60.5, 60.9, 61.2, 106.5, 106.9, 129.6, 133.2, 136.2, 137.5, 158.3, 159.3, 163.7, 165.4. HRMS for $C_{34}H_{38}O_{12}$: Calcd 638.2363; found 638.2369.

4.5.2. 1,4-Bis[(2,5-dicyano-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene) methyl] benzene 9. (from terephthaldialdehyde 0.30 g, 2.24 mmol, **7a** 0.78 g, 4.43 mmol). Recrystallization from acetic acid gave yellow microcrystals of **9** (0.82 g, 82%). Mp 291–292°C. IR (KBr): $\tilde{\nu}$=2214, 1712, 1618, 1569, 1449, 1434, 1386 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=4.35 (s, 12H, 4OMe), 7.42 (s, 2H), 7.57 (s, 4H). HRMS for $C_{26}H_{18}N_4O_4$: Calcd 450.1328; found 450.1322.

4.5.3. 1,4-Bis[(2,3,4,5-tetrachloro-2,4-cyclopentadien-1-ylidene) methyl] benzene 10. (from terephthaldialdhyde 0.1 g 0.75 mmol, **4** 0.30 g, 1.47 mmol). Compound **10** was obtained in 84% (0.31 g) as yellow microcrystals. Mp >250°C (dec.). ^{1}H NMR (DMSO) δ=7.74 (s, 4H), 7.91 (s, 2H). HRMS for $C_{18}H_6Cl_8$:: Calcd 501.7978; found 501.7981.

4.5.4. 1,4-Bis[(2,5-dicarboethyloxy-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene)methyl] thiophene 11. (from thiophene-3,4-dicarboxaldehyde 0.1 g, 0.71 mmol, **7b** 0.346 g, 1.43 mmol) Compound **11** was isolated after

chromatography on silicagel (methylene chloride with 2% of ethyl acetate) as a red oil in 50% yield. ^{1}H NMR ($CDCl_3$): δ=1.03 (t, 6H, J=7.2 Hz), 1.37 (t, 6H, J=7.2), 3.81 (q, 4H, J=7.1 Hz), 4.03 (s, 12H), 4.33 (q, 4H, 7.1), 6.93 (s, 2H), 7.89 (s, 2H). ^{13}C NMR: δ=13.8, 14.4, 60.6, 61.3, 61.4, 106.6, 106.7, 127.5, 131.3, 133.3, 144.3, 158.4, 159.5, 163.5, 165.5. HRMS for $C_{32}H_{36}O_{12}S$: Calcd 644.1927; found 644.1913.

4.5.5. 1,4-Bis[(2,5-dicyano-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene) methyl] thiophene 12. (from thiophene-3,4-dicarboxaldehyde 0.06 g, 0.43 mmol, **7a** 0.15 g, 0.85 mmol). Compound **12** was obtained in 82% (0.16 g) as deep brown microcrystals. Mp >250°C (dec.). ^{1}H NMR ($CDCl_3$): δ=4.36 (s, 6H, OCH_3), 4.41 (s, 6H, OCH_3), 7.29 (s, 2H), 7.58 (s, 2H). HRMS for $C_{24}H_{16}N_4O_4S$+Na. Calcd 479.0790; found 479.0788.

4.5.6. 1,4-Bis[(2,3,4,5-tetrachloro-2,4-cyclopentadien-1-ylidene) methyl] thiophene 13. (from thiophene-3,4-dicarboxaldehyde 0.1 g, 0.71 mmol, **4** 0.30 g, 1.47 mmol). The precipitate which formed was filtered off from the hot solution, washed with ethanol (10 mL) and dried. Compound **13** was obtained in 88% (0.32 g) as deep brown microcrystals. Mp >250°C (dec.). ^{1}H NMR (DMSO): δ=7.86 (s, 2H), 8.05 (s, 2H). HRMS for $C_{16}H_4Cl_8S$: Calcd 507.7542; found 507.7557.

4.6. 1,2-Bis (2,3,4,5-tetrachloro-2,4-cyclopentadien-1-ylidene) ethane 14

Piperidine (0.1 mL, 1 mmol) was added to a solution of glyoxal bis(dimethylacetal) 0.18 g (1.20 mmol) in 5 mL of acetic acid. After heating the mixture at 70°C for 3 min, tetrachlorocyclopentadiene **4** (0.50 g, 2.45 mmol) was added and the mixture stirred at the same temperature for 30 min. After cooling the mixture to room temperature, the precipitate was filtered off, washed with ethanol and dried. The precipitate was dissolved in minimal amount of toluene and passed through short column of silica gel, evaporation of toluene and recrystalization from chlorobenzene gave 0.20 g of the vinylogue **14** (39%). Mp 228°C. IR (KBr): $\tilde{\nu}$=1584, 1559, 1518, 1275, 1236 cm^{-1}..^{1}H NMR ($CDCl_3$): δ=8.25 (s, 2H). HRMS for $C_{12}H_2Cl_8$: Calcd 425.7665; found 425.7671.

4.7. 1,2-Bis (2,5-dicarbomethyloxy-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene) ethane 15

Piperidine (0.1 mL, 1 mmol) was added to a solution of 0.23 g (1.53 mmol) of glyoxal bis(dimethylacetal) in 7 mL of acetic acid. The mixture was heated at 70°C for 3 min and then cyclopentadiene derivative **7c** (0.75 g, 3.13 mmol) was added. The mixture was heated at the same temperature for 30 min. Water (5 mL) was added after cooling the mixture to room temperature. The resulting precipitate was filtered off washed with water (10 mL) and methanol (5 mL) and dried. Crystalization from ethanol offered the vinylog 15 as yellow microcrystals (0.54 g, 70%). Mp 166–177°C. IR (KBr): $\tilde{\nu}$=1721, 1627, 1584, 1441, 1384, 1234 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=3.86 (s, 6H), 3.88 (s, 6H), 4.00 (s, 6H), 4.04 (s, 6H), 7.86 (s, 2H). HRMS for $C_{24}H_{26}O_{12}$: Calcd 506.1424; found: 506.1429.

4.8. 1,2-Bis (2,5-dicyano-3,4-dimethyloxy-2,4-cyclopentadien-1-ylidene) ethane 16

Piperidine (0.1 mL, 1 mmol) was added to a solution of glyoxal bis(dimethylacetal) 0.17 g (1.13 mmol) in 3 mL of acetic acid. After heating the mixture at 70°C for 3 min, the CP derivative **7a** (0.40 g, 2.27 mmol) was added and the mixture stirred at the same temperature for 30 min. Water (5 mL) was added after cooling the mixture to room temperature. The resulting precipitate was filtered off, washed with water (5 mL) and methanol (5 mL) and dried. Crystalization from acetic acid offered the vinylog **16** as yellow microcrystals (0.38 g, 90%). Mp >300°C. IR (KBr): $\tilde{\nu}$=2215, 1611, 1571, 1446, 1379, 1307 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ=4.35 (s, 6H), 4.40 (s, 6H), 7.91 (s, 2H). HRMS for $C_{20}H_{14}N_4O_4$: Calcd 374.1015; found 374.1023.

4.9. 1,4-Bis (2,3,4,5-tetrachloro-2,4-cyclopentadien-1-ylidene)-2-butene 17

Piperidine (0.3 mL) was added to a solution of 0.22 g of 1,1,4,4-methoxy-2-butene (1.26 mmol) in 5 mL of acetic acid. After heating the mixture at 70°C for 3 min, tetrachlorocylopentadiene **4** (0.55 g, 2.70 mmol) was added and the mixture stirred at the same temperature for 30 min. After cooling the mixture to room temperature, the precipitate was filtered off, washed with ethanol and dried. Crystallization from toluene gave **17** (0.38 g, 62%) as orange microcrystals. Mp >300 °C. IR (KBr): $\tilde{\nu}$=1614, 1560, 1453, 1253, 1241 cm^{-1}. ^{1}H NMR ($CDCl_3$): AA′XX′ system δ=7.16 (′, 2H, ^3J=11.14, ^5J=3.11 Hz), 8.05 (AA′, 2H, ^3J=11.14, ^5J=3.11 Hz). MS for $C_{14}H_4Cl_8$: Calcd 451.78; found 451.73.

4.10. 3-(2,5-Dicyano-3,4-dimethyloxy-2,4-cyclopentadien-1-yl)-4-(2,5-dicyano-3,4-dimethyl-oxy-2,4-cyclopentadien-1-yl)-1-butanal 19

Piperidine (0.1 mL, 1.20 mmol) was added to a solution of 0.25 g of 1,1,4,4-tetramethoxy-2-butene (1.44 mmol) in 5 mL of acetic acid. After heating the mixture at 70°C for 3 min, derivative **7a** (0.50 g, 2.84 mmol) was added and the mixture stirred at the same temperature for 30 min. After cooling the mixture to room temperature, the precipitate was filtered off, washed with methanol and dried. Crystallization from acetic acid gave 0.48 g (80%) of **19** as yellow crystals. Mp >300°C. IR (KBr): $\tilde{\nu}$=2221, 1612, 1558, 1441, 1384 cm^{-1}. ^{1}H NMR ($CDCl_3$): 9.90 (s, 1H, H^e), 6.45 (t, 1H, H^a), 4.35 (s, 3H, OCH_3), 4.28 (s, 6H, 2OCH_3), 4.25 (s, 3H, OCH_3), 4.15 (d, 1H, J=2.48 Hz, H^d), 3.28 (m, 1H, H^b), 3.20 (m, 1H, H^c), 2.92 (m, 1H, H$^{b'}$). HRMS for $C_{22}H_{18}N_4O_5$: Calcd 418.1277; found 418.1275.

4.11. 1,4-Bis(2,5-dicyano-3,4-dimethyloxy-2,4-cyclopentadien-1-yl)-2-cyclohexene 21

To a solution of 0.16 g (1.42 mmol) of 1,4-cyclohexanedione and 0.50 g **7a** (2.84 mmol) in 3 mL of dry DMF, piperidine (0.3 mL) was added and the mixture was stirred at room temperature for 30 min. The solution was diluted with 5 mL of water and acidified with HCl until pH 3.5. The orange precipitate formed was filtered washed with water and dried. The precipitate was dissolved in minimal amount

of CH_2Cl_2 and passed through short column of silica gel. Evaporation of CH_2Cl_2 and crystallization from 1,4-dioxane gave orange crystals of **21** (0.43 g, 71%). Mp 285°C. IR (KBr): $\tilde{\nu}$=2208, 1600, 1565, 1544, 1450, 1388, 1360 cm^{-1}. ^1H NMR ($CDCl_3$): δ=7.90 (s, 2H), 4.85 (s, 12H, 4OCH3), 3.35 (s, 4H). HRMS for $C_{24}H_{18}O_4N_4$: Calcd 426.1339; found 426.1334.

4.12. 1,1′-Bi(cyclopenta-2,4-dien-1-ylidene)-2,2′,5,5′-tetracarbonitrile 24

Cyclopentadiene derivative **7a** (0.50 g, 2.84 mmol) was dissolved in 15 mL of dry THF. *t*-BuOK (0.35 g, 3.12 mmol) was added and the mixture stirred at room temperature for 15 min. The colorless potassium salt **23** was filtered off and dissolved in 10 mL of water. $AgNO_3$ (0.48 g, 2.84 mmol) was added, a black precipitate which formed immediately, was filtered off and dried. The thoroughly dried black precipitate was added to 20 mL of toluene and the suspension was refluxed for 5 h. The solution was filtered and toluene was fully evaporated. The residue was dissolved in minimal amount of dichloromethane and passed through a short silica-gel column. Evaporation of dichloromethane and crystalization from acetic acid gave fulvalene **24** as orange crystals. Yield 0.32 g (64%). Mp 215 (dec.). IR (KBr): $\tilde{\nu}$=2190 (CN), 1570 (C=C) cm^{-1}. ^1H NMR ($CDCl_3$): δ=4.45 (s, 12H). ^{13}C NMR ($CDCl_3$): δ=164.57, 136.54, 113.87, 81.83, 61.12. HRMS for $C_{18}H_{12}N_4O_4$: Calcd 348.0859; found 348.0855.

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