diameter, 0.75 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection with authentic materials (see above). The conversion and product distribution are described in Table I (entry 33).

PET Reaction with DCA. A solution of 11.5 mg (9.24 × 10⁻² mmol) of **1d** and 5.0 μL of *c*-C₇H₁₄ in 5.00 mL of CH₃CN was saturated with DCA. After 2 h of irradiation at λ > 400 nm, 12% of the starting material had reacted and the products given in Table I (entry 31a) were observed in a mass balance of 57%.

Transformations of *syn*-7-(1-Methylethyl)-2,3-diazabicyclo[2.2.1]-hept-2-ene (*syn*-1e). 185-nm Photolysis. A sample of 501 mg (3.63 mmol) of *syn*-1e in 280 mL of *n*-pentane was irradiated for 24 h at 0 °C up to complete conversion in the preparative photolysis apparatus. High-molecular-weight products were removed by filtration over neutral Al₂O₃ (60–230 mesh, activity grade I). The solvent was removed by distillation at 36 °C on a 30-cm Vigreux column until above a final volume of 2 mL and the residue was worked up by means of preparative GC to yield 65.0 mg (16%) of hydrocarbons (1.5-m, 10% SE 30 on Chromosorb WHP; N₂ flow of 1.8 kp/cm²; oven, injector, and detector temperatures of 80, 180, and 180 °C). The retention times in brackets are capillary GC values (50-m, OV 101 column; N₂ flow of 0.50 kp/cm²; oven, injector, and detector temperatures of 60, 175, and 175 °C).

3-(1-Methylethyl)-1,4-pentadiene (4e):[26] R_t = 8.00 (8.58) min, isolated yield of ca. 5 mg (ca. 0.045 mmol), relative yield of 5%.

***anti*-5-(1-Methylethyl)bicyclo[2.1.0]pentane (*anti*-2e):** R_t = 14.0 (11.2) min, isolated yield of ca. 10 mg (ca. 0.091 mmol), relative yield of 16%. IR (CDCl₃, registered with a mixture of *syn*-2e and *anti*-2e) 3040, 2960, 2930, 2900, 2860, 1463, 1380, 1363, 1315, 1270, 1258, 1212, 820 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.68 (m_c, 2 H, 5-H, 6-H), 0.96 (d, $J_{7,6} = J_{7',6}$ = 6.3 Hz, 6 H, 7-H, 7'-H), 1.28–1.37 (m, 4 H, 2-H_n, 3-H_n, 1-H, 4-H), 2.02 (m, 2 H, 2-H_x, 3-H_x); ¹³C NMR (CDCl₃, 100.6 MHz, the C–H coupling constants were determined in a fully coupled ¹³C NMR experiment) δ 20.5 (d, J_{CH} = 174 Hz, C-1, C-4), 22.6 (q, J_{CH} = 124 Hz, C-7, C-7'), 23.0 (t, J_{CH} = 134 Hz, C-2, C-3), 30.3 (d, J_{CH} = 125 Hz, C-6), 37.4 (d, J_{CH} = 159 Hz, C-5); GC–MS (70 eV), m/e 110 (1%, M⁺), 95 (44), 93 (6), 81 (9), 79 (6), 77 (5), 69 (13), 68 (13), 67 (100), 66 (13), 65 (7), 55 (15), 53 (8), 44 (10), 43 (8), 41 (32), 39 (19), 29 (7), 27 (10).

***syn*-5-(1-Methylethyl)bicyclo[2.1.0]pentane (*syn*-2e):** R_t = 14.0 (11.5) min, isolated yield of ca. 40 mg (ca. 0.36 mmol), relative yield of 65%;

¹H NMR (CDCl₃, 400 MHz) δ 0.44 (dt, $J_{5,6}$ = 10.1 Hz, $J_{5,1} = J_{5,4}$ = 5.9 Hz, 1 H, 5-H), 1.01 (d, $J_{7,6} = J_{7',6}$ = 6.7 Hz, 6 H, 7-H, 7'-H), 1.28–1.37 (m, 2 H, 2-H_n, 3-H_n), 1.55 (m_c, 2 H, 1-H, 4-H), 1.65 (m_c, 1 H, 6-H), 2.02 (m, 2 H, 2-H_x, 3-H_x); ¹³C NMR (CDCl₃, 100.6 MHz) δ 17.3 (d, J_{CH} = 175 Hz, C-1, C-4), 18.7 (t, J_{CH} = 136 Hz, C-2, C-3), 19.5 (d, J_{CH} = 126 Hz, C-6), 22.3 (q, J_{CH} = 124 Hz, C-7, C-7'), 30.7 (d, J_{CH} = 150 Hz, C-5); GC–MS (70 eV), m/e 110 (0.7%, M⁺), 95 (5), 68 (9), 67 (100), 66 (16), 65 (7), 43 (5), 41 (19), 40 (5), 39 (11), 27 (7).

1-(1-Methylethyl)cyclopentene (3e):[28] R_t = 16.2 (12.7) min, isolated yield of ca. 10 mg (ca. 0.091 mmol), relative yield of 14%. The mass balance, conversion, and product distribution are described in Table I (entry 37).

---

(28) Apparu, M.; Crandall, J. K. *J. Org. Chem.* **1984**, *49*, 2125.

New Extended π-Electron Donors. Tetrathiafulvalene Systems with Heterocyclic Spacer Groups

Thomas K. Hansen,[†] **M. V. Lakshmikantham,**[‡] **Michael P. Cava,**[*,‡]
Renée E. Niziurski-Mann,[‡] **Frank Jensen,**[†] **and Jan Becher**[†]

Contribution from the Departments of Chemistry. The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487-0336, and Odense University, 5230 Odense M, Denmark. Received October 31, 1991. Revised Manuscript Received February 14, 1992

Abstract: Nine new heterocyclic π-electron donors **10a–c**, **11a–c**, and **12a–c** based upon the well-known TTF (tetrathiafulvalene) system, but incorporating a pyrrole, thiophene, or furan ring between the 1,3-thiole rings, have been synthesized. The compounds show two single-electron reversible oxidation waves in cyclic voltammetry. Some TCNQ complexes and conductivity measurements are reported, indicating the new compounds to be good candidates for "organic metals". The influence of the central conjugated system on redox properties is discussed using MNDO-PM3 calculations.

Introduction

The unusual properties of TTF (**1**), to behave as a reversible electron donor and to form conducting charge-transfer complexes with various acceptor molecules, have stimulated much interest during the past 20 years in the synthesis of a wide variety of TTF analogs.[1] Many of these bear substituents at the 4,5-positions,

while, in others, some or all of the sulfur atoms have been replaced by other chalcogens.[2] Among these, some partially oxidized salts of BEDT–TTF (**2**)[3] have been of particular interest, since they

---

(1) For general reviews see: (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209. (b) Narita, M.; Pittman, C. *Synthesis* **1976**, 489. (c) Schukat, G.; Richter, A.; Fanghänel, E. *Sulfur Rep.* **1987**, *7* (3), 155.
(2) (a) Yoneda, S.; Kawase, T.; Inaba, M.; Yoshida, Z. *J. Org. Chem.* **1978**, *43*, 595. (b) Lerstrup, K.; Lee, M.; Wiygul, F.; Kistenmacher, T.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1983**, 294.

†Odense University.
‡The University of Alabama.

Table I. Cyclic Voltammetric Data for the Title Compounds[a] and Computed MNDO-PM3 Ionization Potentials

	E_1, V	$E_{ox} - E_{red}$, V	E_2, V	$E_{ox} - E_{red}$, V	$E_1 - E_2$, V	$IP_1(E_h)$	$IP_1(\Delta SCF)$
10a	0.20	0.07	0.38	0.06	0.18	7.71	7.46
10b	0.31	0.18	0.58	0.17	0.28	7.76	7.46
10c	0.48	0.06	0.71	0.06	0.23	8.24	7.92
11a	0.32	0.06			0	7.93	7.70
11b	0.38	0.09	0.56	0.09	0.18		
11c	0.58	0.07	0.71	0.07	0.13		
12a	0.39	0.06	0.49	0.06	0.10	8.01	7.80
12b	0.46	0.09	0.65	0.09	0.19		
12c	0.69	0.05	0.79	0.06	0.10		

[a] Experimental conditions: donor (ca. 1×10^{-3} M) and electrolyte $Bu_4N^+PF_6^-$ (ca. 1×10^{-2} M) in acetonitrile or methylene chloride (10b, 11b, 12b) under N_2; versus SCE; Pt electrode; scan rate 80 mV s^{-1}; BAS CV-27 potentiostat.

Figure 1. Bar graph representation of E_1 and E_2 values for new π-extended systems compared with those of nonextended TTF systems and some vinylog derivatives of TTF.

have been found to show ambient-pressure superconductivity.

In recent years, considerable interest has been focused upon the synthesis of extended π-donors in which the two dithiole units of a TTF molecule are separated by one or more olefinic or quinonoid units.[4,5] The recently reported vinylog of BEDT-TTF[4a] 4 is one example of such a system. Some general trends in the redox properties[1] of these extended analogs are the following: (a) a lowering of the oxidation potential due to the increased delocalization of positive charge and (b) a smaller difference between E_1 and E_2 due to reduced Coulombic repulsion in the dication state. These effects are illustrated in the behavior of 5, which shows a considerably lower oxidation potential than TTF and only one two-electron oxidative wave.

When the spacer unit consists of a simple conjugated polyene unit, as in 4 and 5, the energy difference between the reduced and oxidized forms is not significantly influenced by conformational changes of the spacer unit itself. Thus, such compounds obey the general trends stated above. A similar correlation becomes more complicated in the case of the recently reported π-extended systems 3,[6] 6,[7] and 7.[7] In 3, the spacer unit is a reduced thiophene ring. Oxidation of this system to the dication state will enable the ring to rearomatize and produce a more thermodynamically stable system. The opposite is true for the bis(benzothiazole) systems 6 and 7, where initial oxidation of the system causes the phenyl or thienyl spacer group to lose its aromaticity. None of these systems have been reported to obey the "rules for simple π-extended systems", and in all cases they show two single-electron oxidation waves.

The compounds reported in this paper 10a–c, 11a–c, and 12a–c are obviously of the last mentioned type and most resemble 7 in structure.
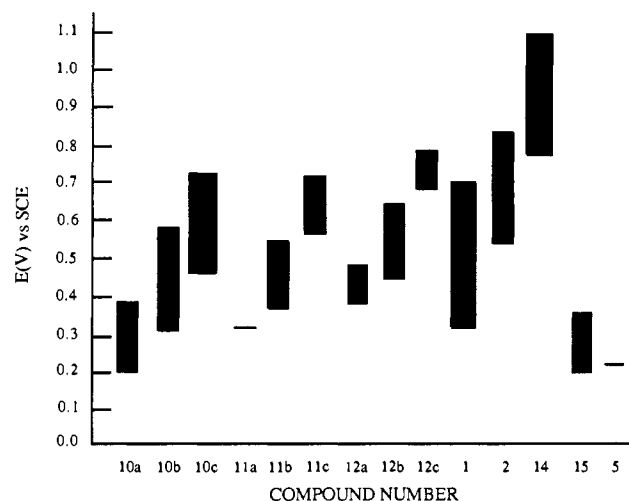
Results and Discussion

The target molecules 10–12 were chosen because their terminal dithiolylidene units cover a range of different substituents in terms of electron-withdrawing effects while their internal units incorporate the three most common five-membered heterocycles. Thus, from the properties of these compounds, we hoped to obtain information on their comparative redox behavior and possibly to

obtain some new extended TTF derivatives with low oxidation potentials and reduced symmetry, identified as desirable properties for organic donors by Wudl et al.[8]

Our synthetic scheme involved the reaction of the appropriate heterocyclic dicarbaldehyde with a dithiolium ylide reagent. Originally, we investigated the use of Wittig-type reactions[9] (Scheme I) for our purpose. The starting phosphonium salts are stable compounds which are available using known methodology. In the case of the highly electron-withdrawing carbomethoxy group of 8c, the reactivity of the phosphorane is enhanced and the desired products 10c, 11c, and 12c are formed in high yield. However, we found the analogous 8a and 8b to react with only one aldehyde group. In the case of 8b, the intermediate monoaldehyde can be isolated in high yield, but under similar conditions, 8a forms TTF as the main product. We assume this to be due to an equilibrium between the phosphonium salt and its dissociation products, the dithiolium salt and triphenylphosphine. This problem was overcome by the use of a Horner–Wittig type reaction (Scheme II).[10] Thus, the readily prepared phosphonates 13a and 13b afforded moderate to high yields of products 10b, 11b, 12a, and 12b. Products 10a and 11a were also obtained, although in low yield. Compound 11a was also prepared in modest yield by hydrolytic decarboxylation[11] of diester 11c (Scheme III).

The yellow unsubstituted compounds 10a, 11a, and 12a are readily oxidized in air, both in solution and in the solid state. The

(3) (a) Williams, J. M.; Wang, H. H.; Emge, T. J.; Geise, U.; Beno, M. A.; Leung, P. C. W.; Douglas, K.; Thorn, R. J.; Schultz, A.; Whangbo, M. *Prog. Inorg. Chem.* **1987**, *35*, 51. (b) Saito, G.; Kagoshima, S. *The Physics and Chemistry of Organic Superconductors*; Springer Verlag: London, 1990. (c) Wang, H.; Beno, M. A.; Geiser, U.; Firestone, M. A.; Webb, K. S.; Nunez, L.; Crabtree, G. W.; Williams, J. M.; Azevedo, J. L. *Inorg. Chem.* **1985**, *24*, 2466 (and references therein).

(4) (a) Hansen, T. K.; Lakshmikantham, M. V.; Cava, M. P.; Metzger, R. M.; Becher, J. *J. Org. Chem.* **1991**, *56*, 2720. (b) Khodorkovskii, V. Yu.; Veselova, L. N.; Neiland, O. Ya *Khim. Geterotsikl. Soedin* **1990**, *130*. (c) Moore, A. J.; Bryce, M. R.; Ando, D. J.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1991**, 320. (d) Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 157. (e) Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1450.

(5) (a) Yoshida, Z.; Kawase, T.; Awajii, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3469. (b) Yoshida, Z.; Kawase, T.; Awaji, H.; Yoneda, S. *Tetrahedron Lett.* **1983**, 3473. (c) Moore, A. J.; Bryce, M. R. *Synthesis* **1991**, 26. (d) Sugimoto, T.; Awaji, H.; Misaki, Y.; Kawase, T.; Yoneda, S.; Yoshida, Z.; Anzai, H. *Chem. Mater.* **1989**, *1*, 535.

(6) Takahasi, K.; Nihira, T.; Shibata, K. *Tetrahedron Lett.* **1989**, *30*, 2091.

(7) Bryce, M. B.; Fleckenstein, E.; Hünig, S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1777.

(8) Lichtenberger, D.; Johnston, R.; Hinkelmann, K.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1989**, *111*, 3302.

(9) Sato, M.; Gonella, N.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 930.
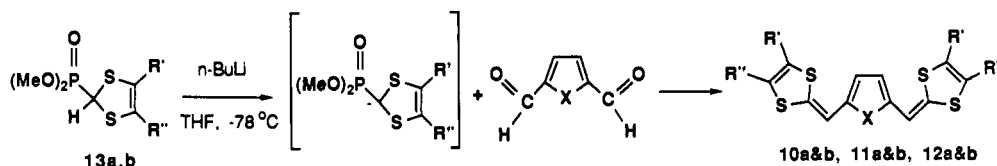
(10) (a) Akiba, K.; Ishikawa, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2674. (b) Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1052.

(11) Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1976**, *41*, 882.
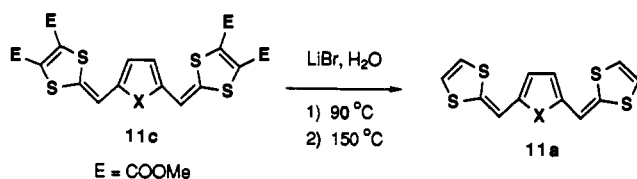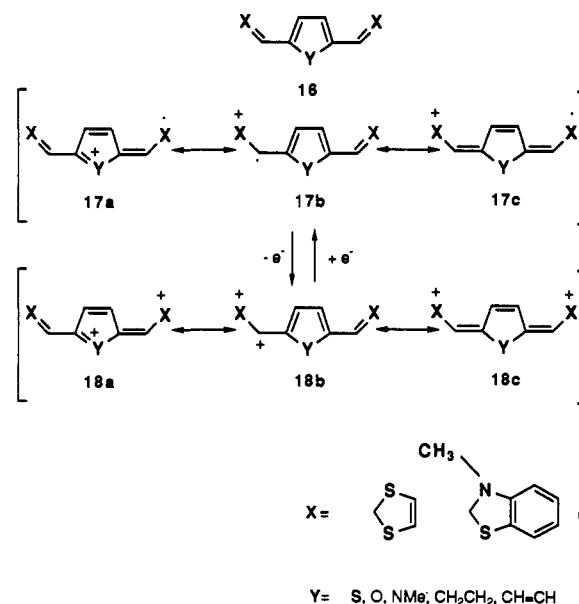
Scheme I
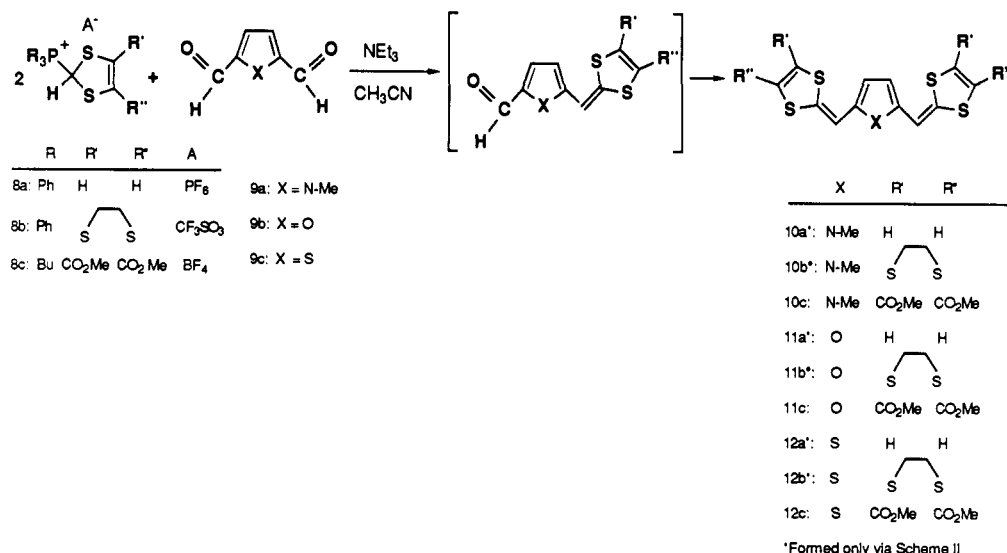
Scheme II

Scheme III

E = COOMe

corresponding ethylenedithio compounds **10b**, **11b**, and **12b**, which are also yellow, are considerably more stable in air. The deep violet or brown derivatives **10c**, **11c**, and **12c** are the most stable to oxidation due to the electron-withdrawing properties of their carbomethoxy substituents.

The redox values of all compounds were determined by cyclic voltammetry. The trends shown by the experimental values which are given in Table I are in good agreement with that shown by the calculated ionization potentials (MNDO-PM3). In Figure 1, the oxidation potentials are shown schematically and compared to those of **1**, **2**, **5**, the diester **14**, and the vinylogue **15**. The height
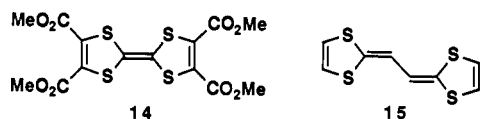
of the bars indicates the difference between E_1 and E_2. The following trends are discernible: (a) The E_1 values of the pyrrole derivatives (**10a–c**) are lower than those of the corresponding furans (**11a–c**), which in turn are lower than those of the thiophenes (**12a–c**). (2) Considering E_2 values, the order is furans $\leq$ pyrroles $<$ thiophenes. This results in a larger difference between E_1 and E_2 for the pyrrole derivatives.

As shown in Figure 1, a comparison of the CV data for compounds **10–12** with those previously reported for simple TTF systems[1c] reveals several interesting features. Of all the compounds listed, the parent TTF shows the largest difference between E_1 and E_2. The addition of one vinyl spacer between the dithiole rings, as in **15**, has the effect of lowering the oxidation potential and reducing the difference between E_1 and E_2. An additional vinyl spacer, as in **5**, does not further lower E_1, but completely eliminates the difference between E_1 and E_2. Increased conjugation and

Scheme IV

Y= S, O, NMe; CH₂CH₂, CH=CH

decreased Coulombic repulsion between the two positive charges can account for these facts, although relaxation in the positive ion to a localized hole may also play a significant role. On the basis of analogy, we would also expect no difference between E_1 and E_2 for compounds **10a**, **11a**, and **12a** (unsubstituted) if participation of the heteroatom were negligible. This evidently is not the case.

The effect of sulfur or carbomethoxy substituents on the TTF system is also apparent from Figure 1. Both have the effect of increasing the oxidation potentials in the extended systems **10–12**. Surprisingly, these substituents cause a decrease in the difference between the E_1 and E_2 values in the case of the simple TTF systems but a corresponding increase in the E_1 and E_2 gap in the case of **10–12** (with the exception of **12c**).

In Scheme IV some relevant resonance structures for radical cations and dications of compounds like **10–12** are shown. These fall into three categories:

5038 *J. Am. Chem. Soc., Vol. 114, No. 13, 1992*

Hansen et al.

(a) Resonance structures **17a** and **18a** represent forms in which the heteroatom of the central ring bears a positive charge. On the basis of analogy to the reactivity sequence in electrophilic substitution, such structures should have the following order of importance: pyrrole $\gg$ furan $>$ thiophene. The greater stability of a positive charge on nitrogen as compared to a positive charge on sulfur or oxygen is exemplified by the relative rates of trifluoroacetylation of pyrrole (5.3×10^7), furan (1.4×10^2), and thiophene (1.0).[12] It may be noted that **17a** will be of lower energy than **18a** due to Coulombic repulsion in the dication state. This accounts for the difference between E_1 and E_2 as well as for the fact that this difference is largest in the pyrrole series, in which the central ring bears the most positive charge.

(b) Structures **17b** and **18b** are contributors in which the central heterocyclic ring is intact and the charge or charges are borne by the dithiole units. Unlike **17b**, **18b** suffers from a strong Coulombic repulsion and should be a negligible contributor. These structures can be part of the explanation of the difference between E_1 and E_2 but cannot explain the differences between the three heterocycles.

(c) Resonance structures of type **17c** and **18c** are likely to be very favored in conjugated nonaromatic systems (i.e. the cationic forms of **4** and **5**). In compounds **10–12**, analogous structures require the loss of aromaticity in the central ring. Aromaticity in the three central heterocycles has been well established as the sequence furan $\ll$ pyrrole $<$ thiophene. The same sequence should correspond to increasing oxidation potentials on the basis of contributions of the type **17c** and **18c**, since these represent contributors of increasingly higher energy. Indeed, this sequence corresponds to the E_2 values in which structures **18a** and **18b** are relatively unimportant due to Coulombic repulsion. The lowering of E_1 for the pyrroles can then be related to the greater tendency of nitrogen to stabilize structures like **17a**.

The theoretical values in Table I for the first ionization potential are calculated by two approximations: $IP_1(E_h)$ is the negative of the HOMO energy for the neutral molecule using Koopmans' theorem, and $IP_1(\Delta SCF)$ is calculated as the energy difference between the neutral molecule and the radical cation. As can be seen from Table I, the MNDO-PM3 method is in both cases able to reproduce the correct order for E_1 of the unsubstituted systems **10a**, **11a**, and **12a**. The IP_1 calculations also reproduce the trend in E_1 as a function of substituent for the three pyrrole derivatives. Inherent in both computational approaches is the neglect of electron correlation and solvent effects, which may be important for these systems. Nevertheless, the correlation between the experimental and computational data suggests that MNDO-PM3 calculations may be of some value in selecting interesting candidates for synthesis.[13] However, one should be aware of their limitations, since attempts in the present case to correlate IP_2 (calculated as the energy difference between the radical cation and the dication) with E_2 were unsuccessful.

Two compounds (**11a** and **10c**) were found to form crystalline charge-transfer complexes with TCNQ in acetonitrile at room temperature. In spite of considerable efforts, it was not possible to obtain crystals of a size large enough for single-crystal conductivity measurements. Consequently, measurements were made on compressed pellets using the two-probe technique in order to determine the order of magnitude of the conductivity of the complexes. Thus, $(11a)_2(TCNQ)_3$ showed a conductivity of 10^{-5} S cm^{-1}, while the complex $(10c)_2$TCNQ showed a conductivity of 10^{-2} S cm^{-1}. These values are typical of many semiconducting organic charge-transfer complexes and appear sufficiently promising to continue work in this area.

Experimental Section

Phosphonates (**13a,b**)[4a,14] and phosphonium salts (**8a,b,c**),[4a,9,13] as well as *N*-methylpyrrole-, furan-, and thiophene-2,5-dicarbaldehyde,[16,17] were

prepared using literature procedures. THF was distilled from sodium and benzophenone prior to use. Acetonitrile was distilled over phosphorus pentoxide and again over potassium carbonate. *n*-BuLi in hexane was obtained from Aldrich and used as received. IR spectra were obtained on a Perkin-Elmer 1280 spectrometer. Mass spectra are EI (70 eV) recorded on a Varian Mat 311A spectrometer. NMR spectra were recorded on a Bruker AM250 spectrometer.

General Experimental Details for 10a, 11a, and 12a (via Scheme II). Phosphonate **13a** (1.06 g; 0.0050 mol) was dissolved in dry THF (30 mL) in a 100-mL three-necked flask with a rubber septum and an N_2 inlet. The mixture was cooled to −78 °C in a dry ice/acetone bath. With cooling, a solution of *n*-BuLi in hexane (3.2 mL; 0.0051 mol from a 1.6 M solution) was added slowly (5 min) with stirring via the septum. After 5 min, a solution of *N*-methylpyrrole-, furan-, or thiophene-2,5-dicarbaldehyde (0.0024 mol) in dry THF (30 mL) was added over 10 min. The cooling bath was removed when addition was complete. The mixture was allowed to stir for 1 h. THF was removed in vacuo, the mixture was extracted with 150 mL of methylene chloride, and the extract was washed with 3 × 20 mL of water, dried with MgSO$_4$(anhyd), and evaporated partly. The remaining solution was quickly filtered through a short Silica column using methylene chloride as eluent. The yellow fraction was immediately evaporated to give **10a**, **11a**, or **12a**. **12a** was relatively stable, whereas **10a** and especially **11a** were unstable in solution and darkened somewhat on the surface in the solid state. However, **11a** could be converted rapidly without isolation to the analytically pure TCNQ complex (see below).

10a: yield 60 mg (8.3%) of yellow crystals; mp 148–9 °C; IR (KBr) ν (cm^{-1}) 1620, 1574, 1456, 1373, 1239; ^{1}H-NMR (CDCl$_3$) δ 6.39 (2 H, s), 6.38 (2 H, s), 6.35 (2 H, d, $J = 7$ Hz), 6.27 (2 H, d, $J = 7$ Hz), 3.43 (3 H, s); MS m/e (%) 309 (M$^+$, 100), 294 (32), 251 (6), 155 (9); HRMS calcd for C$_{13}$H$_{11}$NS$_4$ 308.9774, found 308.9808.

11a: yield 80 mg (11%) of yellow crystals; mp 122–24 °C; IR (KBr) ν (cm^{-1}) 2923, 1579, 1524, 1490, 1302, 1174; ^{1}H-NMR (CDCl$_3$) δ 6.15–6.40 (br m); MS m/e (%) 296 (M$^+$, 100), 267 (5), 251 (6), 194 (9), 148 (18); HRMS calcd for C$_{12}$H$_8$OS$_4$ 295.9458, found 295.9460.

12a: yield 0.32 g (43%) of yellow crystals; mp 133–4 °C; IR (KBr) ν (cm^{-1}) 1569, 1303, 814; ^{1}H-NMR (CDCl$_3$) δ 6.79 (2 H, s), 6.71 (2 H, s), 6.355 (2 H, s), 6.353 (2 H, s); MS m/e (%) 312 (M$^+$, 100), 254 (11), 210 (10), 156 (14). Anal. Calcd for C$_{12}$H$_8$S$_5$: C, 46.15; H, 2.56; S, 51.28. Found: C, 46.03; H, 2.53; S, 50.25.

General Experimental Details for 10b, 11b, and 12b (via Scheme II). Phosphonate **13b** (1.51 g, 0.0050 mol) was dissolved in 30 mL of dry THF under inert atmosphere in a three-necked flask (100 mL) fitted with a rubber septum and cooled to −78 °C in a dry ice/acetone bath. A solution of BuLi in hexane (3.2 mL, 0.0051 mol; 1.6 M solution) was added dropwise via the septum. Five minutes after addition was complete, a solution of *N*-methylpyrrole-, furan-, or thiophene-2,5-dicarbaldehyde (0.0024 mol) in 50 mL of dry THF was added over 20 min and the cooling bath was removed. After 1 h, the mixture was poured into 250 mL of water and the yellow solid was filtered off. **10b** was recrystallized via Soxhlet extraction with methylene chloride; **11b** was recrystallized from chloroform, and **12b**, from toluene.

10b: yield 1.02 g (87%) of yellow crystals; mp 199–200 °C; IR (KBr) ν (cm^{-1}) 1573, 1520, 1456, 1440, 1408, 1374, 1286; ^{1}H-NMR (CDCl$_3$) δ 6.35 (4 H, br s), 3.31 (8 H, s); MS m/e (%) 489 (M$^+$, 1), 384 (1.5), 299 (40), 150 (61), 28 (100). Anal. Calcd for C$_{17}$H$_{15}$NS$_8$: C, 41.72; H, 3.07; N, 2.86; S, 52.35. Found: C, 42.30; H, 3.05; N, 2.77; S, 52.45.

11b: yield 0.75 g (66%) of yellow crystals; mp 213–4 °C; IR (KBr) ν (cm^{-1}) 1600, 1575, 1410, 1287, 920; ^{1}H-NMR (CDCl$_3$) δ 6.37 (2 H, s), 6.17 (2 H, s), 3.32 (8 H, s); MS m/e (%) 476 (M$^+$, 3), 448 (1), 328 (21), 150 (18), 91 (100). Anal. Calcd for C$_{16}$H$_{12}$OS$_8$: C, 40.34; H, 2.52; S, 53.78. Found: C, 40.78; H, 2.60; S, 53.10.

12b: yield 0.60 g (51%) of yellow crystals; mp 230–1 °C; IR (KBr) ν (cm^{-1}) 1569, 1520, 1409, 1286; ^{1}H-NMR (CDCl$_3$) δ 6.78 (2 H, s), 6.64 (2 H, s), 3.33 (8 H, s); MS m/e (%) 492 (M$^+$, 13), 464 (7), 302 (25), 150 (61), 28 (100). Anal. Calcd for C$_{16}$H$_{12}$S$_9$: C, 39.02; H, 2.43; S, 58.53. Found: C, 38.85; H, 2.44; S, 57.70.

General Experimental Details for 10c, 11c, and 12c (via Scheme I). Phosphonium salt **8c**[9] (5.07 g, 0.01 mol) and furan- or thiophene-2,5-dicarbaldehyde (0.004 mol) were dissolved in 50 mL of dry acetonitrile. To the stirred solution was added 5 mL of triethylamine, and stirring was continued for 5 h in the cases of **11c** and **12c**. Water (25 mL) was added slowly. The precipitated solid was collected and recrystallized from methylene chloride/hexane. In the case of *N*-methyl-2,5-diformylpyrrole (0.004 mol), because of the low solubility of the intermediate mono-

---

(12) Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*; Van Nostrand Reinhold: London, 1978; p 186.

(13) Bowadt, S.; Jensen, F. *Synth. Met.* **1989**, *32*, 179.

(14) Bryce, M. R.; Moore, A. J. *Synth. Met.* **1988**, *27*, B.557.

(15) Gonnella, N.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369.

(16) Loader, C. E.; Barnett, G. H.; Anderson, H. J. *Can. J. Chem.* **1982**, *60*, 383.

(17) Feringa, B. L.; Hulst, R.; Rikers, R.; Brandsma, L. *Synthesis* **1988**, 316.

aldehyde, it was necessary to use a large amount of **8c** (up to 10 g) and a large volume (150 mL) of acetonitrile and to add the phosphonium salt in small portions over at least 24 h. When TLC indicated that all yellow monoaldehyde was converted, the volume was reduced to half and the same workup procedure was followed.

10c: yield 1.90 g (88%) of violet crystals; mp 188 °C; IR (KBr) ν (cm⁻¹) 1729, 1586, 1434, 1263; ¹H-NMR (CDCl₃) δ 6.32 (2 H, s), 6.28 (2 H, s), 3.83 (6 H, s), 3.82 (6 H, s), 3.42 (3 H, s); MS *m/e* (%) 541 (M⁺, 100), 483 (78), 381 (19), 366 (18). Anal. Calcd for C₂₁H₁₉NO₈S₄: C, 46.58; H, 3.51; N, 2.59; S, 23.66. Found: C, 46.61; H, 3.51; N, 2.64; S, 23.69.

11c: yield 2.09 g (99%) of brown crystals; mp 89 °C; IR (KBr) ν (cm⁻¹) 1741, 1588, 1434, 1263, 1030; ¹H-NMR (CDCl₃) δ 6.43 (2 H, s), 6.32 (2 H s), 3.97 (6 H, s), 3.96 (6 H, s); MS *m/e* (%) 528 (M⁺, 100), 470 (5), 354 (11), 264 (8). Anal. Calcd for C₂₀H₁₆O₉S₄: C, 45.45; H, 3.03; S, 24.24. Found: C, 45.53; H, 2.82; S, 24.00.

12c: yield 1.98 g (91%) of brown crystals; mp 149 °C; IR (KBr) ν (cm⁻¹) 1731, 1585, 1434, 1260; ¹H-NMR (CDCl₃) δ 6.81 (2 H, s), 6.58 (2 H, s), 3.87 (6 H, s), 3.87 (6 H, s); MS *m/e* (%) 544 (M⁺, 100), 486 (5), 370 (19), 272 (6). Anal. Calcd for C₂₀H₁₆NO₈S₄: C, 44.12; H, 2.94; S, 29.41. Found: C, 44.59; H, 3.02; S, 28.90.

11a via Decarbomethoxylation of 11c (Scheme III). In a 25-mL round-bottomed flask were placed **11c** (0.53 g, 0.001 mol), LiBr, H₂O (0.46 g, 0.0011 mol), and 5 mL of HMPA (no purification). The mixture was heated to 90 °C in an oil bath, and the reaction was monitored by TLC. Initially several spots (staining green with iodine) appeared. When only one was left (ca. 50–70 min), the temperature was increased to 150

°C and maintained (70–80 min) until TLC showed only one clear yellow spot (staining reddish-brown with iodine). The reaction mixture was poured into 100 mL of water, and the resulting mixture was extracted with 3 × 50 mL of methylene chloride. The combined extracts were washed with 2 × 25 mL of sodium chloride solution and once with 25 mL of water, then dried with MgSO₄, treated with a little decolorizing carbon, and filtered. The methylene chloride was evaporated to afford **11a** (66 mg, 23%).

TCNQ Complexes. The complexes were synthesized by mixing a concentrated solution of the donor in acetonitrile with a solution containing an excess of TCNQ in acetonitrile. Immediately, a dark solution resulted, from which the analytically pure TCNQ complex separated. Anal. Calcd for (**10c**)₂(TCNQ), C₅₄H₄₂O₁₆N₆S₈: C, 50.38; H, 3.27; N, 6.53. Found: C, 50.43; H, 3.29; N, 6.98. Calcd for (**11a**)₂(TCNQ)₃, C₆₀H₂₈O₂N₁₂S₈: C, 59.80; H, 2.32; N, 13.95; S, 21.26. Found: C, 59.53; H, 2.37; N, 13.39; S, 21.19.

# New Ultraviolet Stabilizers: 3- and 5-(2'-Hydroxyphenyl)pyrazoles

Javier Catalán,*,† Fernando Fabero,† Rosa M. Claramunt,*,‡ M. Dolores Santa Maria,‡ M. de la Concepción Foces-Foces,§ Felix Hernández Cano,§ Martín Martínez-Ripoll,§ José Elguero,‖ and Roberto Sastre⊥

Contribution from the Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain, Departamento de Química Orgánica y Biología, UNED, 28040 Madrid, Spain, U.E.I. de Cristalografía, Instituto de Química Física "Rocasolano", CSIC, 28006 Madrid, Spain, Instituto de Química Médica, CSIC, 28006 Madrid, Spain, and Instituto de Ciencia y Tecnología de Polímeros, CSIC, 28006 Madrid, Spain. Received October 11, 1991

Abstract: A new class of ultraviolet stabilizers, the *C*-(2'-hydroxyphenyl)pyrazoles, is described. The combined use of X-ray crystallography [3(5)-(2'-hydroxyphenyl)pyrazole (**5**), 1-methyl-3-(2'-hydroxyphenyl)pyrazole (**7**), and 1-methyl-5-(2'-hydroxyphenyl)pyrazole (**8**)], NMR (¹H and ¹³C), and UV spectroscopies allows the determination of the major tautomers, the coplanarity of both rings if present, and the existence of hydrogen bonds. Compounds **5** and **7**, in which there is an intramolecular hydrogen bond (IMHB), do not fluoresce in cyclohexane. Solvent and temperature experiments prove that for these compounds in cyclohexane proton transfer took place in the excited singlet state but not in the triplet state (phosphorescence) and that the latter one is of higher energy than the former. The fact that the absorptions of planar 1-methyl-3-(2'-methoxyphenyl)pyrazole (**9**) and nonplanar 1-methyl-5-(2'-methoxyphenyl)pyrazole (**10**) are quite different whereas their emissions are very similar suggests that **10** might behave as a laser dye in the UV region (from an excited planar form to a ground state nonplanar form). Finally, the photostability of (2'-hydroxyphenyl)- and (2'-methoxyphenyl)pyrazoles was determined, compound **7** being even more stable than Tinuvin P.

Introduction

In previous papers,[1,2] we have discussed the photostability of some *N*-(2'-hydroxyphenyl)pyrazoles (general formula **I**) and their application to photoprotection of polystyrene. Some of these compounds show low emission quantum yields and a high stability

I   Tinuvin P
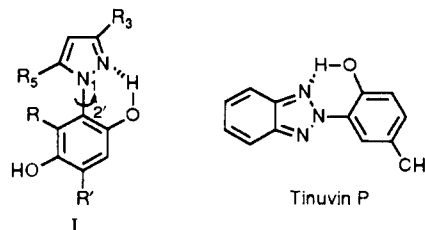
* Authors to whom correspondence should be addressed.
† Departamento de Química, UAM.
‡ Departamento de Química Orgánica y Biología, UNED.
§ Instituto Rocasolano, CSIC.
‖ Instituto de Química Médica, CSIC.
⊥ Instituto de Ciencia y Tecnología de Polímeros, CSIC.

to ultraviolet light. However, the radiationless deactivation of the absorbed ultraviolet energy could not be explained as being