Novel structural units for electropolymerizable compounds: pyrimidiniumolate-functionalized thiophenes[1]

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The synthesis of pyrimidiniumolates with a thiophene unit (**3a**–**c**) is reported. The electrooxidation of **3a** leads to a conductive polymer. Some quantum chemical data for **3a**–**c** and the parent system **5** are given [semiempirical calculations (AM1, PM3), *ab initio* data and density functional theoretical results].

Research on conducting polymers has increased enormously in the last decade.[2–4] Despite these efforts, the control of the long-range order of these materials constitutes a challenge in this field, and improving the order and linear assembly of the monomers during electrooxidation is still a major task.[5,6] Thiophenes and derivatives thereof especially have been investigated quite intensively.[7] Recently, a liquid crystalline thiophene derivative has been reported[9] that leads to a highly conductive polymer upon electrooxidation. Fluorinated alkyl side chains and electron withdrawing groups have also been introduced for this reason.[9] It seemed to us that dipolar heterocycles (mesoionic systems, mesomeric betaines *etc.*)[10,11] are especially suitable for this purpose, because it is likely that a large dipole moment would increase the order of the monomeric units. We now report the synthesis of pyrimidiniumolates **3a**–**c** and the electropolymerisation of **3a**.

Experimental

Mp values were determined using a Tottoli apparatus. IR spectra were measured using a Paragon 1000 FTIR spectrometer (Perkin-Elmer). Mass spectra: MAT 8230 (Finnigan). NMR spectra were recorded on AM 500 (Bruker) and EM390 (Varian) instruments using tetramethylsilane as an internal standard. *J* Values are in Hz. UV: DMR 10 (Zeiss).

Bis(2,4,6-trichlorophenyl)2-(3-thienyl)malonate (1b)

A mixture of 2-(3-thienyl)malonic acid **1a** (Aldrich; 0.95 g, 5 mmol), 2,4,6-trichlorophenol (1.96 g, 10 mmol) and phosphorus oxychloride (1.80 g, 20 mmol) was heated to 90 °C for 1 h. The reaction mixture was cooled to room temp., poured on 50 g of ice–water and extracted with diethyl ether. The organic layers were washed with water, dried (Na_2SO_4), and the solvent evaporated. Recrystallization from isopropyl alcohol–pentane gave **1b** (2.47 g, 90%) as unstable dark yellow crystals with mp 103.5 °C. MS *m/z* (rel. intensity) 320 ($M^+ - C_7H_2Cl_3O_2 + H$, 2), 281 (0.6), 196 (11.1), 167 (3.1), 160 (2.6), 124 (28.2), 97 (100); $C_{12}H_7O_2{}^{35}SCl_3$ (calc. 319.92325, found 319.92330), $C_{12}H_7O_2{}^{35}S^{37}ClCl_2$ (calc. 321.92029, found 321.92020), $C_{12}H_7O_2{}^{35}S^{37}Cl_2Cl$ (calc. 323.91733, found 323.91920); δ_H (90 MHz, $CDCl_3$) 5.45 (s, 1H), 7.25 (m, 1H), 7.35 (s, 4H), 7.6 (m, 2 H); ν_{max} (KBr)/cm^{-1} 3080, 1790, 1765, 1565, 1445.

General procedure for the synthesis of pyrimidiniumolates 3

A mixture of the malonate **1b** (0.55 g, 1 mmol) and the corresponding *N*,*N*′-dimethylamidine **2a**–**c** (1 mmol) in 5 ml of dry anisole was heated to 80 °C for 3 min. After cooling to room temp., 20 ml of diethyl ether was added. After stirring for 6 h at room temp., the precipitate was filtered and recrystallized from ethanol–diethyl ether.

3a: Pale yellow crystals (180 mg, 60%) with mp 203 °C. MS *m/z* (rel intensity) 298 (64), 271 (7), 270 (36), 255 (17), 124 (9), 119 (9), 118 (100), 92 (9), 77 (41); ν_{max} (KBr)/cm^{-1} 3078 (w), 1646 (vs), 1332 (w), 1254 (m), 1026 (w), 845 (m), 798 (m, sh), 781 (m), 723 (w), 631 (w), 448 (w); UV (acetonitrile) λ_{max}/nm (log ε) 208 (4.398), 223 (4.313), 268 (3.62), 354 (3.705); δ_H (500 MHz, $CDCl_3$) 3.25 (s, 6H), 7.38 (dd, 1H, *J* 5.12, *J* 3.11), 7.68–7.80 (m, 5H), 8.18 (dd 1H, *J* 3.16, *J* 1.15), 8.23 (dd, 1H, *J* 5.11, *J* 1.18); δ_C ($CDCl_3$) 34.41, 93.35, 120.52, 121.77, 126.67, 129.03, 129.50, 129.70, 131.26, 135.42, 157.18, 157.87 (Found: C, 63.8; H, 4.5%. Calc. for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73%).

3b: Pale yellow crystals (268 mg, 71%) with mp 325 °C (decomp.). MS *m/z* (rel intensity) 378 (22), 376 (21), 350 (12), 348 (12), 198 (29), 196 (28), 140 (10), 126 (16), 125 (20), 124 (17), 123 (16), 120 (10); ν_{max} (KBr)/cm^{-1} 1643 (vs), 1550 (w), 1526 (w), 1473 (m), 1425 (w), 1333 (w), 1255 (m), 1012 (m), 841 (m), 790 (m), 697 (w), 630 (w); UV (acetonitrile) λ_{max}/nm (log ε) 225 (4.267), 270 (3.526), 358 (3.553); δ_H (500 MHz, [$^2H_6$]DMSO) 3.25 (s, 6H), 7.39 (dd, 1 H, *J* 5.10, *J* 3.16), 7.73 (d, 2 Aryl-H), 7.90 (d, 2 Aryl-H), 8.17 (dd, 1 H, *J* 5.10, *J* 1.22), 8.23 (dd, 1 H, *J* 3.16, *J* 1.22). Calc. for $C_{16}H_{13}N_2O_2SBr$: 377.98605. Found: 377.98600.

3c: Pale yellow crystals (257 mg, 68%) with mp 338 °C (decomp.). MS *m/z* (rel intensity) 378 (M^+, 90), 377 (20), 376 (90), 351 (10), 350 (58), 349 (14), 348 (59), 335 (17), 333 (16), 198 (98), 196 (100), 157 (22), 155 (22), 124 (35), 123 (10), 117 (33), 102 (20); ν_{max} (KBr)/cm^{-1} 1648 (vs), 1555 (m), 1516 (w), 1470 (w), 1383 (m), 1332 (w), 1287 (w), 1251 (m), 853 (m), 789 (m), 685 (w), 628 (w); UV (acetonitrile) λ_{max}/nm (log ε) 228 (sh, 4.142), 272 (3.401), 362 (3.468); δ_H (500 MHz, [$^2H_6$]DMSO) 3.14 (s, 6H), 7.39 (dd, 1 H, *J* 5.11, *J* 3.17), 7.67 (t, 1 Aryl-H), 7.80 (d, 1 Aryl-H), 7.92 (d, 1 Aryl-H), 8.09 (s, 1 Aryl-H), 8.17 (dd, 1H, *J* 5.11, *J* 1.23), 8.24 (dd, 1 H, *J* 3.17, *J* 1.23). Calc. for $C_{16}H_{13}N_2O_2SBr$: 377.98605. Found: 377.98670.

Electropolymerization of 3a

A solution of 100 mg of **3a** and 100 mg of $LiClO_4$ in 20 ml of acetonitrile was electrolysed for 30 min (on 0.8 cm^2 platinum electrodes, $U = 1.80$ V). After this process the electrode was rinsed with acetonitrile. The polymer was removed mechanically, washed with hot acetonitrile and dried. Yield: 20 mg of grey polymer material, aspect similar to graphite powder. The polymer is insoluble in most common solvents at room temp. (slightly soluble in hot acetonitrile). The polymerisation and additionally the conductivity measurements have also been carried out in the BASF laboratories.

Results and Discussion

Pyrimidiniumolates have been known since 1971.[12–14] The dipolar structure of this system leads to a high dipole moment[15] in the direction of the longitudinal molecular axis, calculated by semiempirical methods[16] as 11.35 D (PM3; AM1: 10.83 D) for **3a** (Scheme 1). Pyrimidiniumolates can be prepared quite easily[12–14] by treatment of *N*,*N*′-disubstituted amidines with reactive malonic acid derivatives like acid chlorides or trichlorophenyl esters (magic esters; TCPM procedure by Kappe and co-workers), using solvents such as bromobenzene or anisole. Thiophene derivatives can undergo anodic polymerization in acetonitrile to form electrically conducting polymers. By varying the groups R^1 and R^2, the resulting total dipole strength of the monomer can be adjusted over a wide range. In this paper, the synthesis and electropolymerization of pyrimidiniumolate-functionalized thiophene monomers (**3a**–**c**) are described. Using thienylmalonic acid (**1a**) as starting material, the ester **1b** was available by treatment with 2,4,6-trichlorophenol–$POCl_3$ in 90% yield. Amidines[17] can be prepared by a variety of methods. *N*,*N*′-Dimethylamidines of type **2** are synthesized most conveniently[18] either from the corresponding imidoyl chlorides[19] on treatment with methylamine or from thiuronium salts[20,21] on treatment with methylamine. Heating ester **1b** with amidines **2a**–**c** in anisole gives pyrimidiniumolates **3a**–**c** as pale yellow crystals in satisfactory yields. The electropolymerization of **3a** was carried out on a gold disc electrode using acetonitrile/$LiClO_4$ as solvent/electrolyte. As is shown in Fig. 1, a 100 mV s^{-1} potential scan exhibits a strong anodic oxidation wave at +1.50 V. Microscopic analysis of the polymer-coated gold electrodes showed the formation of small dendritic crystals on an amorphous base layer of polymeric material. A cyclic voltammogram of the monomer-free polymer with increasing scan rates is also shown in Fig. 1. Preliminary measurements indicate that this polymer exhibits a conductivity of approximately 10^{-3} S cm^{-1}. Further improvements of this methodology may give rise to materials which could be of interest in the field of electroconductive/electroluminescent polymer applications.

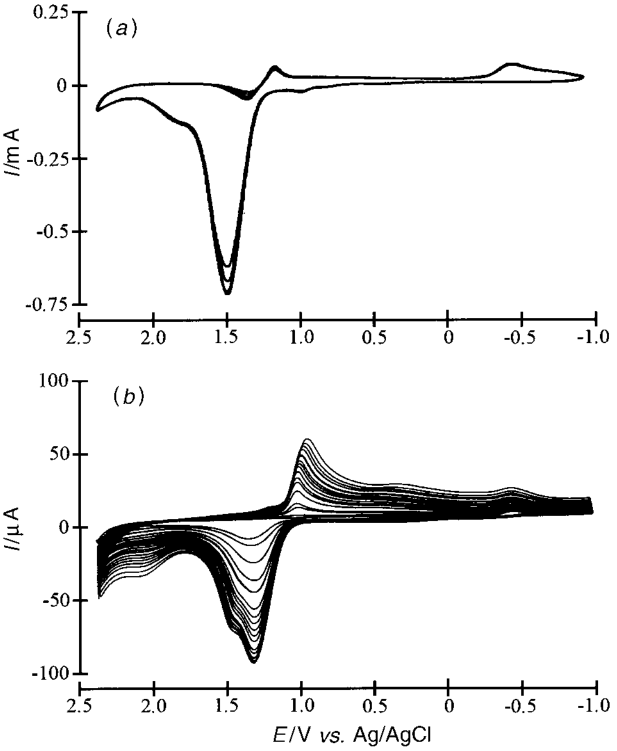


Fig. 1 (*a*) Cyclic voltammogram of **3a** on Au disc electrode, in 0.1 M $LiClO_4$ MeCN. Scan rate 100 mV s^{-1}. (*b*) Cyclic voltammogram of a film of poly-**3a** on Au, in 0.1 M $LiClO_4$ MeCN. Scan rate 20–340 mV s^{-1} by increments of 20 mV s^{-1}.

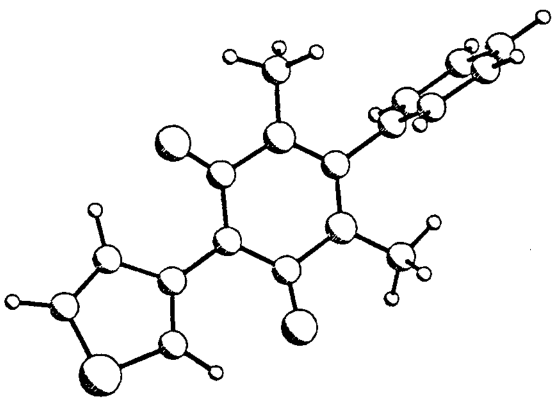
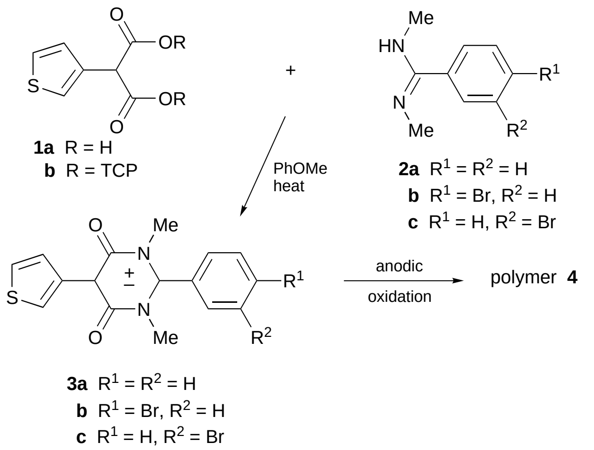


Fig. 2 Calculated geometry of **3a** (AM1)



The structure of the polymer is—as in other related cases—not known with certainty. If the polymerisation takes place at position 2 and 5 of the monomer, several structures are of course possible (2–5′–2′–5″–2″ ... *etc*., 2–2′–5′–5″–2″ ... *etc*.; ′ and ″ refer to polymerisation sites of the monomer). To gain some insight into the geometry of compounds **3**, semiempirical optimizations[22] have been performed, resulting in the following geometry (for **3a**, see Fig. 2). The phenyl ring is nearly perpendicular to the pyrimidiniumolate system (AM1: 90.5°, PM3: 90.2°) whereas the thiophene ring is twisted by 19.8° (AM1, PM3: 46.2°). The rotational barriers for the phenyl ring and the thiophene ring have been investigated in some detail (Fig. 3, AM1 values). Whereas for the former rotation a barrier of 17.2 kcal mol^{-1} (1 cal = 4.184 J) was found—irrespective of the fact of whether ω(a–b–c–d) was fixed or not—the rotational barrier of the thiophene ring is 2.8 kcal mol^{-1} [ω(e–f–g–h) was fixed to 90°]. The electrochemical properties of the resulting polymer should not be affected significantly by the twisting angle of the phenyl group. As expected the dipole moment of compounds **3** depends to a large extent upon substituents. Semiempirical calculations show that on changing the substituent R^1 there is an increase of the dipole strength from approximately 5.1 (5.7) to 12.9 (13.4) Debye (Table 1). The geometrical features of **3** (bond lengths, bond angles) are in line with expectations and with X-ray data.[23] *Ab initio* calculations for the parent system **5** (see Table 2) with density functional methods[24,25]—especially when Becke's non-local three-parameter exchange and correlation functional[26] in conjunction with the Lee–Yang–Parr correlation functional[27] is used—give an excellent picture of this molecule. These results are in agreement with DFT studies on other heterocyclic systems with unusual structure elements (nonclassical furoxans,[28] furoxans,[29,30] benzofuroxans,[29,30] furazans, benzofurazans and related compounds[30,31]).

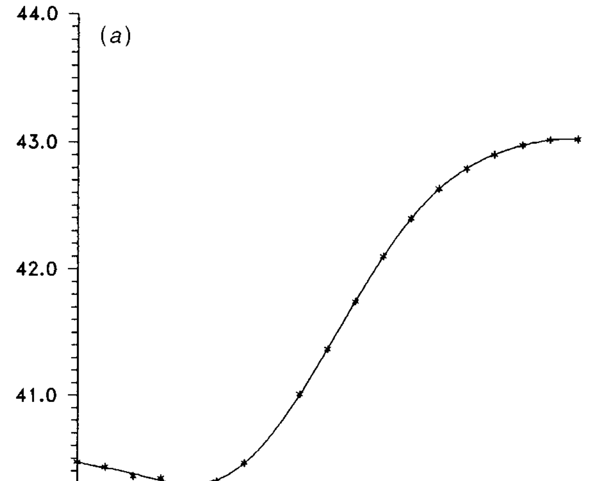


Fig. 3 Rotational barrier for (*a*) thienyl ring rotation [0° ≤ ω(a–b–c–d) ≤ 90°, ω(e–f–g–h) = 90°] and (*b*) phenyl ring rotation in **3a** [0° ≤ ω(e–f–g–h) ≤ 180°, ω(a–b–c–d) = 19.8°] (AM1 values)

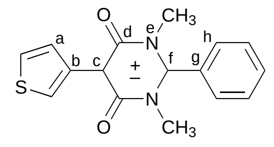
Table 1 Calculated dipole moments of pyrimidiniumolates of type **3**

R^1 (R^2=H)	dipole moment/ Debye (AM1 values)	dipole moment/ Debye (PM3 values)
-NO_2	5.09	5.74
-Br	9.05	10.15
-H	10.83	11.35
-OMe	11.50	12.03
-NEt_2	12.85	13.39

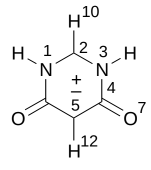
Table 2 Calculated geometry of compound **5**; distances *r* in Å

method	$r_{1,2}$	$r_{3,4}$	$r_{4,5}$	$r_{4,7}$	$r_{2,10}$	$r_{5,12}$
AM1[a]	1.343	1.465	1.412	1.243	1.116	1.096
PM3[a]	1.352	1.492	1.406	1.223	1.104	1.094
rhf/6-311g**	1.296	1.466	1.402	1.194	1.075	1.070
mp2/6-31g*	1.317	1.481	1.409	1.231	1.086	1.083
b3lyp/6-31g*	1.317	1.491	1.411	1.222	1.086	1.082
b3lyp/6-311g**	1.313	1.493	1.409	1.215	1.085	1.080
exp[b]	1.33	1.48	1.41	1.22	—	—

[a] The program systems MOPAC,[22] GAUSSIAN92[24] and G92/DFT[25] were used. [b] For 1,2,3,5-tetraphenylpyrimidiniumolate.[23]



3a



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In conclusion it can be stated that dipolar systems of type **3** (**5**) may serve as potentially useful starting materials for conductive polymers.

The continued support of our work by the Fonds der Chemischen Industrie is gratefully acknowledged. Thanks are due to Dr H. Naarmann, BASF, for conductivity measurements.

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Paper 7/04922F; *Received* 9th *July*, 1997