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New Family of Redox-Active Heterocycles

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Redox-active heterocycles are intrinsically interesting species which play important roles in biological catalysis and materials science. This rich area is represented by flavins, polythiophenes, and tetrathiafulvalenes. The functional role of these heterocycles is tied to their ability to exist in multiple oxidation states.[2] In many biomolecules, this redox function is central to energy storage and transfer,[3] while in solid state chemistry, redox chemistry controls the formation and nature of electrically conductive superstructures.[4] The present report describes the discovery of a completely new family of redox-active heterocycles which were prepared from inexpensive reagents via an unusual method.

Our studies on the activation of sulfur by donor solvents[5] led us to examine the reaction of elemental sulfur with 1-methylimidazole (MeIm). Thus 2 g of sulfur in 10 mL of MeIm was allowed to react at 110 °C. After 72 h, the dark liquid was evaporated and the oily residue was extracted into 10 mL of DMF, which was diluted with Et_2O to precipitate 4 g of dark red microcrystals of the *N*-methylimidazolium salt $(MeImH)_2[C_6H_2N_4S_4Me_2]$ (70% yield based on S). This reaction is conducted under flowing nitrogen to remove the hydrogen sulfide coproduct (eq 1). The anion is a tetraaza diheterocycle,

$$4MeC_3N_2H_3 + 5S \rightarrow [MeC_3N_2H_4{}^+]_2\{H_2Me_2C_6N_4S_4{}^{2-}\} + H_2S \quad (1)$$

to which we will refer as H_2X^{2-}. $(MeImH)_2H_2X$ dissolves in water upon the addition of NaOH (to deprotonate the $MeImH^+$), and treatment of these solutions with PPh_4Cl afforded the corresponding $(PPh_4)_2H_2X$. This salt is freely soluble in polar organic solvents although the solutions are quite oxygen sensitive. Key spectroscopic data bearing on solution structure of H_2X^{2-} include the single C*H*$_3$ resonance in the ^1H NMR spectra and sharp, intense IR bands assigned to ν_{NH} and $\nu_{C=S}$.[6] Single-crystal X-ray diffraction analysis of the $PPh_4{}^+$ salt revealed a planar and centrosymmetric anion (Figure 1).[7] The two N*H* atoms were located crystallographically.

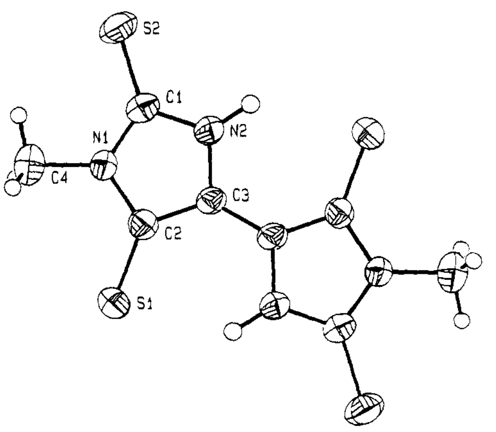
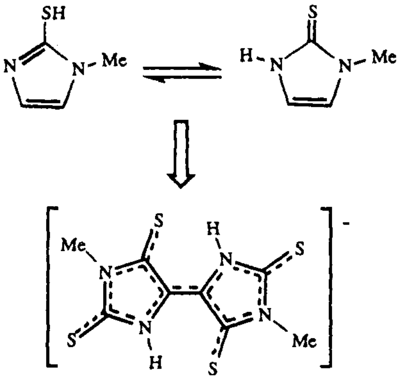


Figure 1. Structure of the monoanion in the 1:1 salt $(PPh_4)H_2Me_2C_6N_4S_4$. The structure of the dianion in the 2:1 salt is similar. Both the monoanion and the dianion are centrosymmetric. Important bond lengths (Å; data for the 2:1 salt are given in brackets): S(1)−C(2) 1.662(5) [1.763(3)]; S(2)−C(1) 1.664(5) [1.696(3)]; N(1)−C(1) 1.362(6) [1.415(3)]; N(1)−C(2) 1.391(6) [1.359(3)]; N(1)−C(4) 1.446(7) [1.444(3)]; N(2)−C(1) 1.357(6) [1.347(3)]; N(2)−C(3) 1.375(6) [1.394(3)]; C(2)−C(3) 1.400(6) [1.364(3)]; C(3)−C(3)′ 1.388(9) [1.435(5)].

Scheme 1



The dianion H_2X^{2-} clearly results from the 4,4′-coupling of two MeIm rings, the remaining four CH centers being converted to thiocarbonyls. At least half of the C−S bonds are formed prior to the coupling process based on the following reaction (Scheme 1). DMF solutions of 1-methyl-2-mercaptoimidazole (MeImS)[8] react with S_8 (145 °C, 8 h) to give purple solutions, and dilution of this mixture with an MeCN solution of Ph_4PBr followed by cooling at −20 °C, afforded black crystals of $(Ph_4P)H_2X$ in 54% yield.[9] This procedure can be readily conducted on a multigram scale. The anion thus generated differs from the aforementioned H_2X^{2-} by one electron, and the paramagnetism of H_2X^- was confirmed by Evans' NMR method ($\mu = 1.7\ \mu_B$).[10]

A crystallographic study of $(PPh_4)H_2X$ again revealed a centrosymmetric structure. The geometries of the monoanion and dianion differ only subtly,[11] the most noteworthy changes being associated with the pair of C2−S1 bonds which are

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[1] (a) School of Chemical Sciences. (b) Institut für Anorganische Chemie.

[2] Leading references: Vögtle, F. *Supramolecular Chemistry*; J. Wiley: New York, 1991.

[3] Cusanovich, M. A.; Meyer, T. E.; Bartsch, R. G. In *Chemistry and Biochemistry of Flavoenzymes*; Muller, F., Ed.; CRC Press: Boca Raton, FL, 1991.

[4] *Organic Superconductors (Including Fullerenes). Synthesis, Structure, Properties, and Theory*; Prentice Hall: Engelwood Cliffs, NJ, 1992.

[5] Paul, P. P.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 3316 and references therein.

[6] For the $MeImH^+$ salt: Anal. Calcd for $C_{16}H_{22}N_8S_4$ (found): C, 42.26 (42.19); H, 4.88 (4.79); N, 24.65 (24.25); S, 28.2 (28.71). IR (KBr): 3026, 3229 cm^{-1}. For the $PPh_4{}^+$ salt: Anal. Calcd for $C_{56}H_{48}N_4P_2S_4$ (found): C, 69.45 (69.66); H, 5.01 (5.54); N, 5.79 (5.71); P, 6.39 (6.82); S, 13.26 (13.19). IR (KBr): 3231 (ν_{NH}), 1108 (ν_{CS}) cm^{-1}. ^1H NMR (CD_2Cl_2): 3.46 (s, 6H), 7.6−7.7 ppm (m, 40H), 13.6 (s, 2H, NH). ^{13}C NMR (CD_2Cl_2): 167.5, 122.6, 121.7, 36.1.

[7] Crystal data for $C_{56}H_{48}N_4P_2S_4$: red translucent, monoclinic, $P2_1/n$, $a = 11.839(2)$ Å, $b = 16.120(5)$ Å, $c = 13.012$ Å, $\beta = 92.27(3)°$, $V = 2481.1(10)$ Å^3, $Z = 4$; $T = 198$ K; $R = 0.0399$; $R_w = 0.0863$; $s = 1.051$. Enraf-Nonius CAD4 diffractometer, 4561 measured reflections, Mo Kα, 4361 independent ($R_{int} = 0.0333$) and 4361 observed reflections [$I > 2\sigma(I)$]. The structure of the $(MeImH^+)_2$ salt was also determined.

[8] *The Tautomerism of Heterocycles*; Elguero, J., Marzin, C., Katritzky, A. R., Linda, P., Eds.; Academic Press: New York, 1976.

[9] For $PPh_4[H_2X]$: Anal. Calcd for $C_{32}H_{28}N_4PS_4$ (found): C, 61.22 (61.02); H, 4.46 (4.23); N, 8.93 (8.84); S, 20.45 (20.36); P, 4.94 (4.78). IR (KBr): 3203 (ν_{NH}), 1105 cm^{-1}. UV−vis (CH_2Cl_2), λ (nm): 238, 252, 358, 440, 478, 518, 768. For $NBu_4[H_2X]$: Anal. Calcd for $C_{24}H_{44}N_5S_4$ (found): C, 54.30 (54.23); H, 8.35 (8.56); N, 13.19 (13.13); S, 24.15 (22.25). IR: 3230 cm^{-1} (ν_{NH}).

[10] The ^1H NMR spectrum only shows the broadened resonances for the phenyl groups of $PPh_4{}^+$; the methyl resonances were not observed.

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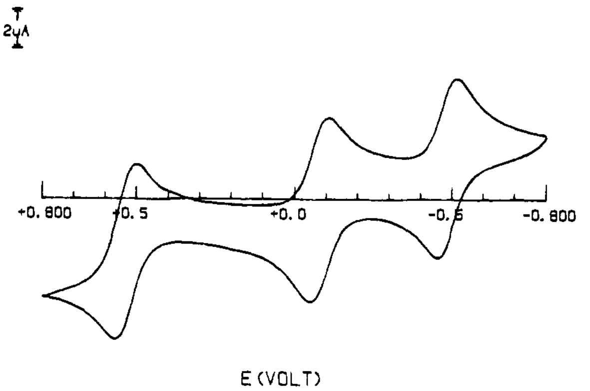

Figure 2. Cyclic voltammogram of a 10^{-3} M MeCN solution of $(PPh_4)H_2Me_2C_6N_4S_4$ (supporting electrolyte, 0.1 M NEt_4BF_4; scan rate = 200 mV/s; reference electrode = Ag/AgCl; working and auxiliary electrodes, Pt; *iR* correction). The wave at ~+550 mV is for the ferrocene internal standard.

substantially shorter in the monoanion (1.662(5) Å) than in the dianion (1.726(3) Å for H_2X^{2-}).[12] The radical anion H_2X^- adopts a more delocalized structure than H_2X^{2-} as revealed by the narrow range for the eleven intra- and inter-ring C−C and C−N distances of 1.357−1.391 Å (vs 1.347−1.435 Å for H_2X^{2-}).

Cyclic voltammetric experiments reveal that $(PPh_4)H_2X$ undergoes 1e oxidation at ~0 mV (to give H_2X^0) and 1e reduction at −482 mV (potentials vs Ag/AgCl, Figure 2). The couples are fully reversible based on the differences in the peak potentials (ΔE_p) which are within 10 mV of an internal ferrocene standard. Furthermore, plots of current vs the square root of the scan rate were linear for both redox events, indicating a diffusion-controlled process (no rearrangement). Very few organic compounds undergo two redox events at such mild potentials.

Motivated by the electrochemical results, we investigated the chemical oxidation of H_2X^-. Acetonitrile solutions of PPh_4H_2X react with 0.5 equiv of iodine to precipitate green microcrystals of H_2X (eq 2).[13] This species is easily obtained in pure form.

$$H_2Me_2C_6N_4S_4^- + 0.5I_2 \rightarrow H_2Me_2C_6N_4S_4 + I^- \quad (2)$$

We observe a sharp ν_{NH} band in its IR spectrum and a series of strong bands in the region appropriate for $\nu_{C=S}$. Suspensions of H_2X and H_2X^{2-} quickly conproportionate to give H_2X^-. The structure of the neutral species cannot yet be definitively assigned although the facility with which it reverts to soluble anions suggests that it is molecular. Two possible structures for H_2X include a cyclic persulfide or a tetrathione (thioindigoid[14]).[15] The very low solubility of H_2X has thwarted attempts to grow crystals. Further work has shown that H_2X behaves as a weak acid since it dissolves in MeCN only upon addition of Et_3N. These experiments open the way for exploring the structural chemistry of the third oxidation state, not to mention examining the pH dependence of the redox properties of H_2X.

In summary, a new family of heterocycles has been prepared easily and from readily available starting reagents. These species are of special interest since they display both multielectron redox and acid/base properties. Recent work has also shown that HX^- binds metal ions.

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Supplementary Material Available: Experimental procedures and spectroscopic data for new compounds and crystallographic information including crystal, data collection, and refinement details, bond angles and distances, atomic coordinates, and thermal parameters (22 pages); observed and calculated structure factors (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[11] Crystal data for $C_{32}H_{28}N_4PS_4$: black, monoclinic, *C*2/*c*, $a = 16.664(5)$ Å, $b = 7.724(2)$ Å, $c = 24.185(6)$ Å, $\beta = 97.46(2)°$, $V = 3086.6(14)$ Å^3, $Z = 4$, $T = 293$ K, Mo Kα, $R = 0.0566$, $R_w = 0.0916$, $s = 1.051$. Enraf-Nonius CAD4 diffractometer, 2779 measured reflections, 2702 independent ($R_{int} = 0.0450$) and 1269 observed reflections [$I > 2\sigma(I)$].

[12] A discussion of C−S multiple bonding as well as some relevant chemistry of mercaptoimidazoles: Freeman, F.; Ziller, J. W.; Po, H. N.; Keindl, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 2586.

[13] Procedure: A solution of 2 g (3.77 mmol) of $(Bu_4N)[XH_2]$ in 100 mL of MeCN was treated with 0.48 g (1.89 mmol) of solid I_2. After 3 h the green crystals were collected and washed with MeCN and Et_2O. Yield: 0.74 g (68%). Anal. Calcd for $C_8H_8N_4S_4$ (found): C, 33.31 (33.44); H, 2.78 (2.86); N, 19.43 (19.56); S, 44.49 (43.76). EIMS (70 eV): *m/z* 288. IR: 3223 (ν_{NH}), 1263, 1229, 1141, 1108 cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.65 (s). UV−vis (CH_2Cl_2), λ (nm): 238, 272, 454, 550, 588.

[14] For a recent discussion of thioxoindigoid compounds, see: Schroth, W.; Hintzsche, E.; Felicetti, M.; Spitzer, R.; Sieler, J.; Kempe, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 739; *Angew. Chem.* **1994**, *106*, 808.

[15] These two structures are as follows: