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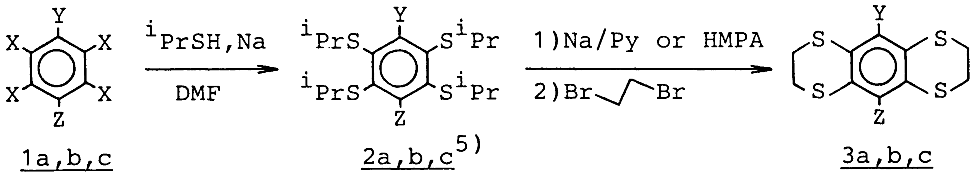
Synthesis and Electrochemical Properties of 2,3,6,7-Tetrahydro-1,4,5,8-tetrathiaanthracene (HTA) and Its Derivatives[1]

Tatsuya NABESHIMA, Satoru IWATA, Naomichi FURUKAWA,*
Kenji MORIHASHI, and Osamu KIKUCHI
Department of Chemistry, University of Tsukuba,
Tsukuba, Ibaraki 305

2,3,6,7-Tetrahydro-1,4,5,8-tetrathiaanthracene (HTA), 9-amino-HTA, 9-acetyl-HTA, 9,10-dimethyl-HTA, and 1,4,5,8-tetrathiaanthracene have been synthesized. Electrochemical properties and preparation of the charge transfer complexes of HTAs with several acceptors are also reported.

Recently, the design and synthesis of new aromatic compounds bearing polythiasubstituents are an interesting and important project in the sulfur chemistry, because the studies on their cation radical, dication, and polycation are expected to provide a variety of scopes in elucidating their basic structures and electronic delocalization in the molecules.[2] Furthermore, introduction of ethylenedithio group into tetrathiafulvalene is, for example, an effective chemical modification to furnish higher transition temperature of superconduction.[3] In this communication we describe the preparation of 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaanthracene (HTA, 3a), its derivatives with functional group(s) at benzene ring and 1,4,5,8-tetrathiaanthracene (TA, 6) to test the electrochemical properties and ability of charge transfer complex formation.

3,4-Dimethyl-1,2,4,5-tetrakis(isopropylthio)benzene (Me_2-TPTB, 2b), and 3-amino-TPTB (2c) were prepared according to a similar procedure for TPTB (2a) reported by Bechgaard.[4] TPTB (13 mmol) was treated with sodium (70 mmol) at 100-105 °C in pyridine or hexamethylphosphoramide (HMPA) to generate the corresponding tetrathiolate anion in situ,[6,7] followed by addition of dibromoethane (29 mmol) at 5 °C to produce 3 (Scheme 1). The crude product thus obtained was purified by silica gel column chromatography and/or preparative HPLC.[8] Friedel-Crafts acylation took place to give monoacetyl-HTA (3d) in 29% yield. Dehydrogenation of HTA was achieved either by the Pummerer reaction[9] of the monoxide of 3a or treatment of SO_2Cl_2, followed by elimination in quinoline,[10] affording 5 and 6 in

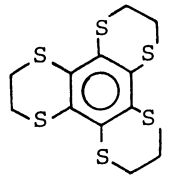


	a	b	c
X	Cl	Br	Cl
Y	H	Me	NH_2
Z	H	Me	H

Scheme 1. Synthetic route to HTAs.

12% and 20% yields, respectively (Scheme 2). The structures of HTA and the derivatives were determined by NMR, IR, MS spectra, or elemental analyses.[11)]

Redox potentials of HTAs were measured by cyclic voltammetry in acetonitrile. As we expected, NH_2-HTA has the lowest redox potential (E_p=0.90 V) among 3a-3d, 2,3,6,7-tetrahydro-1,4,5,8-tetrathiaphenanthrene (HTP, 7), and 2,3,6,7,10,11-hexahydro-1,4,5,8,9,12-hexathiatriphenylene (HTT, 8). Onyl 6 shows reversible two step oxidation potential ($E^{\circ}_{1/2}$=0.98, 1.19 V) and the first potential is lower than that of 3a (1.13 V) owing to the stabilization of cation radical by the double bond (Table 1). A good linear relationship between the peak potentials and their σ^+ values[12)] was obtained, giving rise to ρ value of 0.354. As we expected, the E_p values become lower with increasing the electron donating ability of a substituent in the phenyl ring.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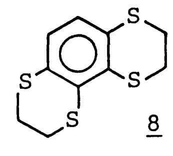
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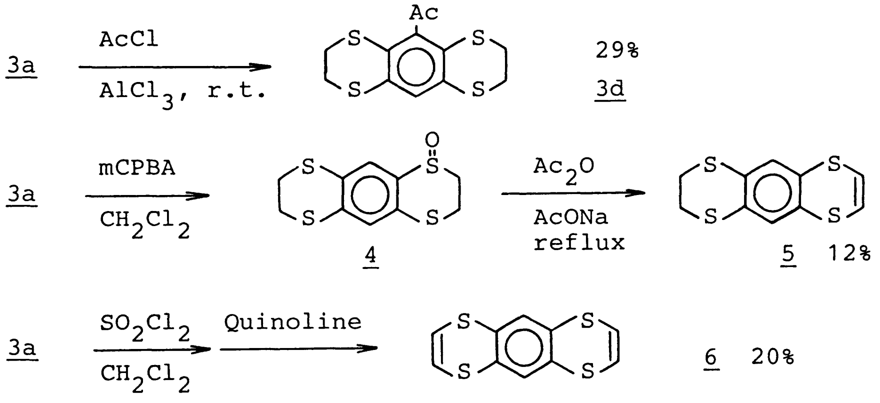

Scheme 2.

CT complexes of HTAs and a suitable electron acceptor such as TCNQ, TCNE, and DDQ, were easily obtained by mixing 3a and a donor in acetonitrile at room temperature. Recrystallization of the crude black precipitates gave glossy black or purple needles. Elemental analyses of the crystals indicate formation of a 1:1 CT complex (Table 2). The CN stretching vibration of 3a-TCNQ (ν=2220 cm^{-1}) and 3b-TCNQ (2219 cm^{-1}) suggests that a partial charge transfer occurs.[13]

Table 1. Redox potentials of HTA derivatives

Compound[a]	E_p[b]	$E^\circ_{1/2}$[b]	E_p- 0.03[8]
HTA(3a)	1.17	1.13	
HTP(7)	1.19	1.14	1.17
HTT(8)	1.13	1.07	1.10
Me_2-HTA(3b)	1.08	1.04	
NH_2-HTA(3c)	0.90	irre.	
Ac-HTA(3d)	1.28	1.22	
TA(6)	1.02	0.98	
	1.23	1.19	

a) In CH_3CN with n-$Bu_4N^+ClO_4^-$(0.1 M) at r.t.
b) V vs. SCE, scan speed 200 mV/s, this work

Stable cation radical of 3a, 7, and 8 was generated by dissolving in concd sulfuric acid at room temperature, resulting in blue or purple solution(e.g. λ_{max} in H_2SO_4; 3a, 530 nm, 876 nm; 7, 401 nm, 736 nm). The colors of the cation radical solution do not change for at least several weeks at room temperature. Their ESR spectra in H_2SO_4 or $AlCl_3$-CH_3NO_2 strongly support the formation of cation radical. Cation radical was also produced as very stable powder by the reaction of HTA with $SbCl_5$ in $CHCl_3$. The salt can be stored for several months at room temperature and the properties of the radical were also characterized by ESR spectroscopy. Detailed ESR study concerning the conformation of radical cations dependent on temperature and theoretical treatment will be reported elsewhere.

These results open a way to the detailed study on the chemistry of sulfur cation radicals and to a new type of electron donors for CT complexes.

Table 2. Charge transfer complexes of HTA with acceptors

Acceptor	Color	Mp(dec.)/°C	Acceptor:HTA (mole ratio)
TCNQ	violet	239-240	1 : 1
TCNE	dark violet	222-223	1 : 1
DDQ	black	200-202	1 : 1

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11) 3a; ^{1}H NMR($CDCl_3$) δ 7.00(s, Ar, 2H), 3.22(s, 8H), ^{13}C NMR δ 29.36, 128.23, 128.64; IR(KBr) 2977, 2914, 2357, 1432, 1412, 1295, 1263, 1112, 949, 871, 834, 655, 438 cm^{-1}; Mp 224-224.5 °C; Anal. Found: C, 46.20; H, 3.88%. Calcd for $C_{10}H_{10}S_4$: C, 46.47; H, 3.90%. 3b; ^{1}H NMR 3.20(s, 8H), 2.43(s, Me, 6H); IR 2921, 2905, 1439, 1411, 1383, 1371, 1333, 1320, 1284, 1168, 1142, 1130, 1014, 987, 954, 851, 663 cm^{-1}; Mp 160.0-160.5 °C; MS(m/z) 286(M^+). 3c; ^{1}H NMR 6.77(s, 1H), 4.45(br.s, NH_2, 2H), 3.19(s, 8H); IR 3453, 3352, 2916, 1587, 1542, 1515, 1414, 1384, 1290, 1097, 1085, 837 cm^{-1}; MS(m/z) 273(M^+). 3d; ^{1}H NMR 7.12(s, 1H), 3.3-3.7(m, 8H), 2.55(s, Me, 3H); IR 2940, 1695, 1430, 1410, 1390, 1355, 1290, 1253, 1220, 1185, 1175, 1160, 1113, 940, 870, 610, 525 cm^{-1}; MS(m/z) 302(M^+). 6; ^{1}H NMR 7.16(s, 2H), 6.50(s, 4H); IR 3030, 1551, 1432, 1420, 1297, 1112, 893, 868, 803, 688 cm^{-1}; Mp 204-205 °C; MS(m/z) 254(M^+); Anal. Found: C, 46.58; H, 2.48%. Calcd for $C_{10}H_6S_4$: C, 47.21; H, 2.43%.

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