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Benzoxazinophenoxazines: neutral and charged species

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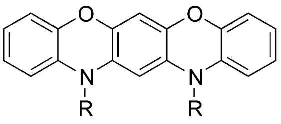
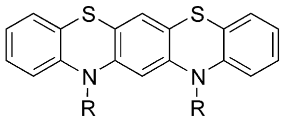
Abstract—A new electron-donor, benzoxazinophenoxazine **1**, was synthesized. It showed a low oxidation potential of +0.21 ~ +0.23 V versus SCE. The neutral molecule, its radical cation salts, and charge transfer complexes were synthesized and characterized. © 2001 Elsevier Science Ltd. All rights reserved.

The synthesis and characterization of electron-donating compounds are important not only in their chemistries but also in their material sciences including their solid-state properties, e.g. conductivity, magnetism, and electroluminescence. To date, many studies have focussed on 6π- or 7π-electronic systems in five-membered heterocyclic rings (e.g. thiophenes[1] or TTFs[1–3]). Although 8π-electronic systems in six-membered heterocyclic rings (e.g. phenoxazines and phenothiazines) are well known as good electron-donors, studies of such compounds have revealed little.[4–6]

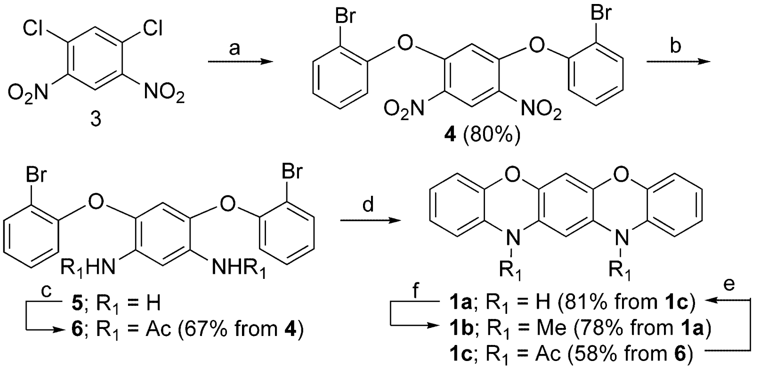


1a; R = H, **1b**; R = Me



2a; R = H, **2b**; R = Me

The benzoxazino- and benzothiazino-condensed phenoxazines and phenothiazines, **1** and **2**, are interesting compounds expected to have superior electron-donating ability. The sulfur-compound **2** has recently been synthesized by two groups: Müllen's group[7] used nitrene-induced cyclization (Cadogan cyclization[8]) and Silberg's group used a more convenient sulfur-bridging method[9,10]. Electrochemical studies of the neutral **2** and spectral studies (UV–vis and EPR) of the radical cations, charge transfer complexes, and deprotonated radical species have been reported, but the solid-state properties of these species have not been clarified. In contrast to **2**, the oxygen analogue **1**, which is expected to be a better electron-donor, has not been described in the literature. Obviously, **1** cannot be synthesized by Silberg's method because of the lack of a suitable oxygen-bridging method. We report the synthesis of **1**,



Scheme 1. *Reagents and conditions*: (a) *o*-bromophenol (2 equiv.), NaH/DMSO, 90°C, 90 min; (b) $SnCl_2·2H_2O$/EtOH, 70°C, 40 min; (c) Ac_2O, 0°C, 15 min; (d) Cu, K_2CO_3/nitrobenzene, 180–185°C, 50 min; (e) KOH (20 equiv.)/EtOH, rt, 25 min; (f) *n*-BuLi, Me_2SO_4/THF-toluene (1:2).

Keywords: benzoxazinophenoxazine; charge transfer complex; radical cation; conductivity.

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its radical cation $\mathbf{1}^{+}$, and charge-transfer complexes together with their properties.

Synthesis of 1,4-benzoxazino[2,3-*b*]phenoxazine (**1a**) and the *N*-methyl derivative (**1b**) was achieved through an intramolecular Ullmann coupling as a key step as illustrated in Scheme 1. The nucleophilic aromatic substitution reaction of 1,5-dichloro-2,4-dinitrobenzene with 2-bromophenolate in DMSO gave **4** with 80% yield. Reduction of **4** followed by acetylation provided **6** in good yield. Intramolecular Ullmann coupling giving **1c** proceeded with moderate yield by heating at 180–185°C for 50 min. Hydrolysis of **1c** gave **1a** with good yield. The methylation through lithiation in THF:toluene = 1:2 gave **1b** with 78% yield. A similar approach was possible for the known sulfur analogue **2a**, which was hardly soluble in many organic solvents; thus, *N*-methylation under similar conditions leading to **2b** was difficult. The compound **2b** was successfully prepared (72% yield) in DMSO using dimsyl sodium as a base and dimethyl sulfate as a methylation reagent.

The oxidation potentials of the oxygen derivatives **1a**,**b** are shown in Table 1 with those of the sulfur analogues **2a**,**b**. The oxygen derivatives **1a**,**b** have lower oxidation potentials than the sulfur derivatives **2a**,**b**.[‡] The first oxidation step (E_1) was reversible for the N–H and N–Me derivatives, **1a**,**b** and **2a**,**b**. The second oxidation step (E_2) was irreversible for the N–H derivatives **1a** and **2a**, and the N–Me oxygen derivative **1b**, but reversible for the sulfur derivative **2b** (Fig. 1). The E_1-values for these ring-fused compounds are smaller than the oxidation potential of *N*-methylphenoxazine (+0.59 V under similar conditions) or *N*-methylphenothiazine (+0.76 V under similar conditions), showing an efficient ring-fusion effect. The E_1-values of the oxygen derivatives **1a**,**b** are even smaller than TTF (+0.30 V under similar conditions).

Table 1. Oxidation potential of **1a**–**2b** and the related compounds[a]

Compd	E_1	E_2
1a	$+0.21^{b}$	$+0.43^{c}$
1b	$+0.23^{b}$	$+0.74^{c}$
2a	$+0.30^{b}$	$+0.51^{c}$
2b	$+0.50^{b}$	$+0.85^{b}$

[a] V versus S.C.E. measured in DMF in the presence of $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) with the sweep rate of 50 mV/s.

[b] Half wave potential.

[c] Peak potential.

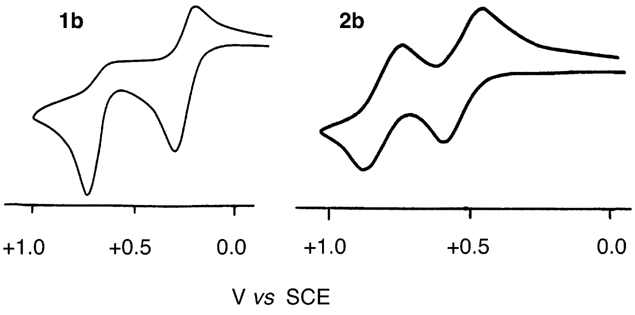

Figure 1. Cyclic volutammograms of **1b** and **2b** in DMF.

Because of the low oxidation potentials, the oxygen derivatives **1** can be expected to form charge-transfer (CT) complexes with suitable electron-acceptors. For instance, when **1b** was mixed with an equivalent

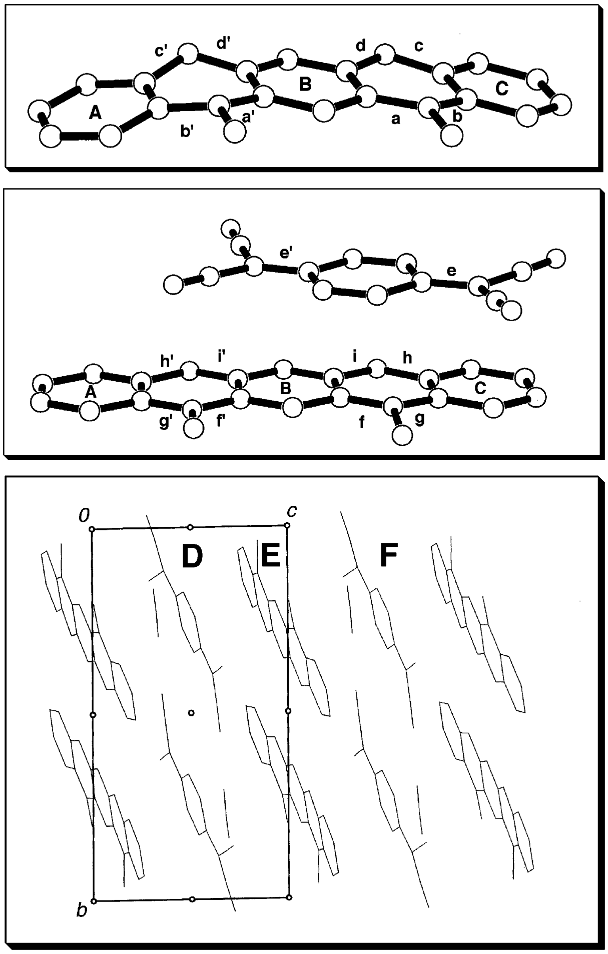

Figure 2. Molecular structure of the neutral **1b** (top), the charge transfer complex **1b**-TCNQ·CH_3CN (middle), and the crystal packing structure of **1b**-TCNQ·CH_3CN (bottom); in the middle figure, CH_3CN solvent molecules incorporated in the crystal lattice was omitted for clarity; bond length (Å): a,a′ = 1.41, 1.41; b,b′ = 1.40, 1.40; c,c′ = 1.38, 1.39; d,d′ = 1.38, 1.40; e,e′ = 1.40, 1.40; f,f′ = 1.38, 1.38; g,g′ = 1.41, 1.40, h,h′ = 1.38, 1.39; i,i′ = 1.37, 1.36, dihedral angle (°) for the neutral **1a**: plane A/B = 18.3, A/C = 24.4, B/C = 6.1, dihedral angle (°) for the **1a**-TCNQ·CH_3CN: A/B = 2.2, A/C = 4.2, B/C = 2.1.

[‡] The difference in oxidation potentials between the phenoxazines and phenothiazines is especially large for the N–Me derivatives. This is probably related to the planarity of these cation radical states. The planar N–Me phenothiazine radical cations would experience higher steric repulsion between the N–Me group and the hydrogens at peri-positions because of the longer C–S bond length (compared to the C–O bond length).

amount of TCNQ, dark-green solids were precipitated. Recrystallization from CH_3CN gave a pure CT complex with a formula of **1b**-TCNQ·CH_3CN. The IR spectrum showed 2189 cm^{-1} (KBr) as a CN stretching vibrational absorption, indicating that the degree of charge-transfer was 0.81.[11]

Fig. 2 compares the structures of neutral **1b** and CT-complex **1b**-TCNQ·CH_3CN as well as the crystal packing structure of **1b**-TCNQ·CH_3CN.[§] While the neutral **1b** has a shallow butterfly structure (Fig. 2, top), the CT complex has an almost planar structure (middle). Furthermore, the length of the C–C double bond (e or e′ bond in Fig. 2, middle; 1.40 Å) of the dicyanomethylene moiety of TCNQ is an intermediate value between those of the neutral TCNQ (1.37 Å[12]) and K^+TCNQ^-(1.42 Å[13]), suggesting the partial charge transfer character in accordance with the IR spectrum. The bond length differences for the structure of the donor moiety between the charged and neutral species were small. The crystal packing structure of **1b**-TCNQ·CH_3CN is also shown (Fig. 2, bottom) with the symmetry elements for the space group $P\bar{1}$ (No. 2). The molecules, TCNQ (**D** in Fig. 2, bottom), **1b** (**E**), and TCNQ (**F**) are almost in parallel planes and the distance between these planes is about 3.2 Å for **D**, **E**-planes, and about 3.3 Å for **E**, **F**-planes. These values are shorter than twice the van der Waals radii of aromatic rings (1.77 Å for benzene),[14] which indicates good orbital overlap between the electron-donor and -acceptor. Acetonitrile solvents (linear molecules indicated in Fig. 2, bottom) are located around the charged TCNQ and these components make a mixed stack along the *c*-axis.

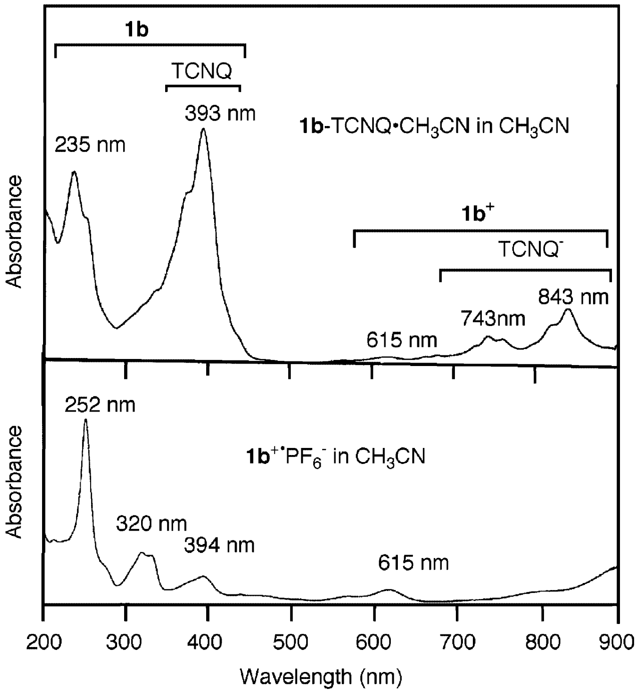

Figure 3. UV–vis spectra of **1b**-TCNQ·CH_3CN (upper) and $\mathbf{1b}^+PF^{6-}$ (lower) in CH_3CN.

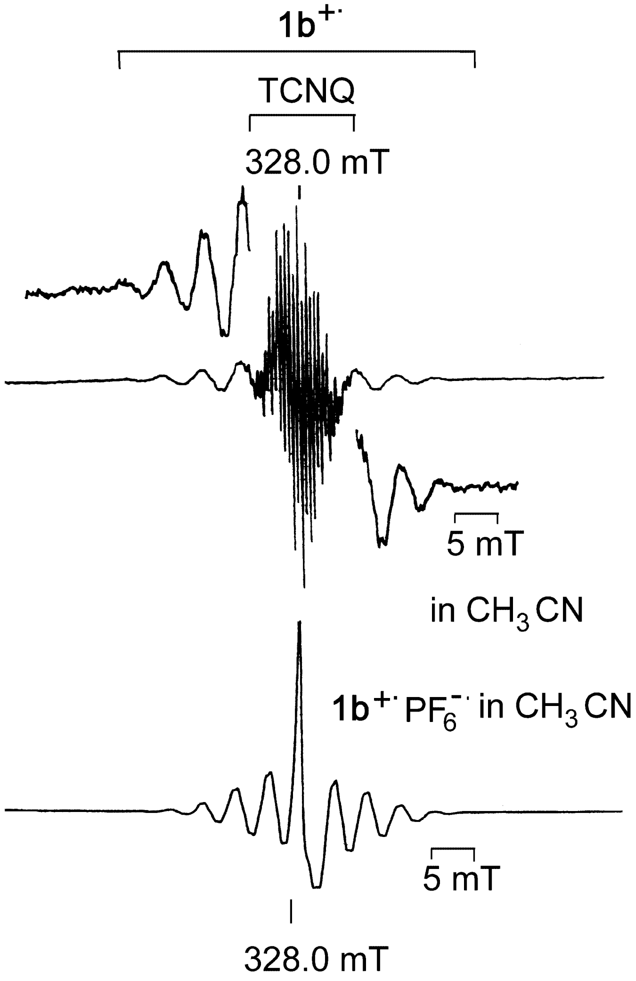

Figure 4. Solution EPR spectra of **1b**-TCNQ·CH_3CN (upper) and $\mathbf{1b}^+PF^{6-}$ (lower) in CH_3CN.

Table 2. The charge transfer complexes and radical ion salts with physical properties

Compd.[a]	Method	Color	Solvent	Conductivity (S cm^{-1})
1a-TCNQ	Mixing	Blue	CH_3CN	7.8×10^{-6}
1b-TCNQ	Mixing	Dark green	CH_3CN	9.9×10^{-4}
$\mathbf{1b}^+ClO_4^-$	Electrolysis	Dark green	THF	5.6×10^{-7}
$\mathbf{1b}_2{}^+I_3^-$	Electrolysis	Dark green	PhCl	3.0×10^{-5}
$\mathbf{1b}^+PF_6^-$	Electrolysis	Dark green	THF	9.8×10^{-6}

[a] The chemical formula accords with the elemental analysis within ±0.3% except for **1a**-TCNQ(±0.5%).

[§] Crystal data of **1b**; $C_{20}H_{16}N_2O_2$, monoclinic, Space group $P2_{1/c}$ (No.14), $a=15.133(1)$, $b=13.167(1)$, $c=16.902(2)$ Å, $\beta=114.758(6)°$, $V=3058.3(4)$ Å^3, $Z=8$, $D_c=1.374$ g cm^{-3}; Cu Kα radiation ($\lambda=1.54178$ Å); $2\theta<130.2°$; 5219 unique reflections of which 3323 were treated as observed [$I>3\sigma(I)$]; $R=0.057$. $R_w=0.086$, Crystal data of **1b**-TCNQ·CH_3CN; $C_{34}H_{23}N_7O_2$, triclinic, space group $P\bar{1}$ (No. 2), $a=12.423(3)$, $b=15.764(4)$, $c=8.130(2)$ Å, $\alpha=90.84(2)$, $\beta=108.47(2)$, $\gamma=67.98(2)°$; $V=1390.2(7)$ Å^3, $Z=2$, $D_c=1.342$ g cm^{-3}; Mo Kα radiation ($\lambda=0.71069$ Å; $2\theta<55.0°$; 6394 unique reflections of which 4606 were treated as observed [$I>3\sigma(I)$]; $R=0.053$. $R_w=0.087$. These data have been deposited with the Cambridge Crystallographic Data Center (CCDC 163017 for **1b**, CCDC 163016 for **1b**-TCNQ·CH_3CN).

In CH_3CN solution, the CT complex (**1b**-TCNQ·CH_3CN) did not show the charge transfer absorption band.[15] Instead, neutral and charged species were observed (Fig. 3). The presence of the neutral species is in accordance with the partial charge transfer character of **1b**-TCNQ·CH_3CN. The spectral assignment of $\mathbf{1b}^+$ was achieved by comparison with $\mathbf{1b}^+PF^{6-}$ prepared electrochemically.

Similarly, the EPR spectrum of the CT complex (**1b**-TCNQ·CH_3CN) in CH_3CN solution showed mixed signals due to the TCNQ radical anion[16] and $\mathbf{1b}^+$. Identification of $\mathbf{1b}^+$-signals was achieved by comparing with $\mathbf{1b}^+PF_6^-$ ($g=2.0034$, formally nine lines with splitting of ca 4.5 G) (Fig. 4).

Table 2 lists the colors and formulas (determined by elementary analysis) of the CT-complexes or the radical ion salts prepared by mixing with TCNQ or by electrolysis in the presence of suitable electrolytes. In contrast to **1a** and **1b**, the sulfur analogues did not give complexes with well-definable elemental composition under similar conditions. The conductivity for the powdered sample of **1b**-TCNQ·CH_3CN showed a low conductivity (3×10^{-7} S cm^{-1}). However, removing the incorporated CH_3CN solvent by heating under vacuum increased the conductivity sharply. The value in Table 2 is for the powdered sample whose elemental analysis coincided with the formula of **1b**-TCNQ. The conductivity for other salts (powdered samples) is also summarized in Table 2, showing that these compounds are semiconductors with 10^{-3}–10^{-7} S cm^{-1}.

Compounds data for **1a** and **1b** are presented in the footnote.¶

References

1. Bäuerle, P. In *Electronic Materials*: *The Oligomer Approach*; Müllen, K.; Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; pp. 105–197.
2. Ishiguro, T.; Yamabe, K.; Saito, G. In *Organic Superconductors*; Fulde, P., Ed.; Springer: Telos, 1998; pp. 125–220.
3. Kobayashi, H.; Kobayashi, A.; Cassoux, P. *Chem. Soc. Rev.* **2000**, *29*, 315–324.
4. Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2945–2949.
5. Oza, A. T. *Czech. J. Phys.* **1983**, *B33*, 1148–1153.
6. Kozawa, K.; Hoshizaki, T.; Uchida, T. *Bull. Chem. Soc.* **1991**, *64*, 2039–2044.
7. Kistenmacher, A.; Baumgarten, M.; Enkelmann, V.; Pawlik, J.; Müllen, K. *J. Org. Chem.* **1994**, *59*, 2743–2747.
8. Cadogan, J. I. G. *Synthesis* **1969**, *1*, 11–17.
9. Silberg, I. A.; Cristea, C. *Hetreocyclic Commun.* **1996**, *2*, 117–124.
10. Jitaru, M.; Cristea, C.; Silberg, I. A. *Rev. Roum. Chim.* **1999**, *44*, 863–866.
11. Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442–2443.
12. Long, R. E.; Sparks, R. A.; Trueblood, K. N. *Acta Crystallogr.* **1965**, *18*, 932–939.
13. Konno, M.; Ishii, T.; Saito, Y. *Acta Crystallogr.* **1977**, *B33*, 763–770.
14. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
15. Mulliken, R. S.; Person, W. B. *Molecular Complexes*; John Wiley & Sons: New York, 1969; pp. 1–298.
16. Rataiczak, R. D.; Jones, M. T.; Reeder, J. R. *Mol. Phys.* **1985**, *56*, 65–77.

¶ Compounds data: **1a**; pale yellow powder, mp>300°C, MS (EI) 288 (M$^+$), ^{1}H NMR (300 MHz, in DMSO-d_6): δ 7.93 (s, 2H), 6.72–6.67 (m, 2H), 6.54–6.50 (m, 4H), 6.40 (d, 2H, $J=7.5$ Hz), 6.07 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (75.45 MHz, in DMSO-d_6): δ 142.37, 135.35, 132.26, 127.56, 123.67, 120.09, 114.94, 113.16, 103.63, 98.79. This compound is rather unstable under aerated conditions. **1b**; colorless plate, mp=198°C, MS (FAB) 605 (MH$^+$), ^{1}H NMR (300 MHz, in DMSO-d_6): δ 6.89–6.83 (m, 2H), 6.70–6.66 (m, 6H), 6.28 (s, 1H), 6.12 (s, 1H), 3.06 (s, 6H); ^{13}C NMR (75.45 MHz, in DMSO-d_6): δ 144.45, 137.74, 134.70, 130.37, 124.04, 120.75, 114.76, 112.01, 103.58, 97.50, 31.17.