# Synthesis, Properties, and Metallic Cation Radical Salts of a New Class of Electron π-Donors: 2,7-Disubstituted Naphtho[1,8-*de*:5,4-*d′e′*]bis[1,3]thiazines

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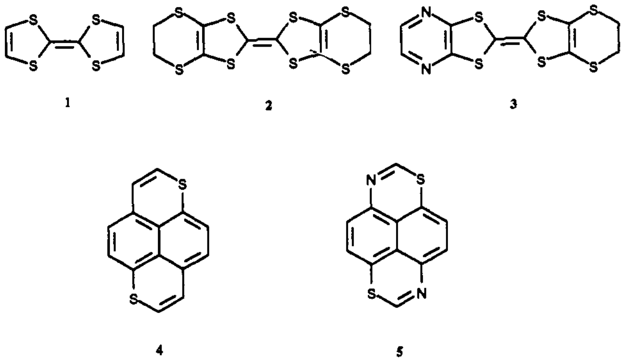
**Abstract:** The first 2,7-disubstituted naphtho[1,8-*de*:5,4-*d′e′*]bis[1,3]thiazines have been prepared from 4,8-dibromo-1,5-diaminonaphthalene, in two steps, via intramolecular nucleophilic substitution. They are shown to be two-stage, electron π-donors and form highly conducting cation radical (CR) salts with $I_3^-$, $IBr_2^-$, and $PF_6^-$ as counterions. Noteworthy is the $IBr_2^-$ salt of 2,7-bis(methylthio)naphtho[1,8-*de*:5,4-*d′e′*]bis[1,3]thiazine ((**10a**)$(IBr_2)_{0.46}$), which crystallizes in the triclinic system, space group $P\bar{1}$, $a = 4.226(1)$ Å, $b = 8.6877(1)$ Å, $c = 11.481(2)$ Å, $\alpha = 105.30(1)°$, $\beta = 90.94(1)°$, $\gamma = 100.13(1)°$, $Z = 1$. It shows a room temperature conductivity of $\sigma_{RT} = 250$ S/cm and exhibits metallic behavior down to 125 K. All of the CR salts reported here have very similar crystal structures typical of segregated stacking. Several S- -S but also interestingly C- -C intermolecular contacts have been observed.

## I. Introduction

The last 20 years have witnessed an intensive research effort in the field of molecular organic conductors.[1] The largest body of work has been devoted to the synthesis and study of charge transfer (CT) complexes and cation radical (CR) salts of tetrathiafulvalene (TTF, **1**) (Chart 1) and its derivatives.[2] Unsubstituted TTF forms several highly conducting salts which are characterized by one-dimensional (1-D) stacking.[3] They all suffer from the Peierls instability and thus are insulators at lower temperatures. Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **2**) on the other hand, forms a number of CR salts which are shown to be 2-D conductors[4] and, despite their moderate room temperature (RT) conductivities, become, in certain cases, superconductors[5] at low temperatures. The increased dimensionality of the BEDT-TTF salts is related to an infinite network of intermolecular S- -S contacts involving not only the sulfur atoms of the TTF skeleton but also the external ones. In fact, the importance of the close interactions has been recognized earlier, after the discovery of superconductivity in the $(SN)_x$ polymer.[6] There, it was considered that the absence of low-dimensional instabilities was due to the significant overlapping of the 1-D $(SN)_x$ chains through S- -S as well as S- -N interactions.[7] The same kind of contacts have also been observed in the TTF-TCNQ (TCNQ = tetracyanoquinodimethane) CT complex.[8] Today, there are few examples of metallic salts based on substituted TTFs (e.g. PEDT-TTF, **3**) which are forming 2-D[9] and even quasi 3-D[10] conducting networks through the same type of interactions. The importance of the S- -N contacts in these cases is illustrated by the fact that the average distance between neighboring donor molecules in the PEDT-TTF salts[11] is closer than that in the BEDT-TTF ones, providing in this way an increased overlapping which, in turn, results in higher conductivities.

**Chart 1**



Therefore it is interesting to look for quasi 1-D conductors which could retain their highly conducting properties down at low temperatures through S- -S and S- -N interactions. π-Electron donors which are known to stack and hence form 1-D electronic systems are, among others, polynuclear arenes such as perylene[12] and pyrene.[13] Recently, dithiapyrene (**4**) and its derivatives have been synthesized and shown to form highly conducting salts.[14,15] Our potential candidate was naphtho[1,8-

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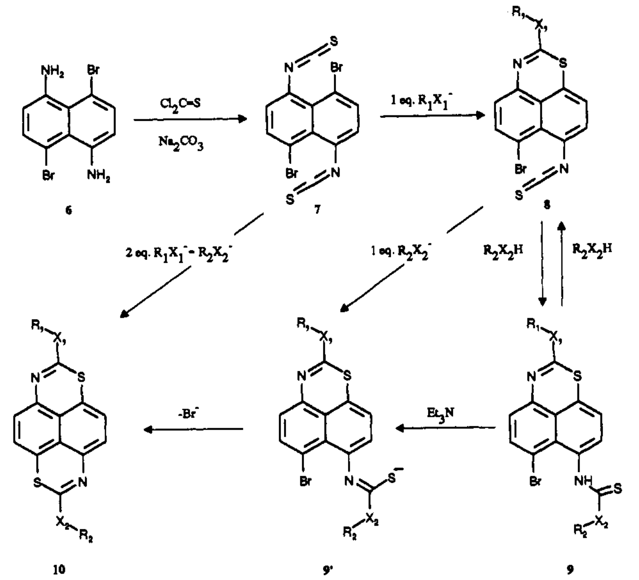
**Scheme 1**[a]



[a] **a**: $X_1, X_2 = S$; $R_1, R_2 = CH_3$. **b**: $X_1, X_2 = S$; $R_1, R_2 = (CH_2)_3CH_3$. **c**: $X_1, X_2 = S$; $R_1, R_2 = (^aCH_2)_{11}CH_3$. **d**: $X_1, X_2 = S$; $R_1, R_2$ = phenyl. **e**: $X_1, X_2 = O$; $R_1, R_2 = CH_3$. **f**: $X_1, X_2 = O$; $R_1, R_2 = (CH_2)_3CH_3$. **g**: $X_1, X_2 = O$; $R_1, R_2$ = phenyl. **h**: $X_1, X_2 = Se$; $R_1, R_2 = CH_3$. **ac**: $X_1, X_2 = S$; $R_1 = CH_3$; $R_2 = (CH_2)_{11}CH_3$. **ba**: $X_1, X_2 = S$; $R_1 = (CH_2)_3CH_3$; $R_2 = CH_3$. **be**: $X_1 = S$; $X_2 = O$; $R_1 = (CH_2)_3CH_3$; $R_2 = CH_3$. **ea**: $X_1 = O$; $X_2 = S$; $R_1, R_2 = CH_3$.

*de*:5,4-*d'e'*]bis[1,3]thiazine (**5**) and its derivatives. For example, 2,7-bis(methylthio)naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazine (**10a**), according to AM1 and PM3 calculations,[16] is predicted to be a centrosymmetric and flat molecule with ionization potential lower than of that of pyrene, meeting some of the necessary prerequisites[17] to form a compact and homogeneous stacking. Moreover, the incorporation of S and N in the pyrene skeleton could provide the desired intermolecular contacts.

Here we report on the synthesis and physical properties of the first examples of 2,7-disubstituted naphtho[1,8-*de*:5,4-*d'e'*]bis-[1,3]thiazines as well as of their highly conducting salts.

## II. Results and Discussion

**Synthesis.** The synthetic route that we applied was similar to the one reported for the preparation of 2-sulfur-substituted 2-thiazolines.[18] In all cases 4,8-dibromo-1,5-diisothiocyanatonaphthalene (**7**), synthesized from 4,8-dibromo-1,5-diaminonaphthalene (**6**) and thiophosgene[19] in the presence of $Na_2CO_3$ (30% yield), was used as the starting material. Several attempts to synthesize naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazine (**5**) by using a variety of reducing reagents[20] always led to intractable material of presumably polymeric nature. However, in the presence of nucleophiles such as alcoholates, thiolates, and selenolates, ring closure occurs smoothly to form 2,7-disubstituted naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazines (**10**) in good yields (Scheme 1). The reaction proceeds by an attack of the appropriate nucleophile on the carbon of the isothiocyanate group followed by nucleophilic displacement of the aryl bromide by the intermediately formed thiolate (e.g. **8** → **9'** → **10**). The ring-formation reaction can be carried out either by using alkali metal salts of the desired nucleophiles or, when the substituent was sulfur, by using free thiols in the presence of a base (e.g. $Et_3N$). The intermediate thioamides **9** of the latter procedure have been isolated, indicating that the first ring-closure reaction is considerably faster than the second one. Thioamides **9** are rather unstable, and even in the solid state, they both eliminate thiol (hence their odor) to form **8**, and HBr to form **5**. 2-Substituted-4-bromo-5-isothiocyanatonaphtho[1,8-*de*][1,3]thiazines (**8**) can be synthesized by reacting equimolar amounts of **7** and the desired nucleophile. Nevertheless, in certain cases, despite the different reaction conditions applied, formation of corresponding **10** was inevitable, and thus, the yields were moderate. Compounds **8** can be further reacted with different nucleophiles, giving rise to nonsymmetrical **10**. Surprisingly, often formation of the two related symmetrical derivatives **10** has been observed. This is probably due to a nucleophilic attack on the carbon of the thiazine ring (instead of an attack on the carbon of the isothiocyanate group) with subsequent elimination of the substituent in the form of the new nucleophile (Scheme 2). So, it is possible that all three combinations (symmetrical and the two unsymmetrical products) can be formed. This side-product formation is even more pronounced when the symmetrical derivatives are less soluble (in the reaction medium) than the unsymmetrical one and, thus, are preferentially precipitating (see attempted synthesis of 2-(dodecylthio-7-(methylthio)naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]-thiazine (**10ca**) in the Experimental Section).

**Scheme 2**

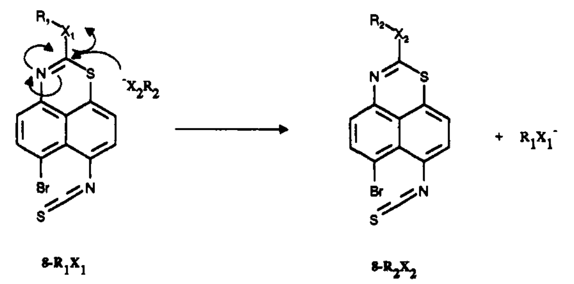


Table 1. Oxidation Potentials[a] of TTF, TMTSeF, pyrene, **10a**, **10b**, and **10d–g**

| | TTF | TMT-SeF | pyrene | **10a** | **10b** | **10d** | **10e** | **10f** | **10g** |
|---|---|---|---|---|---|---|---|---|---|
| $E_1^{ox}$ | 0.520 | 0.530 | 1.410 | 0.860 | 0.850 | 0.840 | 0.840 | 0.790 | 0.890 |
| $E_2^{ox}$ | 0.880 | 1.010 | | 1.320 | 1.330 | 1.290 | 1.330 | 1.320 | 1.390 |
| $\Delta E$ | 0.360 | 0.480 | | 0.460 | 0.480 | 0.450 | 0.490 | 0.530 | 0.500 |

[a] *V* vs SCE (for experimental conditions see text).

The structures were established by means of $^1H$ and $^{13}C$ NMR as well as mass spectroscopy. In addition, IR spectra are indicative of the ring formation judging from the disappearance of the characteristic band due to N=C=S stretching (at ca. 2100 cm$^{-1}$) with concomitant appearance of a new band due to the C=N stretching (ca. 1550 cm$^{-1}$).

2,7-Disubstituted naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazines (**10**) are yellow-orange crystalline substances that, mostly, melt without decomposition.

**Cyclic Voltammetry.** The electrochemical behavior of some selected new compounds, as well as of TTF, teramethyltetraselenafulvalene (TMTSeF), and pyrene as reference compounds, was studied in $CH_2Cl_2$ (although the oxidation potential does not usually depend on the solvent used, we observed a significant solvent effect for both TTF and TMTSeF: for example, 400 mV in benzonitrile/520 mV in $CH_2Cl_2$ for TTF and 470 mV in benzonitrile/530 mV in $CH_2Cl_2$ for TMTSeF). The collected data are summarized in Table 1. All of the new compounds exhibited two well-defined reversible oxidation waves. The values of the first half-wave oxidation potentials ($E_1^{ox}$) lie between those of TTF and pyrene, indicating a moderate donor strength. This

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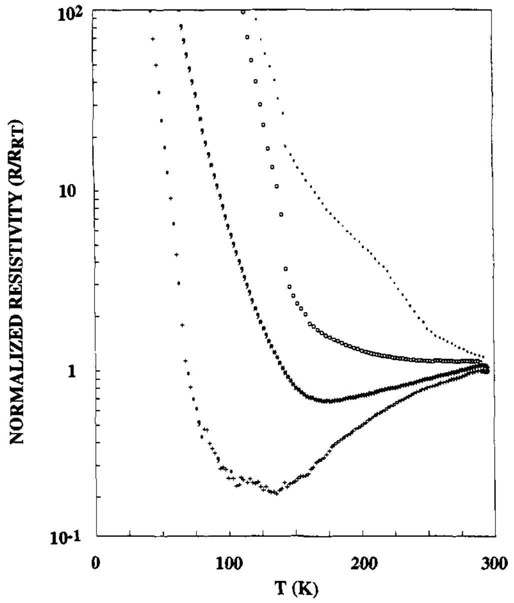

**Figure 1.** Temperature dependence of the normalized resistivity of (a) (**10a**)$_2$PF$_6$ (□) cooling circle, (●) warming circle, (b) (**10a**)(I$_3$)$_{0.46}$ (*) and (c) (**10a**)(IBr$_2$)$_{0.46}$ (+).

is illustrated by the inability of the new $\pi$-donors to form any complexes with TCNQ (no reaction takes place). The difference between the values of the second and the first half-wave oxidation potentials ($\Delta E$), a parameter related with the on-site Coulombic repulsion, is comparable with the one of TMTSeF, an electron donor which forms highly conducting and even superconducting salts.[2b,c] The reduction voltammograms of the compounds **10a**, **10d**, **10e**, and **10g** show some asymmetry in the first reduction waves in contrast with the ones of **10b** and **10f**. This suggests that the dications of the former compounds are insoluble and, due to strong adhesion on the electrode, are more difficult to reduce. It was found that the type of substitution has very little influence on the redox properties of the new systems.

**CR Salts.** Cation radical salts of **10a** with PF$_6^-$ and IBr$_2^-$ as counterions have been grown by standard electrochemical techniques (see Experimental Section for details), while the I$_3^-$ salt has been formed by direct oxidation of **10a** with I$_2$ in appropriate solvents in yields over 80%. High-quality crystals of the latter salt have been grown by a diffusion method. (**10a**)$_2$PF$_6$ grew in the form of long (1 cm), thick, black needles with metallic luster. It shows a RT conductivity of 25 S/cm and temperature-independent behavior down to ca. 200 K, where a transition to the semiconducting state takes place (Figure 1a). The hysteresis observed upon the warming circle of the conductivity measurements could be related to a freezing–defreezing process of the PF$_6^-$ anions which are rotating at RT. (**10a**)(I$_3$)$_{0.46}$ (golden needles) and (**10a**)(IBr$_2$)$_{0.46}$ (black, shiny, thick needles) show RT conductivities of 150 and 250 S/cm (midvalues), respectively. They both exhibit metallic behavior with a metal-to-insulator transition at low temperatures (175 K for the I$_3^-$ salt and ca. 125 K for the IBr$_2^-$ one) (Figure 1b and c, respectively). In this context it is noteworthy to mention that the 2,7-bis(methylthio)dithiapyrene (MTDTPY) iodide, which is the closest comparison to (**10a**)(I$_3$)$_{0.46}$, shows only semiconducting properties and a RT conductivity which is 1 order of magnitude[15b] lower. (**10h**)(I$_3$)$_{0.46}$ was formed by a diffusion method. It has the appearance of golden, long, thick needles. Its RT conductivity is 50 S/cm, and it exhibits temperature-independent behavior down to ca. 200 K, where a transition to the insulating state takes place.

2,7-Disubstituted naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazines are expected to form CT complexes only with strong, organic, electron acceptors, since their first oxidation potentials are relatively high.

**Crystal Structures.** All of the three compounds presented here are isostructural, and thus only the crystal structure projections of (**10a**)$_2$PF$_6$ are shown. As one sees in Figure 2, the donor molecules are stacking in columns along the *a*-axis (which coincides with the long needle-axis) with an interplanar spacing of 3.38(1) Å for both (**10a**)$_2$PF$_6$ and (**10a**)(IBr$_2$)$_{0.46}$, and 3.40(1) Å for (**10a**)(I$_3$)$_{0.46}$. The uniform, close packing of the centrosymmetric organic species is promoted by their planarity: only a slight deviation of S$_2$ (0.10(1) Å) and of C$_7$ (0.07(1) Å) could be detected (Figure 3a). The overlapping mode is of the ring-over-bond type (Figure 3b), resembling the one observed in $\beta$-MTDTPY-TCNQ.[15b] Two different types of transverse S- -S contacts designated as $d_1$ and $d_2$ are observed, forming a two-dimensional network spread along the *ac* plane (Figure 2). Their distances lie well below the sum of the corresponding van der Waals radii: 3.566(3) Å, 3.477(3) Å for the PF$_6^-$ compound, 3.495(6) Å, 3.508(6) Å for the I$_3^-$ one, and 3.538(5) Å, 3.673(6) Å for the IBr$_2^-$ one. In the crystal structure projection along the *a*-axis, a strong interaction ($d_4$) between the methyl groups of neighboring organic molecules, approximately along the *bc* plane, is also observed (Figure 4). The C- -C distances are 3.75(1) Å for the PF$_6^-$ compound, 3.781(1) Å for the I$_3^-$ one, and 3.437(2) Å for the IBr$_2^-$ one. The combination of the S- -S and C- -C interactions induces the formation of robust channels aligned parallel to the conducting columns. Inside these channels, the counterions either have their fixed positions (PF$_6^-$ salt) or they are arranged in linear chains, parallel to the stacking axis, with some positional disorder (I$_3^-$ and IBr$_2^-$ salts). The present crystal structures have a lot of similarities with the one reported by Tanaka et al. for (MTDTPY)(PF$_6$)$_{0.67}$.[15c] It is noteworthy that the metallic character of these compounds is enhanced as the unit cell volume decreases, obviously following the decrease of the anion size. This is probably due to a tighter intercolumnar packing, since the interplanar spacing varies only slightly. This may also reflect the importance of the C- -C contacts, which are clearly the strongest in (**10a**)(IBr$_2$)$_{0.46}$. In this context it cannot be excluded that combination of **10a** with smaller anions is likely to provide compounds with superior conducting properties. The desired intrastack S- -N interactions ($d_3$) are slightly longer (3.57–3.59 Å) than the sum of the van der Waals radii (3.40 Å) due to the molecular slippage induced by the overlapping mode (Figure 2b). They could be probably achieved in such an overlapping mode where a sulfur atom of one molecule lies on the top of a nitrogen atom of the next molecule in the stack, provided that the intracolumnar spacing remains the same as in the present cases or becomes shorter. Since the present examples clearly demonstrate that a larger substituent masks preferentially the nitrogen atom and thus prohibits the transverse contacts, interstack S- -N interactions can be possibly expected only in systems based on unsubstituted or utmost methyl-substituted naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazines.

Unfortunately, attempts to solve the crystal structure of the neutral $\pi$-donor **10a** to correlate of the bond lengths and angles of the charged and uncharged species have proved unsuccessful because of an order–disorder (OD) structure.[21]

## III. Experimental Section

**General Methods.** All the solvents used were purchased from Fluka AG (of analytical grade purity). The chromatography columns were packed with Merck-Kieselgel 60 (70–230 mesh) and eluted with the solvents mentioned in each specific case. The TLC plates used were Merck Kieselgel 60 F$_{254}$. All melting points were taken on a Büchi 535 capillary melting point apparatus and are uncorrected. The absorption spectra were measured on a Shimadzu UV-160 spectrophotometer. The IR spectra were recorded on a Perkin-Elmer 781 spectrometer. $^1$H NMR spectra have been recorded on Bruker AC-250 (250 MHz), Bruker AM-400 (400 MHz), and Varian 500 (500 MHz) spectrometers. $^{13}$C NMR spectra were recorded on a Varian XL-300 (75.5 MHz) spectrometer.

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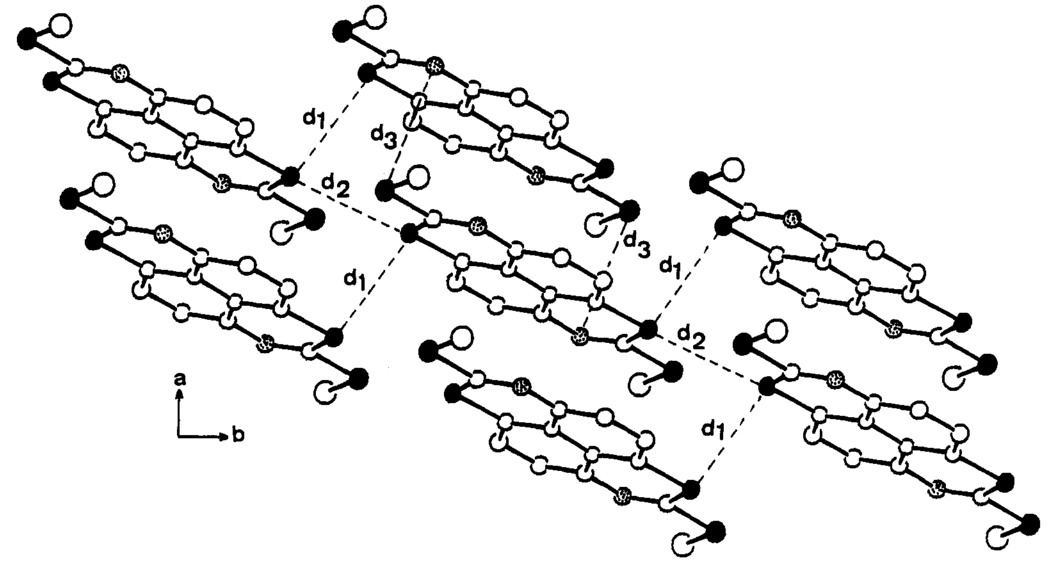

**Figure 2.** Crystal structure projection of $(\mathbf{10a})_2PF_6$ onto the *ac* plane. Sulfur atoms are shown as full circles, nitrogen atoms as dotted circles.

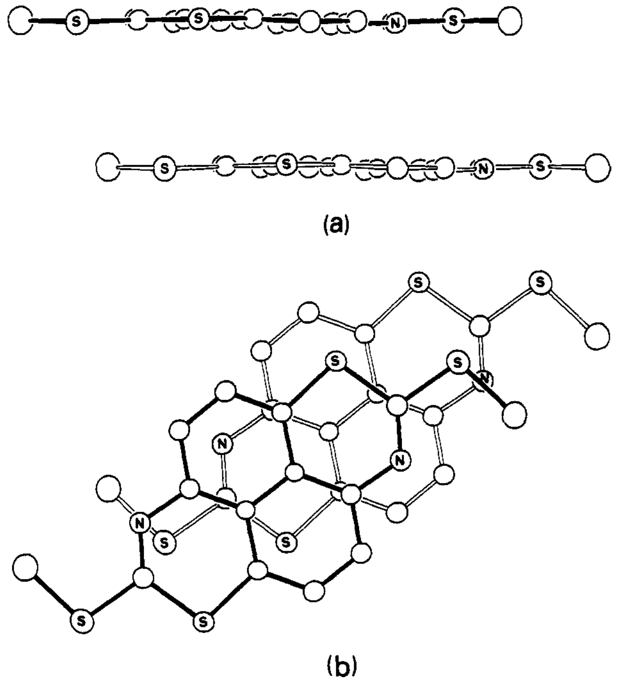

**Figure 3.** Overlapping mode in $(\mathbf{10a})_2PF_6$. The view direction is (a) parallel and (b) perpendicular to the molecular plane.

All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. $^{13}C$ NMR assignments were confirmed by $^1H$ coupled $^{13}C$ spectra. Mass spectra have been recorded with a direct inlet method on a Finnigan MAP 212 spectrometer.

**4,8-Dibromo-1,5-diaminonaphthalene (6).**[22] 4,8-Dibromo-1,5-ditoluene-*p*-sulfonamidonaphthalene[22] (15 g, 24 mmol) was dissolved in 75 mL of concentrated $H_2SO_4$. The solution was stirred overnight under light exclusion and then it was poured onto 450 g of ice. From the resulting violet solution precipitated, after a few minutes, a light beige-violet solid which was filtered off and washed with a minimum amount of cold water. The light-sensitive title material, in the form of the $H_2SO_4$ salt, was immediately applied, without drying, to the next step.

**4,8-Dibromo-1,5-diisothiocyanatonaphthalene (7).** The crude product of the previous step was suspended in a mixture of 150 mL of $H_2O$ and 150 mL of $CH_2Cl_2$, and under vigorous stirring, 18 g (170 mmol) of solid $Na_2CO_3$ was added. To the resulting emulsion a solution of 6.3 g (54 mmol) of thiophosgene in 30 mL of $CH_2Cl_2$ was added dropwise. The reaction progress was monitored with TLC, and after the starting material as well as the monosubstituted product had been consumed (ca. 2 h), the mixture was extracted with 600 mL of $CH_2Cl_2$. The organic phase was washed twice with 300 mL of water, dried over $MgSO_4$, and finally filtered over a short column of silica gel. The solution was concetrated to 200 mL, where off-white crystals started precipitating. The product was filtered off and air-dried to afford 2.7 g (28% calculated on 4,8-dibromo-1,5-ditoluene-*p*-sulfonamidonaphthalene) of the title material: mp 213–214 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log ε) 383 (4.49), 364 (4.45), 249 (4.52); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.86 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 7.43 (d, 2H, *J* = 8.0 Hz, Ar–*H*); IR $\nu_{max}$ (KBr) $cm^{-1}$ 2095, 1365, 1119, 825; MS *m/e* (relative intensity) 400 ($M^+$, 100%). Anal. Calcd for $C_{12}H_4Br_2N_2S_2$: C, 36.02; H, 1.01; Br, 39.94; N, 7.00; S, 16.03. Found: C, 36.12; H, 1.08; Br, 39.88; S, 16.03. From the mother liquor, after evaporation to dryness, another 0.35 g (3.6%) of **7** was earned though with an inferior melting point (207–209 °C).

**2,7-Bis(methylthio)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10a).** Sodium thiomethoxide (210 mg, 3 mmol) was added in one portion, under an inert atmosphere, to a stirred suspension of 400 mg (1 mmol) of **7** in 4 mL of dry DMF at 50 °C. The adduct was immediately dissolved, and after a few minutes a yellow-orange crystalline material precipitated from the red solution. The mixture was stirred for another 15 min and was filtered off, and the solid was washed with water and alcohol and finally air-dried. The crude product was recrystallized from toluene to give 216 mg (64%) of **10a** as orange needles: mp 243–244 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log ε) 431 (3.96), 381 (4.11), 280 (4.59), 246 (441); $^1H$ NMR (250 MHz, $CDCl_3$) δ 6.78 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 6.52 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 2.53 (s, 6H, S–C*H*$_3$); IR $\nu_{max}$ (KBr) $cm^{-1}$ 1557, 821; MS *m/e* (relative intensity) 334 ($M^+$, 100%). Anal. Calcd for $C_{14}H_{10}N_2S_4$: C, 50.27; H, 3.01; N, 8.37; S, 38.34. Found: C, 50.29; H, 3.04; N, 8.55; S, 37.91.

**2,7-Bis(*n*-butylthio)naphtho[1,8-*de*:5,4-*d′e′*]bis[1,3]thiazine (10b).** Four hundred milligrams (1 mmol) of **7** was suspended in a solution of 303 mg (3 mmol) of $Et_3N$ and 270 mg (3 mmol) of butanethiol in 15 mL of dry THF under an inert atmosphere. The reaction mixture was heated to reflux, and after ca. 2 h $Et_3N{\cdot}HBr$ started to precipitate. The reaction progress was followed with TLC, and after 3 days the solvent was evaporated under vacuum. The residue was chromatographed on a silica gel column eluting with benzene/hexane, 1:2. The lemon-yellow front zone afforded trace amounts of **8b**; the second orange zone afforded 305 mg (73%) of **10b** as orange leaflets: mp 101–102 °C. The third yellow zone afforded 102 mg (20%) of **9b** as a malodorous orange oil which crystallized on standing. **10b**: UV $\lambda_{max}$ ($CHCl_3$) nm (log ε) 431 (3.95), 383 (4.10), 282 (4.54), 246 (4.36); $^1H$ NMR (250 MHz, $CDCl_3$) δ 6.73 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 6.59 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 3.15 (t, 4H, *J* = 7.0 Hz, S–C*H*$_2$), 1.69 (tt, 4H, *J* = 7.0 Hz, S–CH$_2$–C*H*$_2$), 1.46 (tq, 4H, *J* = 7.0 Hz, S–CH$_2$–CH$_2$–C*H*$_2$), 0.92 (t, 6H, *J* = 7.0 Hz, S–CH$_2$–CH$_2$–CH$_2$–C*H*$_3$); $^{13}C$ NMR (75.5 MHz, $CDCl_3$) 157.4 (s, *C*=N), 139.8 (s, C(1), C(5)), 125.2 (s, C(4), C(8)), 123.2 (d, C(3), C(7)), 122.1 (s, C(4a), C(8a)), 121.6 (d, C(2), C(6)), 31.3 (t, C(2′)), 30.2 (t, C(1′)), 21.9 (t, C(3′)), 13.6 (q, C(4′)); IR $\nu_{max}$ (KBr) $cm^{-1}$ 2981, 1558, 969, 828; MS *m/e* (relative intensity) 418 ($M^+$, 100%). Anal. Calcd for $C_{20}H_{22}N_2S_4$: C, 57.38; H, 5.30; N, 6.69; S, 30.64. Found: C, 57.55; H, 5.31; N, 6.79;

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[22] Whitehurst, J. S. *J. Chem. Soc.* **1951**, 221–226.

**Table 2.** Summary of Crystal Data, Collection Data, and Refinement for (**10a**)$_2$PF$_6$, (**10a**)(I$_3$)$_{0.46}$, and (**10a**)(IBr$_2$)$_{0.46}$

| | (**10a**)$_2$PF$_6$ | (**10a**)(I$_3$)$_{0.46}$ | (**10a**)(IBr$_2$)$_{0.46}$ |
|---|---|---|---|
| formula | C$_{14}$H$_{10}$N$_2$S$_4$·0.5(PF$_6$) | C$_{14}$H$_{10}$N$_2$S$_4$·0.46(I$_3$) | C$_{14}$H$_{10}$N$_2$S$_4$·0.46(IBr$_2$) |
| mol wt | 406.97 | 509.61 | 466.37 |
| crystal system | $P1$ | $P1$ | $P1$ |
| $a$ (Å) | 4.378(1) | 4.357(1) | 4.226(1) |
| $b$ (Å) | 8.291(1) | 8.300(1) | 8.687(1) |
| $c$ (Å) | 12.808(2) | 12.162(2) | 11.481(2) |
| $\alpha$ (deg) | 105.89(1) | 104.79(1) | 105.30(1) |
| $\beta$ (deg) | 91.92(1) | 89.62(1) | 90.94(1) |
| $\gamma$ (deg) | 103.70(1) | 102.65(1) | 100.13(1) |
| $V$ (Å$^3$) | 432.0(3) | 414.4(3) | 399.3(3) |
| $Z$ | 1 | 1 | 1 |
| $d_{calc}$ (g·cm$^{-3}$) | 1.564 | 2.042 | 1.939 |
| crystal size (mm) | 0.51 × 0.23 × 0.02 | 0.50 × 0.16 × 0.10 | 0.50 × 0.41 × 0.21 |
| diffractometer | | Philips PW1100 | |
| radiation (graphite monochr) | Mo K$\alpha$ | Mo K$\alpha$ | Mo K$\alpha$ |
| wavelength (Å) | 0.7107 | 0.7107 | 0.7107 |
| scan mode | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ |
| scan range (2$\theta$) | 6–64 | 6–70 | 6–70 |
| no. of unique reflections | 3148 | 3820 | 3671 |
| no. of observed reflections ($I > 3\sigma(I)$) | 1508 | 1165 | 1099 |
| refinement method | full matrix | full matrix | full matrix |
| no. of parameters | 124 | 97 | 103 |
| $R$ | 0.057 | 0.104 | 0.095 |
| $R_w$ | 0.061 | 0.109 | 0.106 |

to that described for **10b**, by using 1.3 equiv of *n*-butanethiol and Et$_3$N. Silica gel column chromatography with benzene/hexane, 1:2, as eluant afforded 52% **8b** as yellow needles, mp 92–93 °C, together with traces of **10b** and 32% **9b**. **8b**: UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 390 (4.27), 278 (4.45), 250 (4.51); $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.72 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.30 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.02 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.91 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 3.25 (t, 2H, $J$ = 7.0 Hz, S–C$H_2$), 1.72 (tt, 2H, $J$ = 7.0 Hz, S–C$H_2$–C$H_2$), 1.50 (m, 2H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–C$H_2$), 0.98 (t, 3H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–CH$_2$–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2980, 2120, 1551, 926; MS *m/e* (relative intensity) 410 (M$^+$, 100%). Anal. Calcd for C$_{16}$H$_{13}$BrN$_2$S$_3$: C, 46.94; H, 3.20; N, 6.84; S, 23.50. Found: C, 47.03; H, 3.19; N, 6.92; S, 23.39.

**2-(Dodecylthio)-4-bromo-5-isothiocyanatonaphtho[1,8-*de*][1,3]-thiazine (8c).** The title compound was prepared by a similar procedure to that described for **10b**, by using 1.1 equiv of Et$_3$N and dodecanethiol. Column chromatography with dichloromethane/hexane, 1:1, as eluant afforded 79% of **8c** as orange crystals, mp 84–85 °C, together with 13% **9c**. **8c**: UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 390 (4.27), 278 (4.45), 250 (4.55); $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.72 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.31 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.00 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.90 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 3.21 (t, 2H, $J$ = 7.0 Hz, S–C$H_2$), 1.71 (tt, 2H, $J$ = 7.0 Hz, S–C$H_2$–C$H_2$), 1.42, 1.28 (2m, 2H, 16H, S–C$H_2$–CH$_2$–(C$H_2$)$_9$), 0.89 (t, 3H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–CH$_2$–(CH$_2$)$_9$–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2918, 2115, 1550, 925; MS *m/e* (relative intensity) 522 (M$^+$, 100%). Anal. Calcd for C$_{24}$H$_{29}$BrN$_2$S$_3$: C, 55.26; H, 5.60; N, 5.37; Br, 15.32. Found: C, 55.55; H, 5.63; N, 5.47; Br, 15.09.

**2-Methoxy-4-bromo-5-isothiocyanatonaphtho[1,8-*de*][1,3]thiazine (8e).** The title compound was prepared by a similar procedure to that described for **10a** by using 1.1 equiv of sodium methanolate. The formed precipitate was filtered off and washed with a minimum amount of DMF: 23% **10e**. The filtrate was poured into water, and the precipitated solid was filtered off and subsequently subjected to a silica gel column eluting with benzene/hexane, 1:2. The pale-yellow front zone afforded 11% unreacted material **7**; the second lemon-yellow band gave 10% **8e** as pale-yellow crystals, mp 231–232 °C, while the third yellow zone afforded trace amounts of **10e**. **8e**: UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 391 (4.18), 247 (4.38); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.73 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.35 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 7.00 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.96 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 4.02 (s, 3H, O–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2113, 1628, 1218, 1191, 819; MS *m/e* (relative intensity) 352 (M$^+$, 100%). Anal. Calcd for C$_{13}$H$_7$BrN$_2$OS$_2$: C, 44.45; H, 2.01; N, 7.98; Br, 22.75. Found: C, 44.70; H, 2.01; N, 8.11; Br, 22.48.

**Attempted Synthesis of 2-(Dodecylthio)-7-(methylthio)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10ca).** Two hundred and sixty milligrams (0.5 mmol) of **8c** was suspended in 6 mL of dry DMF at 60 °C under an inert atmosphere. Then 42 mg (0.6 mmol, 1.2 equiv) of sodium thiomethoxide was added at once. The adduct disappeared into the red solution, and after ca. 5 min a solid started to precipitate. After 30 more min the mixture was cooled to RT, and the precipitate was filtered off and washed with water and alcohol. Column chromatography over silica gel of the crude product with dichloromethane/hexane, 1:1, as eluant afforded 118 mg (39%) of **10c** as orange needles, together with 50 mg (33%) of **10a** and trace amounts of **10ca**(!). **10c**: mp 96–97 °C; UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 432 (3.96), 383 (4.10), 283 (4.57), 246 (4.40); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.71 (d, 2H, $J$ = 8.0 Hz, Ar–$H$), 6.58 (d, 2H, $J$ = 8.0 Hz, Ar–$H$), 3.12 (t, 4H, $J$ = 7.0 Hz, S–C$H_2$), 1.69 (tt, 4H, $J$ = 7.0 Hz, S–C$H_2$–C$H_2$), 1.40, 1.26 (2m, 4H, 32H, S–C$H_2$–CH$_2$–(C$H_2$)$_9$), 0.89 (t, 6H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–CH$_2$–(CH$_2$)$_9$–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2919, 1561, 962; MS *m/e* (relative intensity) 642 (M$^+$, 100%). Anal. Calcd for C$_{36}$H$_{54}$N$_2$S$_4$: C, 67.24; H, 8.46; N, 4.36; S, 19.94. Found: C, 67.09; H, 8.13; N, 4.28; S, 19.43. **10c** was also synthesized in analogy to **10b**, by using excess dodecanethiol in the presence of Et$_3$N and prolonged refluxing time.

**2-(Methylthio)-7-(dodecylthio)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]-thiazine (10ac).** One hundred and twenty-seven milligrams (0.39 mmol) of **8a** was dissolved in 6 mL of THF under an inert atmosphere; then 87 mg (0.42 mmol) of dodecanethiol and 75 mg (0.75 mmol) of Et$_3$N were added, and the resulting solution was heated to reflux. After 3 days the solvent was vacuum-evaporated and the residue was chromatographed on silica gel with dichloromethane/hexene, 1:2, as eluant. The first lemon-yellow zone afforded traces of starting material, and the second orange zone afforded 29 mg (15%) of **10ac** as orange powder: mp 98–99 °C; UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 430 (3.91), 383 (4.07), 283 (4.53), 245 (4.37); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.74 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.72 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.60 (d, 2H, $J$ = 8.0 Hz, Ar–$H$), 3.13 (t, 2H, $J$ = 7.0 Hz, S–C$H_2$), 2.53 (s, 3H, S–C$H_3$), 1.69 (tt, 2H, $J$ = 7.0 Hz, S–C$H_2$–C$H_2$), 1.40, 1.26 (2m, 2H, 16H, S–C$H_2$–CH$_2$–(C$H_2$)$_9$), 0.89 (t, 3H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–CH$_2$–(CH$_2$)$_9$–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2923, 1568, 908; MS *m/e* (relative intensity) 488 (M$^+$, 100%). Anal. Calcd for C$_{25}$H$_{32}$N$_2$S$_4$: C, 61.43; H, 6.60; N, 5.73; S, 26.24. Found: C, 61.23; H, 6.73; N, 5.46; S, 26.05.

**2-(*n*-Butylthio)-7-(methylthio)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]-thiazine (10ba).** The title compound was prepared by a similar procedure to that described for **10ca** with **8b** as the starting material, by using 1 equiv of sodium thiomethoxide. Column chromatography of the crude product on silica gel with benzene/hexane, 1:2, as eluant afforded (33%) **10ba** as orange needles, mp 121–122 °C, together with 7% **10b** and 5% **10a**: UV $\lambda_{max}$ (CHCl$_3$) nm (log $\epsilon$) 429 (3.96), 382 (4.11), 281 (4.58), 244 (4.42); $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 6.73 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.71 (d, 1H, $J$ = 8.0 Hz, Ar–$H$), 6.59 (d, 2H, $J$ = 8.0 Hz, Ar–$H$), 3.14 (t, 2H, $J$ = 7.0 Hz, S–C$H_2$), 2.52 (s, 3H, S–C$H_3$), 1.68 (tt, 2H, $J$ = 7.0 Hz, S–C$H_2$–C$H_2$), 1.46 (tq, 2H, S–C$H_2$–CH$_2$–C$H_2$), 0.96 (t, 3H, $J$ = 7.0 Hz, S–C$H_2$–CH$_2$–CH$_2$–C$H_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2932, 1557, 981, 908; MS *m/e* (relative intensity) 376 (M$^+$, 100%). Anal. Calcd for C$_{17}$H$_{16}$N$_2$S$_4$: C, 54.22; H, 4,28; N, 7.44; S, 34.06. Found: C, 54.54; H, 4.67; N, 7.18; S, 33.68.

**2-(*n*-Butylthio)-7-methoxynaphtho[1,8-*de*:5,4-*d′e′*]bis[1,3]thiazine (10be).** The title compound was prepared by a similar procedure to that described

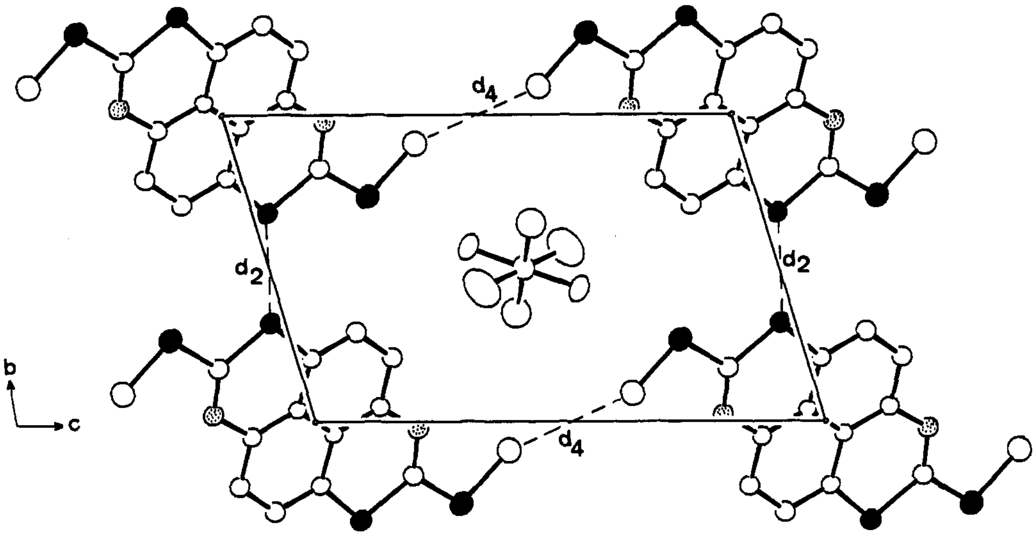

**Figure 4.** Crystal structure projection of $(\mathbf{10a})_2PF_6$ along the *a*-axis. Sulfur atoms are shown as full circles, nitrogen atoms as dotted circles.

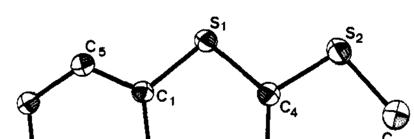

**Figure 5.** ORTEP drawing and atomic numbering scheme of $(\mathbf{10a})_2PF_6$. Thermal ellipsoids are drawn with 50% probability.

S, 30.64. **9b**: $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 8.91 (s, br, 1H, N—H), 7.72 (d, 1H, *J* = 8.0 Hz, Ar—H), 7.36 (d, 1H, *J* = 8.0 Hz, Ar—H), 7.04 (d, 1H, *J* = 8.0 Hz, Ar—H), 6.97 (d, 1H, *J* = 8.0 Hz, Ar—H), 3.25 (m, 4H, S—C*H*$_2$ and NH—C(═S)—S—C*H*$_2$), 1.60 (m, 4H, S—$CH_2$—C*H*$_2$ and NH—C(═S)—S—$CH_2$—C*H*$_2$), 1.45 (m, 4H, S—$CH_2$—$CH_2$—C*H*$_2$ and NH—C(═S)—S—$CH_2$—$CH_2$—C*H*$_2$), 0.91 (m, 4H, S—$CH_2$—$CH_2$—$CH_2$—C*H*$_3$ and NH—C(═S)—S—$CH_2$—$CH_2$—$CH_2$—C*H*$_3$); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 201.4 (s, br, *C*═S), 159.1 (s, *C*═N), 141.2 (s, C(8)), 136.4 (d, C(6)), 130.8 (s, br, C(4)), 130.1 (d, C(2)), 128.4 (s, C(8a)), 123.5 (d, C(7)), 122.7 (s, C(4a)), 119.9 (d, C(3)), 112.0 (s, C(5)), 36.3 (t, C(1″)), 31.3, 30.7 (2t, C(2) and C(2″)), 30.5 (t, C(1′)), 22.1, 21.9 (2t, C(3′) and C(3″)), 13.7 (q, C(4′), C(4″)). A new column chromatography of **9b** after 3 days afforded, besides the unchanged material, 8 mg of **8b** and 7 mg of **10b**.

**2,7-Bis(phenylthio)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10d).** The title compound was prepared by a similar procedure to that described for **10b** by using 3 equiv of thiophenol and $Et_3N$ in DMF. The product precipitated directly from the reaction mixture after a few minutes: 79% orange-red powder (from toluene); mp 299–300 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 433 (3.95), 383 (4.14), 288 (4.50), 247 (4.51); $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 7.64, 7.43, 7.21 (3m, 4H, 4H, 2H, S-*Ph*), 6.56 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 6.48 (d, 2H, *J* = 8.0 Hz, Ar-*H*); IR $\nu_{max}$ (KBr) cm$^{-1}$ 1557, 983; MS *m/e* (relative intensity) 458 (M$^+$, 100%). Anal. Calcd for $C_{24}H_{14}N_2S_4$: C, 62.85; H, 3.08; N, 6.11; S, 27.97. Found: C, 63.16; H, 3.17; N, 6.02; S, 27.77.

**2,7-Bis(methoxy)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10e).** The title compound was prepared by a similar procedure to that described for **10a** by using 2.5 equiv of sodium methoxide: 58% lemon-yellow needles (from toluene); mp 279–280 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 418 (3.86), 373 (4.04), 248 (4.03); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.71 (s, 4H, Ar-*H*), 3.94 (s, 6H, O–C*H*$_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 1651, 1638, 1208, 1182; MS *m/e* (relative intensity) 302 (M$^+$, 100%). Anal. Calcd for $C_{14}H_{10}N_2O_2S_2$: C, 55.61; H, 3.33; N, 9.26; S, 21.21. Found: C, 55.88; H, 3.32; N, 9.19; S, 21.13.

**2,7-Bis(*n*-butoxy)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10f).** The title compound was prepared by a similar procedure to that described for **10a** by using 3 equiv of sodium butoxide. After 2 h of stirring the DMF solution was poured into 50 mL of water and the precipitated solid filtered off, washed with water, and finally air-dried. It was subsequently chromatographed over silica gel with dichloromethane/hexane, 1:1, as eluant: 22% lemon-yellow needles; mp 146–147 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 418 (3.86), 376 (4.01), 250 (4.00); $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 6.68 (s, 4H, Ar–*H*), 4.33 (t, 4H, *J* = 7.0 Hz, O–C*H*$_2$), 1.69 (tt, 4H, *J* = 7.0 Hz, O–$CH_2$–C*H*$_2$), 1.43 (tq, 4H, *J* = 7.0 Hz, O–$CH_2$–$CH_2$–C*H*$_2$), 0.95 (t, 6H, *J* = 7.0 Hz, O–$CH_2$–$CH_2$–$CH_2$–C*H*$_3$); $^{13}$C NMR (75.5 MHz, $CDCl_3$) 157.0 (s, *C*═N), 140.7 (s, C(1), C(5)), 124.8 (s, C(4), C(8)), 122.1 (s, C(4a), C(8a)), 122.0, 121.8 (2d, C(3), C(7) and C(2), C(6)), 68.0 (t, C(1′)), 30.7 (t, C(2′)), 19.2 (t, C(3′)), 13.8 (q, C(4′)); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2962, 1630, 1574, 1178; MS *m/e* (relative intensity) 386 (M$^+$, 41%). Anal. Calcd for $C_{20}H_{22}N_2O_2S_2$: C, 62.15; H, 5.74; N, 7.51; S, 16.48. Found: C, 61.38; H, 5.77; N, 7.51; S, 16.48.

**2,7-Bis(phenoxy)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10g).** The title compound was prepared by a similar procedure to that described for **10a**, by using 2.2 equiv of anhydrous sodium phenolate: 41% lemon-yellow crystals (from toluene); mp 264–265 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 417 (3.84), 373 (4.07), 249 (4.17); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39, 7.21 (2m, 4H, 6H, O–*Ph*), 6.66 (d, 2H, *J* = 8.0 Hz, Ar–*H*), 6.56 (d, 2H, *J* = 8.0 Hz, Ar–*H*); IR $\nu_{max}$ (KBr) cm$^{-1}$ 1632, 1584, 1492, 1210; MS *m/e* (relative intensity) 426 (M$^+$, 100%). Anal. Calcd for $C_{24}H_{14}N_2O_2S_2$: C, 67.59; H, 3.31; N, 6.57; S, 15.04. Found: C, 67.06; H, 3.29; N, 6.79; S, 14.99.

**2,7-Bis(methylseleno)naphtho[1,8-*de*;5,4-*d′e′*]bis[1,3]thiazine (10h).** It was prepared in analogy with **10a** by using 2.3 equiv of lithium selenomethoxide, prepared *in situ* from dimethyl diselenide and $LiEt_3BH$,[23] in THF: 48% red-orange needles; mp 232–233 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 430 (3.93), 382 (4.09), 302 (4.44), 246 (4.37); $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 6.72 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 6.55 (d, 2H, *J* = 8.0 Hz, Ar-*H*) 2.44 (s, 6H, Se–C*H*$_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 1557, 961, 872, 820; MS *m/e* (relative intensity) 430 (M$^+$, 100%). Anal. Calcd for $C_{14}H_{10}N_2S_2Se_2$: C, 39.26; H, 2.35; N, 6.54; S, 14.97. Found: C, 39.46; H, 2.35; N, 6.54; S, 14.97.

**2-(Methylthio)-4-bromo-5-isothiocyanatonaphtho[1,8-*de*][1,3]thiazine (8a).** The title compound was prepared by a similar procedure to that described for **10a**, by using 1.1 equiv of sodium thiomethoxide. The resulting crude product was chromatographed over silica gel with dichloromethane/hexane, 1:1, as eluant. The lemon-yellow front zone afforded 143 mg (26%) of the title material as lemon-yellow crystals; mp 171–172 °C. The second orange zone afforded 7.5% **10a**. **8a**: UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 390 (4.24), 276 (4.41), 249 (4.54); $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 7.75 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 7.32 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 7.08 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 6.92 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 2.62 (s, 3H, S–C*H*$_3$); IR $\nu_{max}$ (KBr) cm$^{-1}$ 2102, 1548, 921; MS *m/e* (relative intensity) 368 (M$^+$, 100%). Anal. Calcd for $C_{13}H_7BrN_2S_3$: C, 42.51; H, 1.92; N, 7.63; S, 26.19. Found: C, 42.62; H, 2.10; N, 7.72; S, 25.81.

**2-(*n*-Butylthio)-4-bromo-5-isothiocyanatonaphtho[1,8-*de*][1,3]thiazine (8b).** The title compound was prepared by a similar procedure

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[23] Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204–1208.

for **10ca** with **8b** as the starting material by using 1 equiv of sodium methoxide. Column chromatography of the crude product over silica gel with benzene/hexane, 1:2, as eluant afforded (40%) **10be** as yellow-orange needles: mp 76–77 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 421 (3.82), 379 (4.09), 259 (4.39); $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 6.80–6.59 (m, 4H, Ar–*H*), 3.96 (s, 3H, O–$CH_3$), 3.16 (t, 2H, *J* = 7.0 Hz, S–$CH_2$), 2.52 (s, 3H, S–$CH_3$), 1.69 (tt, 2H, *J* = 7.0 Hz, S–$CH_2$–$CH_2$), 1.49 (tq, 2H, S–$CH_2$–$CH_2$–$CH_2$), 0.97 (t, 3H, *J* = 7.0 Hz, S–$CH_2$–$CH_2$–$CH_2$–$CH_3$); IR $\nu_{max}$ (KBr) $cm^{-1}$ 2932, 1639, 1571, 1213, 1187, 931, 822; MS *m/e* (relative intensity) 360 ($M^+$, 100%). Anal. Calcd for $C_{17}H_{16}N_2OS_3$: C, 56.64; H, 4.47; N, 7.77; S, 26.68. Found: C, 56.13; H, 4.74; N, 7.72; S, 26.02.

**2-Methoxy-7-(methylthio)naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazine (10ea).** The title compound was prepared by a similar procedure to that described for **10ca** with **8e** as the starting material, by using 1 equiv of sodium thiomethoxide. Column chromatography of the crude product over silica gel with dichloromethane/hexane, 1:2, as eluant afforded (63%) **10ea** as yellow needles: mp 230–231 °C; UV $\lambda_{max}$ ($CHCl_3$) nm (log $\epsilon$) 421 (3.78), 378 (4.01), 259 (4.34); $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.78 (d, 1H, *J* = 8.0 Hz, Ar–*H*), 6.69 (d, 1H, *J* = 8.0 Hz, Ar–*H*), 6.68 (d, 1H, *J* = 8.0 Hz, Ar–*H*), 6.61 (d, 1H, *J* = 8.0 Hz, Ar–*H*), 3.93 (s, 3H, O–$CH_3$), 2.53 (s, 3H, S–$CH_3$); IR $\nu_{max}$ (KBr) $cm^{-1}$ 2949, 1633, 1570, 1180, 821; MS *m/e* (relative intensity) 318 ($M^+$, 100%). Anal. Calcd for $C_{14}H_{10}N_2OS_3$: C, 52.80; H, 3.17; N, 8.80; S, 30.21. Found: C, 52.61; H, 3.18; N, 8.84; S, 29.88.

**Preparation of CR Salts.** The $PF_6^-$ and $IBr_2^-$ salts have been prepared by electrooxidation of the donor in the presence of *n*-$Bu_4NPF_6$ and *n*-$Bu_4NIBr_2$ ($10^{-2}$ mol/L) as supporting electrolytes, respectively, in an H-type cell equipped with 1 mm i.d. Pt electrodes, under a constant current of 0.5 mA, in $CH_2Cl_2$. After 1 week the long, thick needles have been collected and cautiously washed with $CH_2Cl_2$. The $I_3^-$ salt has been prepared by the diffusion method in an H-type cell, using donor and $I_2$ in a 4:3 stoichiometry in toluene or in chlorobenzene/nitrobenzene, 8:2. After 2 weeks the long, thick needles have been collected and washed with $CH_2Cl_2$.

**Electrochemical Measurements.** All measurements were performed in $CH_2Cl_2$ (Fluka, HPLC grade) containing 0.025 M $Bu_4NPF_6$ as supporting electrolyte and a $7 \times 10^{-4}$ M concentration of the substrate studied. All of the potentials were determined under an inert atmosphere, at room temperature, using a stationary Pt disk of 5 mm i.d. as working electrode and a Pt wire as a counter electrode. A commercially available (Beckman) SCE over agar bridge was used as reference electrode. The voltammograms were measured with the help of a AML-471 multipolarograph with integrated XY recorder using two different scanning speeds of 5 and 100 mV/s.

**Electrical Conductivity Measurements.** Electrical conductivities were measured on single crystals of all the salts with a four-probe method in an RMC close-circle-system cryostat. Electrical contacts were done with the help of platinum paste Degussa 308. The temperature dependence of the normalized resistivities is given in Figure 1.

**X-ray Study.** Crystal data, collection data, and refinement details are given in Table 2. Bond lengths of $(\mathbf{10a})_2PF_6$, $(\mathbf{10a})(I_3)_{0.46}$, and $(\mathbf{10a})(IBr_2)_{0.46}$ are summarized in Table 3. On the oscillation photographs of the $(\mathbf{10a})(I_3)_{0.46}$ and $(\mathbf{10a})(IBr_2)_{0.46}$ structures, diffuse scattering in addition to normal Bragg reflections on the planes perpendicular to the *a*-axis was observed. The diffuse layers were indexed on the basis of a superstructure of the anions having periodicities of 9.43 and 9.20 Å for $I_3^-$ and $IBr_2^-$, respectively. According to this model the stoichiometric ratio of **10a** and anions is 1:0.46 in both cases. In the least squares refinements several models for the disordered anions were tested but none of them was really satisfactory. Nevertheless, the crystal packing of $(\mathbf{10a})(I_3)_{0.46}$ could be determined with reasonable accuracy. The periodicity of 9.43 Å of linear $I_3^-$ columns is shorter than that found in $TTT_2I_3$[24] of 9.96 Å. On oscillation photographs of $(\mathbf{10a})_2PF_6$, very weak diffuse streaks appear in the middle between the layers perpendicular to the *a*-axis, indicating a superstructure of $PF_6^-$ with a periodicity of 2*a*. Considering the short *a*-axis and the size of the $PF_6^-$ anion, it is reasonable that only every second cell is occupied by an anion, leading to a ratio of **10a** and $PF_6^-$ of 1:0.5. All non-hydrogen atoms, including those of the anion, were located in Fourier maps. Phosphorous and fluorine atoms were refined with occupation factors of 0.25 and 0.5, respectively. A similar case in which also only every second unit cell was occupied with a $PF_6^-$ anion was observed for $(perylene)(PF_6)_{0.55}$.[11]

**Table 3.** Intramolecular Distances (Å) and Angles (deg) for $(\mathbf{10a})_2PF_6$, $(\mathbf{10a})(I_3)_{0.46}$, and $(\mathbf{10a})(IBr_2)_{0.46}$

| | $(\mathbf{10a})_2PF_6$ | $(\mathbf{10a})(I_3)_{0.46}$ | $(\mathbf{10a})(IBr_2)_{0.46}$ |
|---|---|---|---|
| | Intramolecular Distances | | |
| S(1)–C(1) | 1.73(1) | 1.74(1) | 1.70(2) |
| S(1)–C(4) | 1.75(1) | 1.77(1) | 1.73(2) |
| S(2)–C(4) | 1.75(1) | 1.74(1) | 1.71(2) |
| S(2)–C(7) | 1.81(1) | 1.82(1) | 1.81(2) |
| N(1)–C(3) | 1.41(1) | 1.39(2) | 1.43(2) |
| N(1)–C(4) | 1.27(1) | 1.26(2) | 1.30(2) |
| C(1)–C(2) | 1.42(1) | 1.44(2) | 1.46(2) |
| C(1)–C(5) | 1.40(1) | 1.34(2) | 1.37(2) |
| C(2)–C(2) | 1.43(1) | 1.43(2) | 1.41(2) |
| C(2)–C(3) | 1.40(1) | 1.40(2) | 1.39(2) |
| C(3)–C(6) | 1.38(1) | 1.38(2) | 1.43(2) |
| C(5)–C(6) | 1.41(1) | 1.41(2) | 1.44(2) |
| | Angles | | |
| C(1)–S(1)–C(4) | 100.6(5) | 103.5(8) | 101.7(7) |
| C(4)–S(2)–C(7) | 101.1(6) | 103.2(9) | 100.4(8) |
| C(3)–N(1)–C(4) | 121.4(9) | 121(1) | 122(1) |
| S(1)–C(1)–C(2) | 122.3(8) | 122(1) | 120(1) |
| S(1)–C(1)–C(5) | 116.1(9) | 118(1) | 117(1) |
| C(2)–C(1)–C(5) | 121(1) | 120(1) | 123(1) |
| C(1)–C(2)–C(2) | 116.9(8) | 119(1) | 116(1) |
| C(1)–C(2)–C(3) | 122(1) | 121(1) | 123(1) |
| C(2)–C(2)–C(3) | 120.7(8) | 121(1) | 120(1) |
| N(1)–C(3)–C(2) | 124.1(9) | 126(1) | 125(1) |
| N(1)–C(3)–C(6) | 114.7(8) | 113(1) | 115(1) |
| C(2)–C(3)–C(6) | 121(1) | 121(1) | 120(1) |
| S(1)–C(4)–S(2) | 108.6(7) | 111(1) | 109(1) |
| S(1)–C(4)–N(1) | 129(1) | 127(1) | 128(1) |
| S(2)–C(4)–N(1) | 122.2(8) | 122(1) | 123(1) |
| C(1)–C(5)–C(6) | 120(1) | 121(1) | 120(1) |
| C(3)–C(6)–C(5) | 120(1) | 118(1) | 121(1) |

## IV. Conclusion

We have found a versatile synthesis of the hitherto unknown 2,7-disubstituted naphtho[1,8-*de*:5,4-*d'e'*]bis[1,3]thiazines. We have shown that these compounds behave as reversible redox systems and are forming highly conducting, metallic CR salts in combination with inorganic anions.

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**Supplementary Material Available:** Tables of atomic and thermal parameters (6 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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[24] Smith, D. L.; Luss, H. R. *Acta Crystallogr.* **1977**, *B33*, 1744–1749.