Preparation and structural characterization of naphtho[2,1-*d*:6,5-*d′*]bis([1,2,3]dithiazole) NT and π-stacked mixed valence salt $[NT]_3[BF_4]_2$

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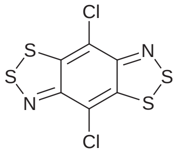
Naphtho[2,1-*d*:6,5-*d′*]bis([1,2,3]dithiazole) NT, prepared by a 'double Herz' condensation of 2,6-diaminonaphthalene with S_2Cl_2, can be electrooxidized to the conductive, π-stacked mixed valence salt $[NT]_3[BF_4]_2$.

The bis([1,2,3]dithiazoles) **1**[1] and **2**[2] represent the first members of a new family of redox active heterocycles with potential applications in the design of molecular conductors.[3] While their oxidation potentials are relatively high, the resulting radical cations are extremely stable, forming crystalline 1:1 salts with inorganic counterions. Compound **1** must be prepared by the condensation of diaminobenzenedithiol with sulfur monochloride, as the use of Herz chemistry,[4] *i.e.* a double ring closure of *p*-phenylenediamine with sulfur monochloride, is not effective; the products of this reaction are largely polymeric.[5] We now report that, in contrast to this behavior, the condensation of 2,6-diaminonaphthalene[6] with sulfur monochloride leads, with remarkable regiospecificity and in good yield, to the 'double Herz' cyclocondensation product naphtho[2,1-*d*-:6,5-*d′*]bis([1,2,3]dithiazole) NT **3**. We also describe the structure and redox chemistry of NT, and its use in the formation of the conductive, π-stacked mixed valence salt $[NT]_3[BF_4]_2$.



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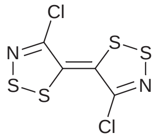

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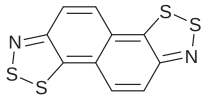

3 NT

In contrast to the complex reaction of 1,5-diaminonaphthalene with S_2Cl_2,[7] the condensation of 2,6-diaminonaphthalene with S_2Cl_2 in the presence of pyridine as auxiliary base proceeds *via* electrophilic ring closure at both *peri*-positions[8] to afford what we presume is an oxidized form (radical cation or dication) of the title compound NT **3**. Chlorination of the remaining C–H positions does not occur. In a typical preparation S_2Cl_2 (30 ml) was added to a slurry of 2,6-diaminonaphthalene (3.00 g, 19.0 mmol) in 20 ml of CH_2Cl_2 and the mixture stirred overnight. Pyridine (9.1 g, 115 mmol) in 15 ml of CH_2Cl_2 was then added dropwise and the mixture stirred for another 2 h. The resulting mixture was filtered, and the solid washed with MeCN (3 × 75 ml) to remove pyridine hydrochloride. The remaining solid was slurried in 100 ml MeCN and reduced with Ph_3Sb (6.8 g, 19.0 mmol) overnight. The resulting red–black precipitate was filtered off, washed with 50 ml of MeCN and dried *in vacuo*. This solid was extracted repeatedly with hot chlorobenzene to give deep blue solutions which yielded golden needles of **3** (NT) (2.5 g, 8.9 mmol, 47%) upon cooling. Further purification by fractional sublimation at 180–130 °C/10^{-2} Torr afforded golden blocks, mp 316–320 °C, UV–VIS ($C_2H_4Cl_2$) λ_{max} (log ε) 622 (4.6) nm.‡

Cyclic voltammetry on solutions of NT in THF (with Pt electrodes and 1 M $Bu^n{}_4NPF_6$ as supporting electrolyte) reveals two reversible oxidation waves with $E_{1/2}$ = 0.41 and 0.66 V *vs.* SCE. These potentials are significantly lower than those observed for **1** (0.93, 1.5 V) and **2** (0.80, 1.25 V),[1,2] and comparable to those found for TTF.[9] Consistently, the intense π–π transition in NT (622 nm) is to longer wavelength of the corresponding absorption maxima in **1** (522 nm) and **2** (565 nm).[1,2] In order to test the potential of NT as a donor for the formation of charge transfer salts we have explored the use of electrocrystallization methods.[10] To date we have found that electrooxidation of NT in a 2:1 mixture of CS_2:$C_2H_4Cl_2$ containing 0.1 M $Bu^n{}_4NBF_4$ as supporting electrolyte, and using Pt electrodes, currents of 3–5 μA, and growth periods of 10–14 days, affords lustrous black needles of the mixed valence salt $[NT]_3[BF_4]_2$. When dissolved in liquid SO_2, lilac colored solutions of $[NT]_3[BF_4]_2$ exhibit a strong and persistent EPR signal of the $[NT]^+$ radical cation (Fig. 1), with g = 2.0106 and a hyperfine coupling pattern based on a_N = 0.235 mT. Additional coupling to two pairs of hydrogens with a_H = 0.079 and 0.048 mT is also observed.

The crystal structures of both NT and $[NT]_3[BF_4]_2$ have been determined by X-ray diffraction.§ In the structure of NT itself the molecules lie on a center of inversion; the packing pattern consists of slipped π-stacks of NT molecules running in the x direction (Fig. 2). In the asymmetric unit of the mixed valence salt $[NT]_3[BF_4]_2$ one NT molecule (A) lies on a center of inversion, while the other molecule (B), along with the BF_4^- ion, adopt general positions. The molecules are packed in layers (Fig. 3) in which the B molecules form dimer units across a center of inversion. These dimers are linked by S···S contacts of 3.407(2) (S3···S5) and 3.250(2) (S4···S6) Å.[11] The B dimers and A molecules adopt an alternating π-stacked arrangement, in which the unique A molecules are slipped relative to the B dimers (Fig. 3). The BF_4^- anions are located between the stacks, bridging B dimers on one side to A molecules on the other.

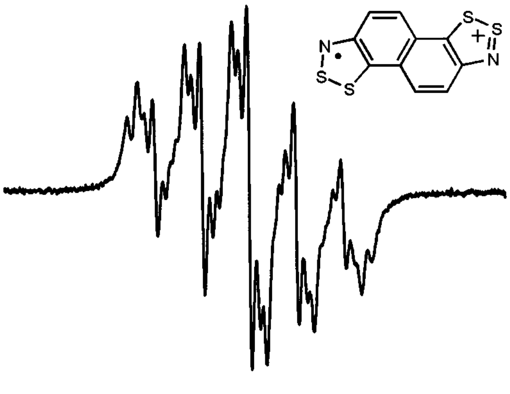

Fig. 1 X-Band EPR spectrum of the $[NT]^+$ radical cation (in liquid SO_2 at 298 K). Sweep width = 2.5 mT.

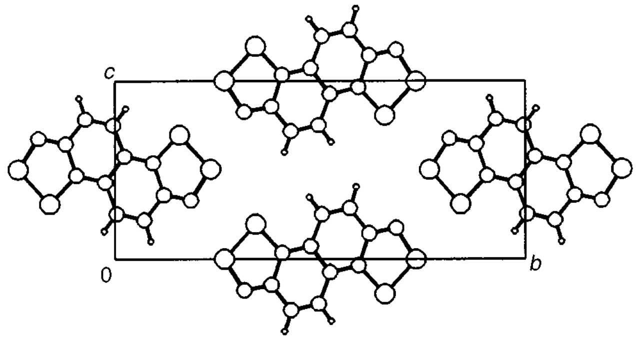

Fig. 2 Crystal packing of NT, viewed along the *x* direction

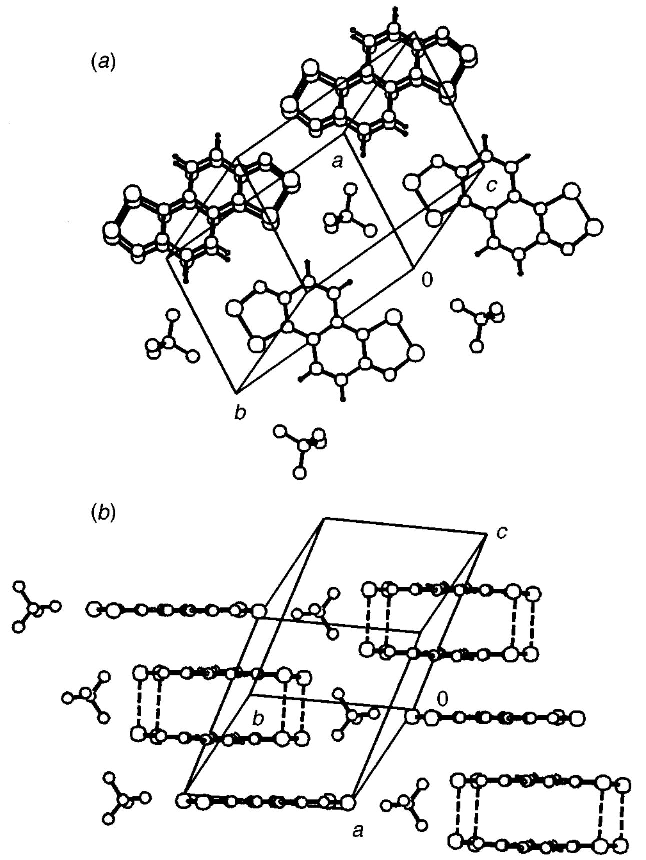

Fig. 3 Crystal packing of $[NT]_3[BF_4]_2$, showing (*a*) layers of neutral molecules and radical cation dimers and (*b*) alternating slipped π-stacks

While the 3:2 stoichiometry of the salt formally implies the presence of a 2/3 positive charge per heterocyclic layer, comparison[12] of the intramolecular distances in NT and $[NT]_3[BF_4]_2$ suggests that the B molecules are nominally oxidized to the radical cation (+1) state, while the A molecules are neutral. The unusual triple-decker[13] stacking pattern found for $[NT]_3[BF_4]_2$ is thus comprised of closed shell ($[NT]_2^{2+}$ and NT) units, and the material is expected to be a semiconductor. Preliminary pressed pellet conductivity measurements on $[NT]_3[BF_4]_2$ nonetheless indicate a relatively high value of σ = *ca.* 10^{-2} S cm^{-1}, indicative of a well developed band structure. More detailed transport property measurements are in progress. Meanwhile, the present results augur well for the use of NT and related bis([1,2,3]dithiazoles) in the design of new conductive charge transfer salts.

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Notes and References

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‡ The proposed formula of NT is in agreement with elemental and mass spectrometric analysis.

§ *Crystal data* for NT and $[NT]_3[BF_4]_2$: Data were collected (at 293 K) on an Enraf-Nonius CAD-4 automated diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using θ–2θ scans to a $2\theta_{max}$ = 50°. The structures were solved by direct methods and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. For NT: $S_4N_2C_{10}H_4$, M = 280.39, monoclinic, space group $P2_1/n$, with a = 3.8784(12), b = 17.2855(14), c = 7.7653(8) Å, β = 102.617 (18)°, V = 508.02(18) Å^3, Z = 2, D_c = 1.83 g cm^{-1}, μ = 0.86 mm^{-1}. 73 Parameters were refined using 901 unique observed reflections [$I > 0.0\ \sigma(I)$] to give R = 0.030, R_w = 0.048. For $[NT]_3[BF_4]_2$: $S_6N_3C_{15}H_6BF_4$, M = 507.39, triclinic, space group $P1$, with a = 9.3225(14), b = 10.650(2), c = 11.302(5) Å, α = 108.04(2), β = 117.32(3), γ = 98.175(14)°, V = 892.6(4) Å^3, Z = 2, D_c = 1.89 g cm^{-1}, μ = 0.78 mm^{-1}. 262 Parameters were refined using 2314 unique observed reflections [$I > 1.0\ \sigma(I)$] to give R = 0.049, R_w = 0.059. CCDC 182/963.

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