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SYNTHESES AND PROPERTIES OF BINAPHTHO[1,8-de]-1,3-DITHIIN-2-YLIDENE AND ITS SELENIUM ANALOGUE

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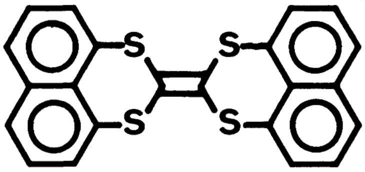
With a view to discovering new electron donors for low-dimensionally metallic materials, the title compounds were prepared via the corresponding 1,8-dichalcogen-bridged naphthalenes. Their donor characters were examined by cyclic voltammetry, as compared with those of the reference compounds.

The discovery of tetrathiafulvalene (TTF), forming charge-transfer salts with low-dimensionally metallic properties, has stirred considerable interest in searching new electron donors which exhibit similar conductivity.[1)] The hitherto unknown binaphtho[1,8-de]-1,3-dithiin-2-ylidene **1** belongs to the same tetrathiaethylene class, but differs structurally from TTF type regarding the fused heterocyclic member. From another viewpoint, it may be regarded as an extended type with ethylene conjugation of 1,8-dichalcogen-bridged naphthalene, which has been noticeable as a novel class of donor.[2-4)] In this context, it is very instructive to examine the properties of **1** as a potential donor. In addition, its selenium analogue **2** looks further promising in expectation of enhanced electron transfer due to introduction of the more polarizable chalcogen. We now report the syntheses and electrochemical properties of **1** and **2**.



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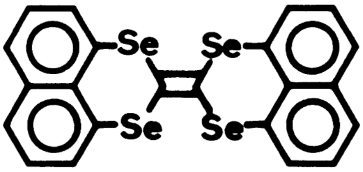

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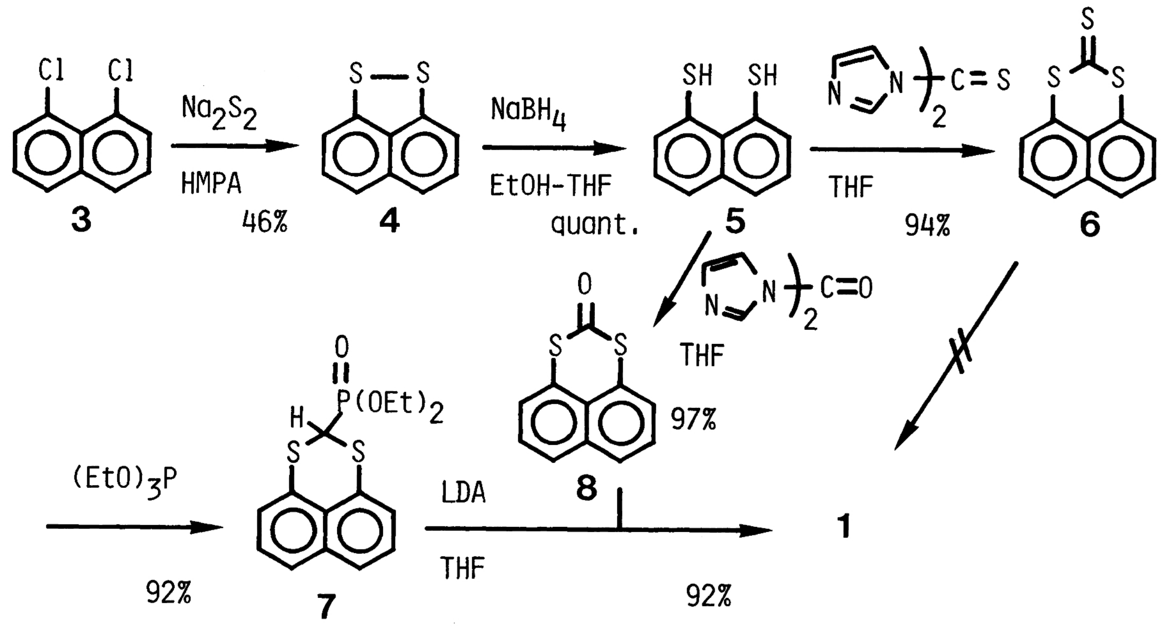
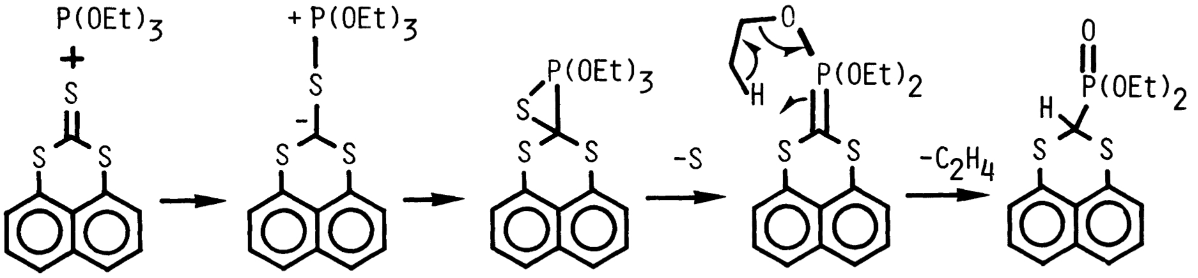
The synthetic route of **1** is shown in Scheme 1. Almost all symmetrical TTF derivatives are generally prepared by coupling of two identical heterocyclic moieties, usually 1,3-dithiole-2-thione or 1,3-dithiolium ion.[5)] Compound **1** is expected to be similarly accessible from desulfurized coupling of naphtho[1,8-de]-1,3-dithiin-2-thione **6**. Nakayama et al. already reported the formation of the precursor **6** as a minor product on photolysis of naphtho[1,8-de]-1,2,3-thiadiazine in carbon disulfide.[6)] We have developed an alternative access via naphtho-[1,8-cd]-1,2-dithiole **4**, which is of choice on large-scale preparation. The intermediate **4** was previously prepared by some methods, i.e., a direct thermal reaction of naphthalene and sulfur,[7)] multistage reactions starting with diazo-



Scheme 1.

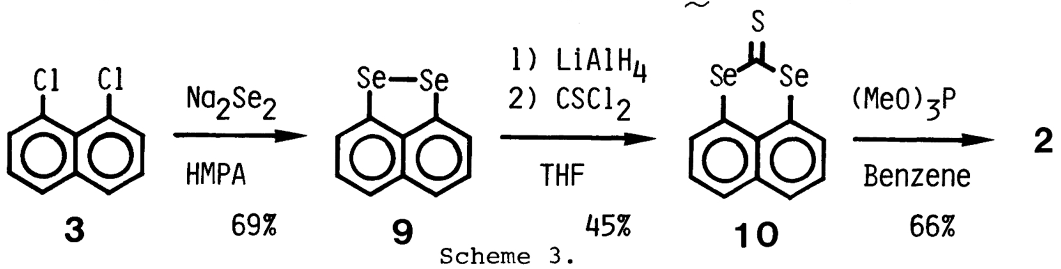
tization of 1-aminonaphthalene-8-sulfonic acid,[8] and a reaction of 1,8-dilithionaphthalene with sulfur.[2] Sandmann's and other groups recently reported direct substitution of unactivated aryl halides involving peri-disubstituted arenes with metal dichalcogenide in a dipolar aprotic solvent.[4,9] In a similar manner, sodium was allowed to react with elemental sulfur at 110 °C in hexamethylphosphoric triamide to form sodium disulfide, which was in situ treated with 1,8-dichloronaphthalene 3[10] at 150 °C, giving 4 in 46% yield.[11] Reduction of 4 with sodium borohydride at RT in tetrahydrofuran-ethanol gave quantitatively naphthalene-1,8-dithiol 5,[12] which was subsequently treated with N,N'-thiocarbonyldiimidazole at -15 °C to afford 6 in 94% yield.[13] All attempts to convert 6 into the target molecule 1 using phosphorus reagents such as triethyl phosphite, trimethyl phosphite, and triphenyl phosphine were unsuccessful. The exclusive product from heating 6 at 110 °C in triethyl phosphite was assigned to diethyl naphtho[1,8-de]-1,3-dithiin-2-yl phosphonate 7 (92% yield),[14] while the other phosphorus reagents led to unidentified products. The formation of 7 is most likely rationalized by a mechanism as shown in Scheme 2.



Scheme 2.

Compound 7 offers an additional approach to 1, because it may be an appropriate reagent for a Wittig modification developed by Wadsworth and Emmons.[15] Thus 7 was treated with lithium diisopropylamide at -78 °C in tetrahydrofuran to generate a phosphonate carbanion, which, however, did not react with thione 6. As the real counterpart, naphtho[1,8-de]-1,3-dithiin-2-one 8 was prepared in 97% yield from a reaction of dithiol 5 and N,N'-carbonyldiimidazole in a similar manner as described for the synthesis of 6.[16] Finally, treatment of the above phosphonate carbanion with 8 gave binaphtho[1,8-de]-1,3-dithiin-2-ylidene 1 in 92% yield.[17]

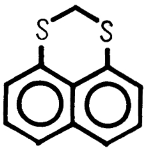
The synthesis of the selenium analogue 2 was carried out in a similar, but shorter route as shown in Scheme 3. Thus a reaction of 3 with sodium diselenide in hexamethylphosphoric triamide at 100 °C gave naphtho[1,8-cd]-1,2-diselenole 9 in 69% yield.[18] The reduction of 9 with lithium aluminium hydride at RT in tetrahydrofuran, followed by treatment with thiophosgene produced naphtho[1,8-de]-1,3-diselenin-2-thione 10 in 45% yield.[19] In contrast to the sulfur case, a reaction of 10 with trimethyl phosphite in refluxed benzene gave directly the desired binaphtho[1,8-de]-1,3-diselenin-2-ylidene 2 in 66% yield.[20]



Scheme 3.

The structures of 1 and 2 were characterized by spectroscopic and elemental analyses. Both ^{1}H-NMR spectra showed aromatic signals consistent with 1,8-symmetrically disubstituted naphthalene. In addition, both MS spectra showed satisfactory molecular ion peaks involving isotopic peaks due to sulfur or selenium.

The cyclic voltammetry of 1 exhibited a reversible redox wave, whose half-wave oxidation potential was situated at 1.14 V vs. a Ag/AgCl reference electrode in benzonitrile (0.1 M Bu_4NClO_4, Pt electrode, 100 mV·s^{-1} scan rate). In contrast, the cyclic voltammetry of naphtho[1,8-de]-1,3-dithiin 11[21] and naphtho-[1,8-de]-2-isopropylidene-1,3-dithiin 12[22] showed irreversible oxidations with somewhat higher peak potentials. Thus the easier oxidation for 1 and the higher stability of the resulting radical cation may be attributed to extended conjugation of π-electrons through the central olefin. On the other hand, the cyclic voltammetry of 2 again showed an irreversible oxidation, though its peak potential was the almost same as that of 1. The introduction of selenium does not serve to enhance the donor character of 2 and rather prompts the resulting radical cation to decompose owing to labile C-Se bond relative to C-S bond.



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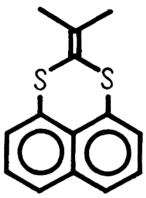

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11) **4**: reddish brown plates from hexane, mp 123 °C (lit.,8) 116 °C).
12) **5**: colorless leaflets from hexane-THF, mp 122 °C, IR(KBr) 2520, 2540 cm^{-1}(S-H).
13) **6**: orange needles from hexane-benzene, mp 201-202 °C (lit.,6) 199-201 °C), IR (KBr) 1040 cm^{-1}(C=S).
14) **7**: colorless columns from hexane-benzene, mp 120 °C, ^{1}H-NMR(CCl$_4$, 60MHz) δ 1.20 (t, J_{CH-CH}=7.4 Hz, 6H, CH$_3$), 4.02 (dq, J_{CH-O-P}=8.4 Hz, J_{CH-CH}=7.4 Hz, 4H, CH$_2$), 4.23 (d, J_{CH-P}=17 Hz, 1H, CHS), 7.2-7.7 (m, 6H, ArH).
15) W. S. Wadsworth, Jr., Org. React., **25**, 77 (1977).
16) **8**: colorless needles from hexane-benzene, mp 140 °C, IR(KBr) 1630 cm^{-1}(C=O).
17) **1**: pale yellow prisms from carbon disulfide, mp 297 °C, ^{1}H-NMR(CS$_2$, 360 MHz) δ 7.22-7.28 (m, 8H, ArH), 7.486 (dd, J=7.37 Hz, J'=1.92 Hz, 4H, ArH).
18) **9**: dark violet needles from hexane, mp 124 °C (lit.,2) 127-129 °C).
19) **10**: orange needles from hexane, mp 153-154 °C, IR(KBr) 1021 cm^{-1}(C=S).
20) **2**: pale yellow fine crystals from toluene, mp 287-287.5 °C, ^{1}H-NMR(CS$_2$, 360 MHz) δ 7.286 (t, J=7.7 Hz, 4H, ArH), 7.476 (bd, J=7.3 Hz, 4H, ArH), 7.610 (bd, J=8.1 Hz, 4H, ArH).
21) Compound **11** was prepared in 26% yield by treatment of **5** with sodium hydride and diiodomethane at RT in THF; colorless plates from hexane-benzene, mp 124-125.5 °C.
22) Compound **12** was prepared in 95% yield from Wadsworth-Emmons reaction of **7** and acetone; colorless prisms from hexane, mp 106 °C, IR(KBr) 1595 cm^{-1}(C=C).

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