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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A NOVEL ORGANOTELLURIUM COMPOUND: DINAPHTHO[2,3-*b*;2',3'-*d*]-TELLUROPHENE

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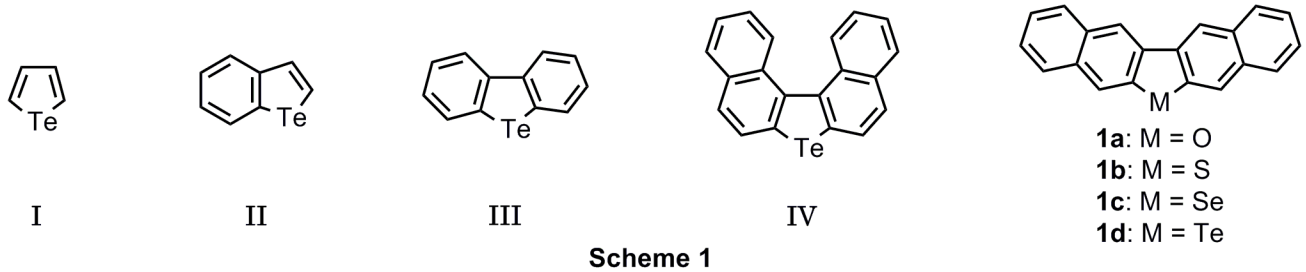
Abstract – The first example of dinaphtho[2,3-*b*;2',3'-*d*]tellurophene (**1d**) has been synthesized by the condensation of tellurium with 3,3'-dilithio-2,2'-binaphthalene. Single crystal X-ray analysis of **1d** revealed that naphthalene and tellurophene rings are almost coplanar. A linear relationship (R^2 = 0.971) between the atomic radius of Group 16 elements and the HOMO-LUMO gap energies of **1a**–**d** was found by density functional theory (DFT) calculations.

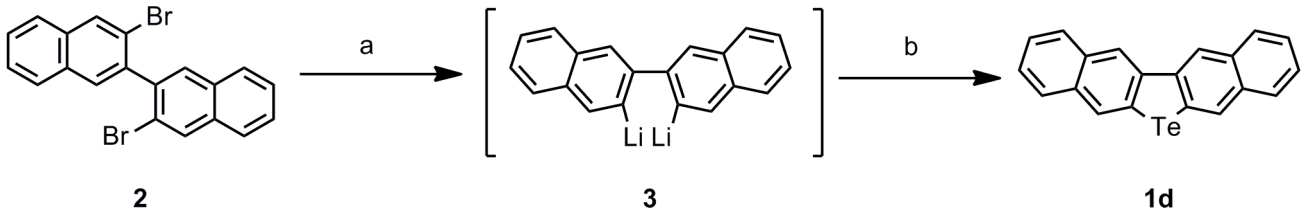
Organotellurium compounds are becoming of increasing interest in a variety of fields, such as in synthesis, crystallography, physical properties, biology and materials science.[1] Among these, the chemistry of the tellurophene,[2] a fully unsaturated five-membered heterocyclic rings containing a tellurium element, has drawn much attention in comparison with thiophene and selenophene. Monocyclic (**I**), benzene ring-fused (**II**) and dibenzo derivatives (**III**) were prepared, and their reactivity as well as their physical properties extensively studied.[1,2] On the other hand, dinaphthotellurophene has been reported in the synthesis of [2,1-*b*;2',1'-*d*]-fused derivative (**IV**) even though there are six kinds of structural isomers by the difference in a position of fused benzene ring.[3] Additionally, dinaphtho[2,3-*b*;2',3'-*d*]heteroles (**1**)



Scheme 1

containing Group 16 elements were known to the synthesis of furan (**1a**: M = O)[4], thiophene (**1b**: M = S)[5,6] and selenophene (**1c**: M = Se)[6] derivatives by many steps. As heteroacene molecules **1b**[5b] and **1c**[6] are expected as organic semiconductor materials, we focused on tellurium analog (**1d**). In this work, we report the synthesis, molecular structure and physical properties of the title compound (**1d**), which was obtained easily from 3,3'-dibromo-2,2'-binaphthalene (**2**). Moreover, the HOMO-LUMO gaps for dinaphthoheteroles (**1**) containing Group 16 elements were determined by density functional theory (DFT) calculations.

Treatment of 3,3'-dibromo-2,2'-binaphthalene (**2**)[7] with *n*-butyllithium in dry THF at -80 ˚C, and subsequently with tellurium powder resulted in ring closure, giving the desired product containing dinaphtho[2,3-*b*;2',3'-*d*]tellurophene (**1d**) in 29% yield,[8] *via* 3,3'-dilithio-2,2'-binaphthalene intermediate (**3**).



Scheme 2. Reagents and conditions: (a) *n*-BuLi, THF, -80 °C, 2 h; (b) Te

The structure of **1d** was elucidated mainly by the HRMS, NMR spectral and combustion analyses.[8] In the ^{1}H- and ^{13}C-NMR spectra of **1d**, all the corresponding aromatic protons and carbons on the two naphthalene rings were found to be equivalent, indicating that **1d** has a highly symmetric structure in $CDCl_3$ solution. The UV-vis spectrum of **1d** showed the λ_{max} at 412 nm, and the peak position was red-shifted compared to **IV** (λ_{max} : 400 nm) in CH_2Cl_2 (Figure 1).

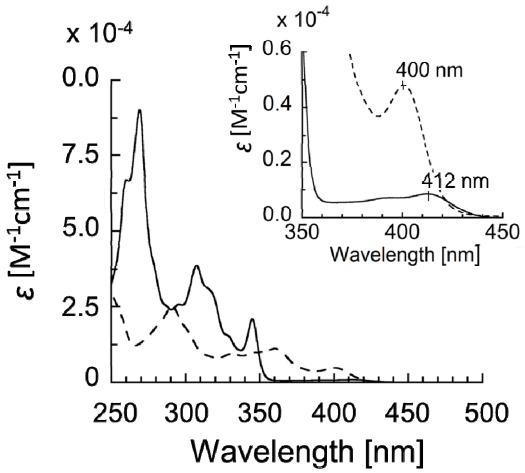


Figure 1. UV/Vis spectra of **1d** (solid line, c = 3.1×10^{-5} M) and **IV** (dashed line, c = 3.4×10^{-5} M) in CH_2Cl_2

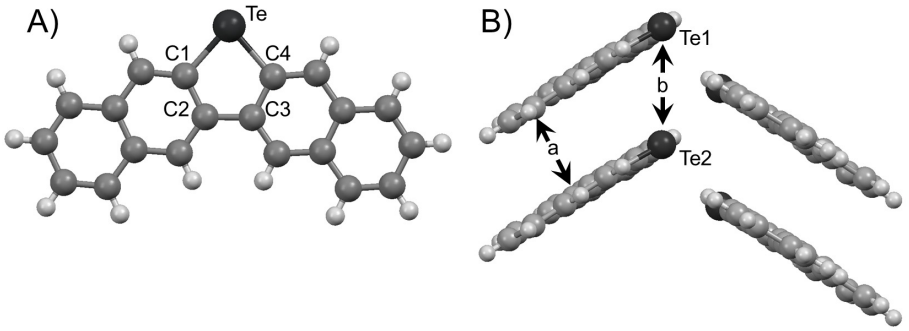


Figure 2. X-Ray structure of **1d** (A), and packing structure (B)

The X-ray structure (A) and its packing structure (B) of **1d** obtained from the single crystal X-ray analysis are illustrated in Figure 2.[9] The results revealed that the naphthalene and the fused tellurophene rings are virtually coplanar (mean deviation 0.034 Å) to each other. The angle between each naphthalene ring defined by ten carbon atoms is 2.81˚. In contrast, the same angle equals 13.88˚ in **1b** (M = S): the structure shows a bent conformation.[5b] Around the five–membered ring moiety of **1d**, the bond lengths [Te-C(1): 2.094(2) Å, Te-C(4): 2.096(2) Å, C(1)-C(2): 1.427(2) Å, C(2)-C(3): 1.472(2) Å and C(3)-C(4): 1.433(2) Å] and bond angles [C(1)-Te-C(4): 82.12(7)˚, Te-C(1)-C(2): 112.33(1)˚, C(1)-C(2)-C(3): 116.87(2)˚, C(2)-C(3)-C(4): 116.33(2)˚, C(3)-C(4)-Te(1): 112.34(1)˚] of the tellurophene ring hardly changed from those of dibenzotellurophene (**III**).[10] The crystal packing is classified into a herringbone-type (Figure 2B), and the interfacial distance (a) of adjacent molecules being 3.55 Å. Moreover, intermolecular interactions between Te(1) and Te(2) atoms are likely to be weak, since the Te(1)–Te(2) distance (b) is 4.18 Å, which corresponds to 95% of the sum of the van der Waals radii (4.40 Å).[10,11]

Table 1. Calculated HOMO-LUMO gap and atomic radius [Å]

Compd.	M	HOMO [eV]	LUMO [eV]	HOMO-LUMO gap [eV]	Atomic radius[a)] [Å]
1a	O	-5.79	-1.90	3.89	0.72
1b	S	-5.66	-1.88	3.78	1.02
1c	Se	-5.55	-1.85	3.70	1.16
1d	Te	-5.36	-1.80	3.56	1.36

a) See ref. 13

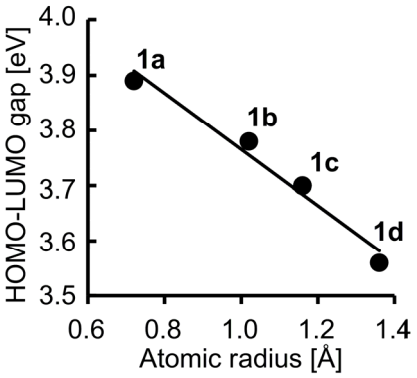


Figure 3. Plots of atomic radius [Å] vs HOMO-LUMO gap [eV] of **1**

To understand the electronic structure and the lowest-energy transition of **1d**, we performed DFT calculations by using the B3-LYP functional. 6-31+G* basis sets were used for carbon and hydrogen

atoms, while a LanL2DZ basis set was used for the heteroatom. The geometry of optimized structure of **1d** agreed very well with that of the X-ray structure. The wavelength for the lowest-energy transition of **1d** and **IV** were estimated to be 412 nm and 402 nm, respectively, reproducing the observed values faithfully. The HOMO-LUMO gap for **1d** was calculated to be 3.56 eV (Table 1), is larger than that for pentacene (calc. 2.21 eV: B3-LYP/6-31+G*).[12] As is clearly seen, the HOMO-LUMO gap energies of **1a**–**d** decrease with increasing the size of the heteroatom, which arisen from the destabilization of the HOMO levels. The plots of atomic radius[13] of Group 16 elements versus the HOMO-LUMO gap energies for **1a**–**d** show linear relationship ($R^2 = 0.971$) (Figure 3). A similar tendency was observed not only in **1** but also in 1-benzoheteroles containing Group 16 elements.[14] It suggests that the HOMO-LUMO gap energies of a heteroacene can be controlled by a proper selection of Group 16 elements.

Further investigation to extend heteroacene chemistry for development of functional materials including electronic devices and to elucidate the chemical/physical properties of these compounds by means of synthetic, theoretical and spectroscopic studies are in progress.

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8. Experimental procedures for **1d**: A *n*-BuLi in hexane (1.65 M, 1.33 mL, 2.2 mmol) was added to a solution of 3,3'-dibromo-2,2'-binaphthalene (412 mg, 1 mmol) in dry THF (12 mL) at -78 ºC under an argon atmosphere. After stirring the reaction mixture for 2 h at the same temperature, tellurium powder (140 mg, 1.1 mmol) was added to the solution in small portions over 15 min period. The reaction mixture was stirred for 1 h at -78 ºC, warmed to 0 °C, and then diluted with CH_2Cl_2 and water. The organic layer was separated, washed with brine, dried over anhydrous magnesium sulfate. After removal of the solvent in vacuo, the resulting residue was recrystallized twice from benzene/CH_2Cl_2 to give **1d** (111 mg, 29% yield) as yellow prism. mp 248-251°C (from benzene - CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.51 (ddd, J = 6.4, 5.5, 3.6 Hz, 2H), 7.52 (ddd, J = 6.4, 5.5, 3.6 Hz, 2H), 7.79 (dd, J = 3.7, 5.5 Hz, 2H), 8.01 (dd, J = 3.7, 5.5 Hz, 2H), 8.25 (2H, s), 8.66 (2H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 122.93 (d), 123.46 (s), 125.82 (d), 126.30 (d), 126.37 (d), 128.46 (d), 131.55 (d), 131.82 (s), 133.47 (s), 142.13 (s); UV/Vis (λ_{max} in CH_2Cl_2): 269 (ε 9010), 307 (3870), 345 (2080), 412 nm (870); LRMS (EI) m/z 382 (M^+); HRMS *m/z* : calcd. for $C_{20}H_{12}Te$: 382.0001. Found: 382.0010; *Anal.* Calcd for $C_{20}H_{12}Te$: C, 63.23; H, 3.18. Found: C, 63.23; H, 3.45.
9. Crystal data: $C_{20}H_{12}Te$, M = 379.90, Monoclinic, a = 11.9754(16), b = 4.1804(5), c = 27.477(4) Å, β = 92.991(3)°, V = 1373.7(3) Å^3, T = 90 K, Space group $P2_1/n$, Z = 4, D_{calc} = 1.837 Mg/m^3. Crystal size 0.16 x 0.10 x 0.05 mm^3, $2\theta_{max}$ = 60.06, 32134 reflections measured, 4003 unique (Rint = 0.0394), μ(Mo Kα) = 2.154 mm^{-1}. The final R_1 and wR_2 were 0.0210 and 0.0466 ($I > 2\sigma(I)$), for 202 parameters. The residual electron densities (peak and hole) were 1.242 e.Å^{-3} and -0.550 e.Å^{-3}. Experimental and refinement details of the X-ray crystallographic structure of compound **1d** can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk), reference code 1010170.
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