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

Mio Matsumura,1 Atsuya Muranaka,2 Naoki Kakusawa,3 Jyoji Kurita,3 Daisuke Hashizume,4 Masanobu Uchiyama,2,5* and Shuji Yasuike1*

1 School of Pharmaceutical Sciences, Aichi Gakuin University, 1-100 Kusumoto-cho, Chikusa-ku, Nagoya 464-8650, Japan. 2 Advanced Elements Chemistry Research Team and Elements Chemistry Laboratory, RIKEN, Wako-shi, Saitama 351-0198, Japan. 3 Faculty of Pharmaceutical Sciences, Hokuriku University, Kanagawa-machi, Kanazawa 920-1181, Japan. 4 Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS), RIKEN, Wako-shi, Saitama 351-0198, Japan. 5 Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: uchiyama@mol.f.u-tokyo.ac.jp, s-yasuik@dpc.agu.ac.jp

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, dinaphthothellurophene 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 (I)
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\(^5\,^6\) 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 (I) containing Group 16 elements were determined by density functional theory (DFT) calculations. Treatment of 3,3’-dibromo-2,2’-binaphthalene (2)\(^3\) 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).

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 \(\lambda_{\text{max}}\) at 412 nm, and the peak position was red-shifted compared to IV (\(\lambda_{\text{max}}\): 400 nm) in CH\(_2\)Cl\(_2\) (Figure 1).

**Scheme 1**

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

**Figure 1.** UV/Vis spectra of 1d (solid line, \(c = 3.1\times10^{-5} \text{ M}\)) and IV (dashed line, \(c = 3.4\times10^{-5} \text{ M}\)) in CH\(_2\)Cl\(_2\).
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. 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. 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). 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).

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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>O</td>
<td>-5.79</td>
<td>-1.90</td>
<td>3.89</td>
<td>0.72</td>
</tr>
<tr>
<td>1b</td>
<td>S</td>
<td>-5.66</td>
<td>-1.88</td>
<td>3.78</td>
<td>1.02</td>
</tr>
<tr>
<td>1c</td>
<td>Se</td>
<td>-5.55</td>
<td>-1.85</td>
<td>3.70</td>
<td>1.16</td>
</tr>
<tr>
<td>1d</td>
<td>Te</td>
<td>-5.36</td>
<td>-1.80</td>
<td>3.56</td>
<td>1.36</td>
</tr>
</tbody>
</table>

a) See ref. 13

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*). 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 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. 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.

ACKNOWLEDGMENT

We thank the RIKEN Integrated Cluster of Clusters (RICC) at RIKEN for the computer resources used for the calculation. We acknowledge financial support from Institute of Pharmaceutical Life Sciences, Aichi Gakuin University and the Special Research Found from Hokuriku University.

REFERENCES AND NOTES


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 °C 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 °C, warmed to 0 °C, and then diluted with CH₂Cl₂ 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/CH₂Cl₂ to give 1d (111 mg, 29% yield) as yellow prism. mp 248-251°C (from benzene - CH₂Cl₂);

1H-NMR (400 MHz, CDCl₃) 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);

13C-NMR (100 MHz, CDCl₃) 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 CH₂Cl₂): 269 (ε 9010), 307 (3870), 345 (2080), 412 nm (870); LRMS (EI) m/z 382 (M⁺); HRMS m/z : calcd. for C₂₀H₁₂Te: 382.0001. Found: 382.0010; Anal. Calcd for C₂₀H₁₂Te: C, 63.23; H, 3.18. Found: C, 63.23; H, 3.45.

9. Crystal data: C₂₀H₁₂Te, 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) Å³, T = 90 K, Space group P2₁/n, Z = 4, Dₑ = 1.37 Mg/m³. Crystal size 0.16 x 0.10 x 0.05 mm³, 2θ_max = 60.06, 32134 reflections measured, 4003 unique (Rint = 0.0394), μ (Mo Kα) = 2.154 mm⁻¹. The final R₁ and wR₂ were 0.0210 and 0.0466 (I > 2σ(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.


