Synthesis and Reaction of 2-Acetylamino-2'-Tellurocyanato-1,1’-Binaphthyl

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Abstract.
2-Acetylamino-2'-tellurocyanato-1,1'-binaphthyl (1) was prepared from the reaction of potassium tellurocyanate with 2-acetylamino-[1,1'-binaphthalene]-2'-diazonium chloride. Treatment of 1 with hydrochloric acid gave bis(2-amino-1,1'-binaphthalene-2'-yl) ditelluride (2) in 65% yield. Reaction of 2 with phenylacetyl chloride and trimethylacetyl chloride gave bis(2-phenylacetylamino-1,1'-binaphthalene-2'-yl) ditelluride (3) and bis(2-trimethylacetylamino-1,1'-binaphthalene-2'-yl) ditelluride (4), respectively. (2-Acetylamino-1,1’-binaphthyl-2'-yl)tellurium tribromide (5) was prepared by reaction of 1 with bromine. Partial reduction of 5 gave the corresponding tellurenyl bromide (6) which in turn reacted with KCN to afford compound 1 in good yield. Alkaline hydrolysis of 1 or reduction of 5 and 6 with hydrazine hydrate in boiling ethanol gave bis (2-acetylamino-1,1’-binaphthalene-2'-yl) ditelluride (7) in good yield. All these new compounds were characterized by elemental analyses, IR, 1H and 13C NMR and mass spectrometry.

Keywords: Tellurocyanate, Binaphthyl, Ditellurides, Tellurenyl bromide.

INTRODUCTION

Chiral binaphthyl compounds have gained interest as ligands in various catalytic reactions,1-4 especially those with different substituents in 2- and 2’-position of the binaphthyl system. Tomoda and coworkers5,6 reported a binaphthyl residue as a chiral auxiliary for selenium. Diazotization of binaphthyl amine, followed by treatment with potassium selenocyanate gave a 24% yield of the desired selenocyanate and similarly the bis(selenocyanate) was prepared from the diamine.5,6

Our previous work7 described the synthesis of the racemic cyclic telluride, 2,7-dihydro-1H-dinaphtho-[c,e]tellurepin, which possessing a C2 axis from the reaction of 2,2’-bis(bromomethyl)-1,1’-binaphthalene with potassium tellurocyanate in dry DMSO. Thus, our previous work on organotellurocyanates8-10 together with the fact that organotelluracyanate compounds are very rare in literature11-13 in compare with organoselenocyanate14 encouraged us to report our results on the synthesis of 2-acetylamino-2'-tellurocyanato-1,1’-binaphthyl. Furthermore, some new binaphthyl
ligands containing tellurium substituents in 2’-position in addition to acetylamino or amino group in 2-position are reported.

**EXPERIMENTAL**

**Physical Measurements**

Infrared spectra were recorded with KBr discs in the range of 4000–200 cm\(^{-1}\) on a Pye-Unicam SP-300s Infrared spectrophotometer. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker MW-250 spectrometers with TMS as an internal reference using CDCl\(_3\) or DMSO-d\(_6\) as a solvent. Mass spectra were measured at 70 eV with a MAT 1125 Finnigan mass spectrometer; peaks shown relative to \(^{130}\)Te. Microanalysis for carbon, hydrogen and nitrogen were obtained on a Carlo-Ebra EA1-108 Elemental Analyzer. All melting points were determined by a Gallenkamp melting point apparatus and are uncorrected.

**Synthesis**

All experimental manipulations were carried out argon atmosphere. The solvents were dried before use by standard methods. 2,2'-Diamino-1,1'-binaphthyl, 15 2-acetylamino-2'-amino-1,1'-binaphthyl\(^{16}\) and 2-acetylamino-[1,1'-binaphthalene]-2'-diazonium chloride\(^{16,17}\) were prepared according to literature methods. Commercial reagents were used without purification. Column chromatography was carried out with silica gel Merck60 (80±230mesh).

**2-Acetylamino-2’-tellurocyanato-1,1’-binaphthyl** (1)

A solution of potassium tellurocyanate was prepared by stirring together tellurium powder (1.28 g, 10 mmol) and dry powdered KCN (0.65 g, 10 mmol) in dry DMSO (70 ml) at 100°C for 1h under argon according to Spencer et al.\(^{18}\) To the resulting pale yellow solution, after cooling to room temperature and diluting with dry DMSO (30 ml), was added dropwise diazolited 2-acetamino-2'-amino-1, 1'-binaphthyl (3.74 g, 10 mmol). The mixture was stirred at room temperature for 6h and filtered. The filtrate was poured into 200 ml of distilled water, which then extracted with dichloromethane (4 x 50 ml). The organic layer was washed with saturated aqueous Na\(_2\)CO\(_3\) and dried over MgSO\(_4\). The solution was evaporated at reduced pressure to give a brown solid. Purification by column chromatography was achieved using silica gel Merck60 (80±230mesh).

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Anal. Calcd for C\(_{23}\)H\(_{16}\)N\(_2\)OTe: C, 59.53; H, 3.48; N, 6.04, Found: C, 59.42; H, 3.38; N, 5.89.

IR (KBr): cm\(^{-1}\), 3300, 3090, 2960, 2890, 2143, 1690, 1560, 1455, 1360, 630, 510, 465.

\(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.65, (sb, 1H, NH), 8.01, (m, 2H, Ar-H), 7.97\)–7.91, (m, 2H, Ar-H), 7.82, (d, \(J(H,H) = 8.2Hz, 1H, Ar-H), 7.52\)–7.45, (m, 2H, Ar-H), 7.33\)–7.24, (m, 2H, Ar-H), 7.20, (d, \(J(H,H) = 8.6Hz, 1H, Ar-H), 7.16\)–7.11, (m, 1H, Ar-H), 6.83, (d, \(J(H,H) = 8.8Hz, 1H, Ar-H), 2.11, (s, 3H, CH\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 182.72, 140.94, 135.90, 133.18, 132.96, 131.67, 130.86, 130.13, 129.67, 128.61, 128.49, 127.69, 127.66, 127.27, 127.08, 126.18, 125.79, 124.08, 121.83, 118.08, 115.87, 101.10, 24.71\).

**Bis(2-amino-1,1’-binaphthalene-2’-yl) ditelluride** (2)

Compound 1 (1.16 g, 2.5 mmol) in a mixture of conc. HCl (20 ml) and dioxane (50 ml) was heated under reflux for 2h. The solution was cooled to room temperature and diluted with 200 ml of water. The solution was made alkaline by addition sufficient amount of 10% NaOH and stirred for 30 min at room temperature. The solution was extracted with toluene (4 x 100 ml). The organic layer was washed with water, dried over Na\(_2\)SO\(_4\) and evaporated to dryness under reduced pressure to give brownish-yellow solid. The product was recrystallized with petroleum ether (60-80°C) to obtain dark orange solid in 65% yield (0.88 g), m.p. 190-191°C.
Bis(2-phenylacetylamino-1,1'-binaphthalene-2'-yl) ditelluride (3).

Anal. Calcd for C₄₀H₂₈N₂Te₂: C, 60.67; H, 3.56; N, 3.53, Found: C, 60.59; H, 3.52; N, 3.36.

IR (KBr): cm⁻¹, 3420, 3310, 3070, 2985, 2870, 1630, 630, 520, 460.

¹H NMR (CDCl₃): δ = 8.01–7.81 (m, 10H, Ar-H), 7.55–7.37 (m, 6H, Ar-H), 7.35–7.16 (m, 6H, Ar-H), 7.10–7.04 (m, 2H, Ar-H), 3.32 (sbr, 4H, NH₂).

¹³C (CDCl₃): δ = 143.24, 141.56, 133.18, 132.78, 130.65, 130.26, 129.85, 128.46, 128.42, 127.74, 127.67, 127.62, 126.74, 125.83, 125.62, 124.51, 123.83, 123.01, 119.63, 114.64.

Bis(2-trimethylacetylamino-1,1'-binaphthalene-2'-yl) ditelluride (4)

This compound was prepared by the same above method, using compound 2 (0.79 g, 1 mmol), trimethylacetyl chloride (0.12 g, 1 mmol) and triethylamine (0.2 g, 2 mmol). Deep-orange precipitate was obtained in 72% yield, m.p. 262-264°C.

Anal. Calcd for C₅₀H₄₄N₂O₂Te₂: C, 62.54; H, 4.61; N, 2.91, Found: C, 62.15; H, 4.58; N, 2.84.

IR (KBr): cm⁻¹, 3290, 3060, 2960, 2870, 1680, 1600, 1390, 1370, 640, 545, 480.

¹H NMR (CDCl₃): δ = 8.62 (sbr, 2H, NH); 8.06–7.72 (m, 16H, Ar-H), 7.38–7.36 (m, 8H, Ar-H), 1.49 (s, 18H, CH₃).

(2-Acetylamino-1,1'-binaphthyl-2'-yl)tellurium tribromide (5)

To a solution of compound 1 (0.93 gm 2 mmol) in 20 ml of dry diethyl ether was added drop by drop a solution of bromine (1.28 g; 8 mmol) in 40 ml of dry diethyl ether. A fine yellow precipitate was formed immediately and soon became almost colorless. Bromine was added until a permanent color of bromine resulted when an additional drop of bromine was added. The solvent was allowed to evaporate at r.t. and a yellow precipitate of the corresponding tribromide was obtained. The product was recrystallized from ethanol, m.p. 192-194°C. Yield: 85%.

Anal. Calcd for C₂₂H₁₆NO₃TeBr₃: C, 38.99; H, 2.37; N, 2.07, Found: C, 38.73; H, 2.17; N, 1.98.

IR (KBr): cm⁻¹, 3280, 3070, 2965, 2890, 1665, 1570, 1460, 1365, 640, 530, 490.

¹H NMR (DMSO-d₆): δ = 9.11 (s, 1H, NH), 8.25 (d, 3J(H,H)= 8.3Hz, 1H, Ar-H), 8.19–7.91 (m, 5H, Ar-H), 7.74–7.64 (m, 1H, Ar-H), 7.52–7.25 (m, 3H, Ar-H), 7.13 (d, 3J(H,H)= 8.3Hz, 1H, Ar-H), 6.82 (d, 3J(H,H)= 8.3 Hz, 1H, Ar-H), 2.09 (s, 3H, CH₃).
(2-Acetylamino-1,1-binaphthyl-2'-yl)tellurenyl bromide (6)
A solid sodium bisulfite (0.31 g, 3 mmol) was added in small portions over a period of 30 min to a stirred suspension of 5 (0.68 g, 1 mmol) in water at 0°C. The resulting mixture was stirred for 30 min at 0°C and filtered. The brownish-red precipitate was dissolved in CH2Cl2, filtered through glass wall and diluted with hexane. The solid product was crystallized from petroleum-ether to yield compound 6 as a red solid in 54% yield, m.p. 102-103°C.
Anal. Calcd for C22H16NOTeBr: C, 51.02; H, 3.11; N, 2.70, Found: C, 50.95; H, 3.25; N, 2.75.
IR (KBr): cm⁻¹, 3280, 3060, 2965, 2895, 1665, 1560, 1460, 1360, 620, 510, 490.
¹H NMR (DMSO-d₆): δ = 9.01(s, 1H, NH), 8.21 (d, J(H,H)= 8.1Hz, 1H, Ar-H), 8.17–7.92 (m, 5H, Ar-H), 7.72–7.61 (m, 1H, Ar-H), 7.51–7.24 (m, 3H, Ar-H), 7.11 (d, J(H,H)= 8.4Hz, 1H, Ar-H), 6.78 (d, J(H,H)= 7.93 Hz, 1H, Ar-H), 2.15 (s, 3H, CH₃).
¹³C NMR (DMSO-d₆): δ = 169.34, 140.23, 135.25, 134.63, 132.20, 131.56, 130.81, 129.57, 129.15, 128.91, 128.64, 128.23, 127.84, 127.13, 126.11, 125.38, 124.74, 124.43, 118.39, 111.89, 25.01.
Bis(2-acetylamino-1,1'-binaphthalene-2'-yl) ditelluride (7)
This compound was prepared by two methods:
Method 1. To a solution of 1 (0.30 g, 0.65 mmol) in ethanol (20 ml) was added a solution of sodium hydroxide (0.16 g, 2.45 mmol) in 15 ml of ethanol. The resulting mixture was stirred for 50 min at 40°C under oxygen atmosphere. An aqueous saturated ammonium chloride was added. The solution was extracted with dichloromethane (4 x 50 ml). The organic layer was dried over Na₂SO₄, and then the solvent removed under reduced pressure. Purification of crude product thus obtained by column chromatography (benzene/ acetone) afforded pure 7 (0.37 g, 65% yield) as an orange solid, m.p. 184-185°C.
Method 2. A suspension of compound 5 or 6 (1 mmol) in 40 ml of ethanol was heated under reflux. Hydrazine hydrate (1.5 g) in 30 ml of ethanol was added dropwise until evolution of nitrogen ceased. The solution was then filtered hot. The filtrate was evaporated to dryness to afford a red precipitate. This product was purified by column chromatography as described in previous method. M.p. 184-185°C. Yield: 82%.
Anal. Calcd for C₄₄H₃₂N₂O₂Te₂: C, 60.33; H, 3.68; N, 3.19, Found: C, 60.21; H, 3.72; N, 2.95.
IR (KBr): cm⁻¹, 3310, 3080, 2980, 2890, 1670, 1455, 1360, 620, 510, 490.
¹H NMR (CDCl₃): δ = 8.61(s, 1H, NH), 8.16–7.86 (m, 6H, Ar-H and NHOCH₃), 7.60–7.51 (m, 1H, Ar-H), 7.47–7.39 (m, 1H, Ar-H), 7.36–7.12 (m, 4H, Ar-H), 7.02 (d, J(H,H) = 7.9 Hz, 1H, Ar-H), 1.97 (s, 3H, CH₃).
¹³C NMR (CDCl₃): δ = 170.87, 142.31, 135.83, 133.14, 132.83, 131.07, 130.66, 130.07, 128.54, 128.39, 127.68, 127.31, 127.16, 126.25, 125.82, 124.48, 124.18, 121.79, 118.38, 112.65, 23.41.
Conversion of (2-Acetylamino-1,1-binaphthyl-2'-yl)tellurenyl bromide (6) to 2-Acetylamino-2'-tellurocyanato-1,1'-binaphthyl (1)
To a stirred solution of (2-acetylamino-1,1-binaphthyl-2'-yl)tellurenyl bromide (0.52 g, 1 mmol) in 20 ml ethanol and 10 ml of water was added KCN (0.065 g, 1 mmol). The resulting solution was stirred for 1 h at room temperature. A white precipitate was formed. The reaction mixture was diluted with H₂O, extracted with CH₂Cl₂, and the organic phase was dried over Na₂SO₄ and filtered. The filtrate was diluted with hexane and the resultant solution was evaporated under reduced pressure to give brownish-red solid. Purification by column chromatography was carried out as described for compound 1 to give a yellow precipitate in 83% yield, m.p. 77°C.
RESULTS AND DISCUSSION

When a solution of KTeCN was treated with 2-acetylamino-[1,1'-binaph-thalene]-2'-diazonium salt under argon atmosphere gave compound 1 (i.e. 2-acetylamino-2'-tellurocyanato-1,1'-binaphthyl) as a pale yellow solid in 32% yield. Treatment of 1 with conc. HCl afforded compound 2 in good yield, Scheme 1. Reaction of 2 with phenylacetyl chloride and trimethylacetyl chloride gave compounds 3 and 4, respectively in good yields (Scheme 1). Compound 1 can be easily converted to the tribromide 5 in 85% yield by its reaction with bromine, Scheme 1. Tellurenyl halides, are unfamiliar compounds compared to the well known selenium analogues.19,20 It is usually difficult to prepare organotellurenyl halides mainly due to the absence of Te← N or Te← O interaction which may lead to unstable compound.19,20 Thus, partial reduction of compound 5 gave the stable tellurenyl bromide (compound 6) in good yield, Scheme 1. The stability of 6 may be attributed to the intramolecular interactions between tellurium and acetylamino group or due to the bulky binaphthyl group. It is worth noting that the first stable tellurenyl compound is 2-naphthylellurenyl iodide,21 which obtained in 1959. Compound 6 was treated with potassium cyanide to afford compound 1 in 83% yield. Compound 7 was prepared by two methods either by alkaline hydrolysis of 1 or by reduction compounds 5 or 6 with hydrazine hydrate in boiling ethanol, Scheme 1.

The IR spectra of all new compounds show bands for naphthyl group at range of 490-460, 640-620 and 3100-3020 cm⁻¹ due to out of plane bending, in plane bending and C-H stretching, respectively. The presence of acetylamino group (i.e. νCO, νNH and δNH) for all compounds (except 2) was confirmed from their IR spectra, see Experimental Section. IR spectra (KBr discs) of all compounds showed medium bands due to N-H stretching vibration in the region 3230-3280 cm⁻¹ and very strong bands in range 1660-1690 cm⁻¹ due to ν(C=O). The IR spectrum of compound 1 shows a strong band at 2140 cm⁻¹ due to ν(Te-CN).9-11 The IR spectrum of 2 shows three bands at 3420, 3310 and 1630 cm⁻¹ due to asymmetrical, symmetrical and deformation of NH₂ group.22,23

The 1H NMR spectra for all compounds were recorded in CDCl₃ or DMSO-d₆ and are presented in Experimental Section. In general, the spectra of all compounds exhibit the expected pattern for these compounds. The 1H NMR spectra of compounds 1, 3, 4, 5, 6 and 7 showed a broad singlet NH signal between 8.05-9.11 ppm and CH₃O signal around 2.0 ppm. Figure 1 represents the spectrum of compound 1. Compound 2 showed a signal due to NH₂ protons at 3.32 ppm. This value is within the typical ranges for aromatic amines.22 The 13C NMR of compounds 1, 6 and 7 show a signal at 24.7, 23.4 and 25.0 ppm, respectively due to methyl of acetamido group, whereas compound 3 shows a signal at 46.7 ppm due to methylene carbon of benzyl group. The spectra of compounds 1, 3, 5, 6 and 7 show a downfield signal between 182.7–169.3 ppm due to carbonyl carbon. These values agree well with literature values.22 Compound 1 shows a signal at 101.1ppm which could be attributed to carbon of Te-CN group.9-11 Figure 2 represents the 13C spectrum of compound 1.

In conclusion, a new series of organotellurium compounds containing binaphthyl group were prepared. These new compounds can be used as multidentate ligands with various transition metal ions and can also be also used in various catalytic reactions.
REFERENCES

1. a) L. Gong, L., C. Müller, C., Celik, M. A., Frenking, G., and Meggers, E., New J. Chem., 2011, 35, 788.
   b) H. Brunner, H. Weber, M., and Zabel, M., Z. Naturforsch. 2003, 58b, 821.
2. a) Cao W., Feng, X., and Liu, X., Org. Biomol. Chem., 2019, 17, 6538.
   b) Vyskočil, Š., Smrčina, M., Hanuš, V., Polášek, M. and Kočovský, P., J. Org. Chem., 1998, 63, 7738.
3. Štěpán Vyskočil, S., Stanislav Jaracz, S., Smrčina, M., Šticha, M., Vladimir Hanuš, V., Polášek, M., and Kočovský, P., J. Org. Chem., 1998, 63, 7727.
4. a) Weseliński, L., Stępniak, P., and Jurczak, J., Synlett., 2009, 14, 2261.
   b) Brunner, H., Weber, H., and Zabel, M., Z. Naturforsch., 2003, 58b, 821.
5. Tom, S., Fujita, K., Iwaoka, M., Phosphorus, Sulfur, Silicon Relat. Elem., 1990, 67, 247.
6. Tom, S. and Iwaoka, M., J. Chem. Soc. Chem. Commun., 1988, 1283.
7. Al-Rubaie, A. Z., Fahad, T. A., Al-Jadaan, S. A. N., Aboud, N. A., J. Organomet. Chem., 2004, 687, 2377.
8. Al-Rubaie, A. Z., Yousif, L. Z., Al-Ba’aj, A. K., J. Organomet. Chem., 2003, 673, 40.
9. Al-Rubaie, A. Z., Al-Jadaan, S. A. N., Polyhedron, 1997, 16, 1241.
10. Al-Rubaie, A. Z., Al-Marzoook, A.Y., Al-Jadaan, S. A. N. (1996). Recl. Trav. Chim. Pays-Bas, 115, 427.
11. Al-Rubaie, A. Z. (2006). New Developments In Organometallic Chemistry Research. Cato, M. A., (Ed., Nova Scientific Publication, USA.
12. Sadekov, I. D., Skopenko, V. V., Burlov, A. S., Ivanova, E. I. and Garnovski, I. D., Russ. J. Gen. Chem., 1997, 67, 1058.
13. a) Toshimitsu, A., (2013). “Organic selenocyanates, tellurocyanates and related compounds “, in PATAI’s Chemistry of Functional Groups, John Wiley & Sons, Ltd., USA.
   b) Toshimitsu, A. and Uemura, S., (1987). “Organic Selenium and Tellurium Compounds”, Vol. 2; in Patai, S., Ed. Wiley & Sons, USA.
14. Guillemín, J.-C., Curr. Org. Chem., 2011, 15, 1670.
15. Zi,G.; Xiang, L.; Zhang, Y.; Q. Wang, Q.; Zhang, Z., Appl. Organometl. Chem., 2007, 21, 177.
16. H. Akimotom H. and Yamada, S., Tetrahedron, 1971, 27, 5999.
17. Brown, K. T., Berry, M. S. and Murdoch, J. R., J. Org. Chem., 1985, 50, 4345.
18. Spencer, H. K., Lakshmikam, M. V. and Cava, M. P., J. Am. Chem. Soc., 1974, 99, 1470.
19. Sadekov, I. D. and Minkin V. I., Russ. J. Org. Chem., 1999, 35, 953.
20. Borisov, A. V., Matsulevich, Zh. V., Fukin, G. K. and Baranov, E. V., Russ. Chem. Bull., 2010, 59, 581 and references therein.
21. Vicentini, G., Giesbrecht; E. L. and Pitombo, R. M., Chem. Ber., 1959, 92, 40.
22. Silverstein, R., Bassier, G., and Morrill, T. (1981). “Spectrometric Identification of Organic Compounds”, J. Wiley and Sons, NY, USA.
23. Al-Rubaie, A. Z., Al-Salim, N. I., and Al-Jaddan, S. A. N., *J. Organomet. Chem.*, 1993, **443**, 67.

Scheme 1. Methods of preparation of compounds 1-7.

R = CH$_2$Ph (3); C(CH$_3$)$_3$ (4)
Figure 1. $^1$H NMR spectrum of compounds 1
Figure 2. $^{13}$C NMR spectrum of compound 1