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SYNTHESES OF NOVEL DIBENZO[*d,f*]HETERONINS INCORPORATING GROUP 15 AND 16 HEAVIER ELEMENTS

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Abstract – Fully unsaturated dibenzo[*d,f*]heteronins incorporating Group 15 (P, As, Sb) and Group 16 (S, Se, Te) heavier elements have been prepared *via* a common 1,8-dilithium intermediate. These heteronins, except for dibenzothionin, are the first examples of fused nine-membered heterocyclic ring. Proton NMR spectra of the heteronins revealed that two olefinic bonds in the heteronin ring have the *cis* configurations and the nine-membered rings exist in a buckled, non-planar conformation.

A variety of fully unsaturated nine-membered heterocyclic rings (heteronins) such as azonines and oxonins have been prepared, and their molecular structures and aromatic character have been studied.¹ However, heteronins containing Group 15 (P, As, Sb) and Group 16 (S, Se, Te) elements have not been reported, except for dibenzothionins (**1a**)² and phosphonins (**2d**).³ We recently reported the syntheses and physical properties of seven-membered (heteroepins)⁴ and ten-membered (heteroecins)⁵ heterocyclic compounds incorporating such heavier elements from the corresponding 1,6- and 1,9-dilithium intermediates, along with their physical properties and thermal stabilities. As part of our studies on the

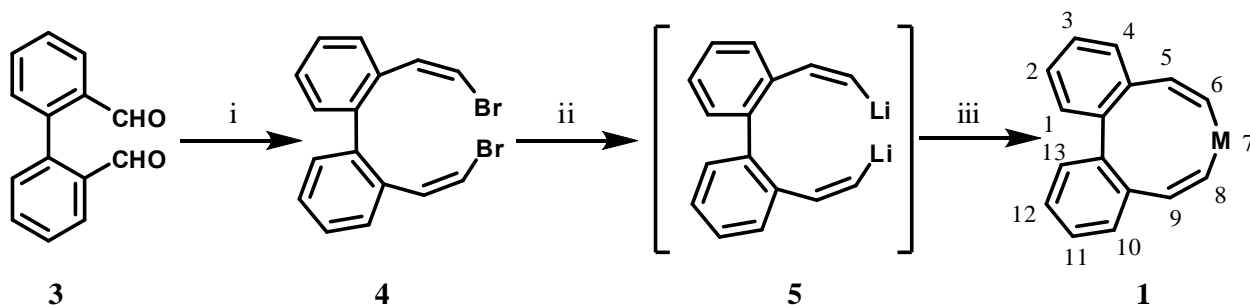


M = a: S, b: Se, c: Te, d: PPh, d': P(O)Ph, e: AsPh, f: SbPh

Scheme 1

synthesis of new heterocyclic compounds incorporating Group 14, 15, and 16 heavier elements, we report here the synthesis and structures of the title dibenzoheteronins (**1a-f**) from (*Z*)-2,2'-bis(2-bromovinyl)biphenyl (**4**) via a common 1,8-dilithium intermediate (**5**).

The key starting compound, (*Z*)-2,2'-bis(2-bromovinyl)biphenyl (**4**),⁶ was prepared stereoselectively in 57% yield by a double Wittig reaction of 2,2'-diformylbiphenyl (**3**)⁷ with bromomethyltriphenylphosphonium bromide.⁸ In the NMR spectrum of **4**, the coupling constant of the vinylic protons ($J_{\alpha, \beta} = 8.1$ Hz) of the bromovinyl moiety supports the all-*cis* configuration. Treatment of **4** with *tert*-butyllithium in dry ether under an argon atmosphere, and then with deuterium oxide resulted 1,8-dideuterio compound in 85% yield.⁹ This result clearly shows the generation of the 1,8-dilithium species (**5**) in high efficiency. However, the reaction of **5** with electrophilic reagents such as $(\text{PhSO}_2)_2\text{S}$, SeCl_4 , TeI_4 , PhPCl_2 , PhAsCl_2 , and PhSbBr_2 gave the desired dibenzo[*d,f*]heteronins (**1a-f**) in low yields (10–17%) as the sole characterizable product.¹⁰ The heteronins (**1**) except for phosphonin (**1d**) were stable enough to be eluted using silica gel column chromatography and isolated in pure form. The phosphorus-containing heteronin (**1d**) is susceptible to air oxidation and was isolated as its P-oxide (**1d'**).



Scheme 2. Reagents and conditions: i, $\text{Ph}_3\text{P}^+\text{CH}_2\text{Br}-\text{Br}$ (x 2), *t*-BuOK, THF, -80 °C to rt, 12 h, 57 %; ii, *t*-BuLi, Et_2O , -80 °C, 5 min; iii, Metal reagents [$(\text{PhSO}_2)_2\text{S}$, SeCl_4 , TeI_4 , PhPCl_2 , PhAsCl_2 or PhSbBr_2], Et_2O , -80 to -10 °C, 2.5 h.

Table 1. Selected $^1\text{H-NMR}$ Spectroscopic Data of Heteronins (**1**) (400 MHz, CDCl_3 : δ).

Compd.	M	6-H and 8-H (α)		5-H and 9-H (β)		$J_{5,6(8,9)}$ (Hz)	Ar
1a	S	5.86		6.52		11.0	7.12–7.40
1b	Se	6.15		6.92		11.0	7.08–7.39
1c	Te	6.45		7.40		11.0	7.02–7.39
1d'	P(O)Ph	6.07	6.15	7.09	7.40	10.6 ^{a)} (13.9) ^{b)}	6.78–7.44
1e	AsPh	5.92	6.13	7.08	7.26	10.1 (13.6)	6.92–7.48
1f	SbPh	6.12	6.37	7.43	7.62	11.4 (13.9)	6.95–7.44

a) $J_{\text{P},6(8)} = 13.6$ and $J_{\text{P},5(9)} = 35.5$ Hz, b) $J_{\text{P},6(8)} = 17.6$ and $J_{\text{P},5(9)} = 33.0$ Hz.

The structures of the heteronins (**1a-c**, **d'**, **e**, **f**) obtained here were established from their spectral properties (HR-MS and $^1\text{H-NMR}$). The $^1\text{H-NMR}$ spectroscopic data of the nine-membered ring protons for **1** are given in Table 1. The spectroscopic data [$^1\text{H-NMR}$ and UV (253 nm, ϵ 5000, EtOH)] and mp (121–123 °C) of the thionin (**1a**) obtained here are in good accordance with those of dibenzo[*d, f*]thionin, reported by Bindra *et al.*² The vinyl proton signals of 6-H and 8-H as well as 5-H and 9-H for the Group 16 heteronins (**1a-c**) exhibit one AB doublet with coupling constant $J_{5,6(8,9)} = 11.0$ Hz. This magnetic equivalence of the olefinic protons implies that **1a-c** have a symmetrical structure in solution with rapid conformational exchange on the NMR time scale, and both olefinic bonds have the *cis* configuration. It is also suggested that, because the vinyl protons of **1a-c** were observed at the relatively high field (δ 5.86–6.45 for 6-H and 8-H, δ 6.52–7.40 for 5-H and 9-H), without the deshielding associated with aromatic character, **1a-c** should be classified as non-aromatic compounds. We have already reported that the vinyl protons of non-aromatic Group 16 3-benzoheteroepins were observed at a higher field (α : δ 5.89–6.79; β : δ 6.72–7.62; $J_{\alpha,\beta} = 9.2$ –9.9 Hz),^{4b} than those of aromatic Group 16 1-benzoheteroles (α : δ 7.39–8.75; β : δ 7.30–8.00; $J_{\alpha,\beta} = 5.5$ –7.0 Hz).¹¹ In the $^1\text{H-NMR}$ spectra of Group 15 heteronins (**1d'**, **e**, **f**), the vinyl proton signals corresponding to 5-H and 9-H as well as 6-H and 8-H were observed in different positions with the coupling constant $J_{5,6} = 10.1$ –10.6 Hz and $J_{8,9} = 13.6$ –13.9 Hz. The magnetic nonequivalence of the olefinic protons implies that these Group 15 heteronins (**1d'**, **e**, **f**) exist in buckled, non-planar conformations. It should be emphasized that both the olefinic bonds of **1d'**, C(5)–C(6) and C(8)–C(9), should have the *cis* configuration.⁵ Quin has recently reported the synthesis and structure of dibenzo[*d, f*]phosphonin P-oxide (**2d'**), which have *cis* and *trans* olefinic bonds, for which two vinyl proton signals were observed at δ 6.04 ($J_{\text{P,H}} = 24$ Hz and $J_{\text{H,H}} = 14$ Hz) and δ 6.08 ($J_{\text{P,H}} = 14$ Hz and $J_{\text{H,H}} = 4$ Hz).^{3a}

All the dibenzoheteronins (**1a-c**, **d'**, **e**, **f**) isolated here displayed relatively high thermal stability and remained unchanged even when heated at 110 °C for 24 h in toluene-*d*₈. The thermal stabilities of these dibenzoheteronins is in contrast to these of benzoheteroepins⁴ and monocyclic heteronins.¹

We have developed a general route for the synthesis of Group 15 (P, As, Sb) and Group 16 (S, Se, Te) fully unsaturated dibenzo[*d, f*]heteronins (**1**) from a common starting material, 2,2'-bis(2-bromovinyl)biphenyl (**4**) *via* 1,8-dilithium intermediate (**5**). All the heteronins obtained here exist in buckled, non-planar conformations and are classified as non-aromatic compounds.

Further studies on the molecular structures and chemical properties of these novel dibenzo[*d, f*]heteronins containing heavier elements are in progress.

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6. **4**: colorless oil; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , $J = \text{Hz}$): δ 6.31 (2H, d, $\beta\text{-H}$), 6.66 (2H, d, $\alpha\text{-H}$), 7.21–7.89 (8H, m, Ar-H), $J_{\alpha,\beta} = 8.1$; HR-MS m/z 361.9327 (M^+ , calc. for $\text{C}_{16}\text{H}_{12}\text{Br}_2$: 361.9307).
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9. 1,8-dideuterio compound: mp 73–74 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , $J = \text{Hz}$): δ 5.08 (2H, d, $\beta\text{-H}$), 6.40 (2H, dt, $\alpha\text{-H}$), 7.14–7.67 (8H, m, Ar-H), $J_{\alpha,\beta} = 8.1$, $J_{\text{H,D}} = 1.0$; HR-MS m/z 208.1221 (M^+ , calc. for $\text{C}_{16}\text{H}_{12}\text{D}_2$: 208.0939).
10. **1a**: 10% yield, mp 121–123 °C (Lit.,² 121–122 °C); **1b**: 16% yield, mp 113–115 °C; **1c**: 14% yield, mp 155–156 °C; **1d'**: 10% yield, colorless oil; **1e**: 10% yield, colorless oil; **1f**: 17% yield, colorless

oil.

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