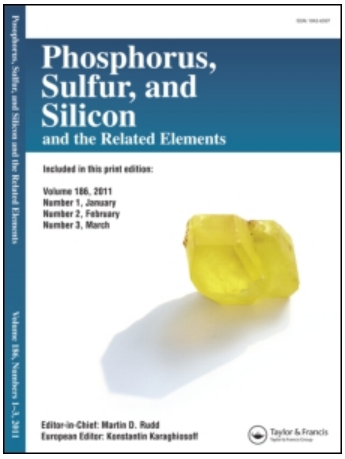

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THROUGH-SPACE INTERACTION OF TETHERED GROUPS IN DIPHOSPHA PERI-SUBSTITUTED NAPHTHALENES

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Online publication date: 12 August 2010

To cite this Article Kilian, Petr , Slawin, Alexandra M. Z. and Woollins, J. Derek(2004) 'THROUGH-SPACE INTERACTION OF TETHERED GROUPS IN DIPHOSPHA PERI-SUBSTITUTED NAPHTHALENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 999 — 1002
To link to this Article: DOI: 10.1080/10426500490427826
URL: http://dx.doi.org/10.1080/10426500490427826

Phosphorus, Sulfur, and Silicon, 179:999–1002, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427826

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THROUGH-SPACE INTERACTION OF TETHERED GROUPS IN DIPHOSPHA PERI-SUBSTITUTED NAPHTHALENES

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(Received August 21, 2003; accepted October 3, 2003)

NMR properties of 1,8-diphosphanaphthalenes with prerequisites for strong through-space interaction were studied. The exceptional magnitude of $^4J(PP)$ 246 Hz was found in Nap[P(NMe$_2$)$_2$][P(OMe)(NMe$_2$)] (Nap = naphthalene-1,8-diyl). The P^{III}, P^V mixed valence systems Nap[P(E)(OMe)$_2$][P(OMe)$_2$] (E = O, S, Se) show much lower magnitudes of through-space interaction than expected.

Keywords: Chalcogenides; phosphorus; strained molecules

In recent years we have been examining the chemistry of 1,8-diphospha naphthalenes.[1] The mismatch between the ideal peri-geometry dictated by rigid organic backbone and the bulk of tethered atoms in peri-positions, results in sub-Van der Waals contacts and significant steric strain, generating unusual chemistry and bonding.[2] The molecule adjusts to the peri-space crowding by twisting of the initially planar aromatic skeleton; further adjustments include out-of-plane and in-plane displacements of peri-atoms (Figure 1). Besides crystallography, the crowding can be assessed by spectral methods, most importantly by NMR and MS. Clearly, as the bulk of the atoms connected to the phosphorus atom increase, the distortion will also increase.

RESULTS AND DISCUSSION

We recently prepared and characterized a series of 1,8-diphospha substituted naphthalenes **1**–**4** with stepwise increased strain (Scheme 1). The products were fully spectrally characterized by multinuclear

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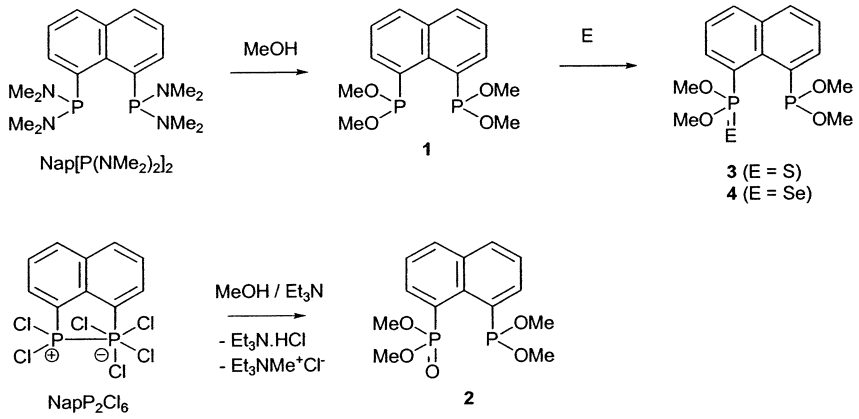

SCHEME 1 Syntheses of univalent P^{III}, P^{III} system **1** and mixed valence P^{III}, P^{V} systems **2–4** from $Nap[P(NMe_2)_2]_2$ and $NapP_2Cl_6$ (Nap = naphthalene-1,8-diyl).

NMR, IR, Ra, and MS spectroscopy and their crystal structures were measured.

NMR properties of compounds **1–4** were studied as they represent systems possessing lone pair(s) available for interaction in the crowded peri-space. Exceptional magnitudes of $^4J(PP)$ were expected due to possibility of through-space interaction. Despite few 1,8-bisphosphano naphthalenes $Nap(PR_2)_2$ being known, the only magnitude of $^4J(PP)$ 199 Hz of P^{III},P^{III}-peri-substituted naphthalene system reported to date was obtained from MAS solid state $^{31}P\{^1H\}$ NMR spectrum of $Nap(PPh_2)_2$.[3] Unfortunately, also the ^{31}P solution NMR spectrum of **1** did not allow determination of its $^4J(PP)$, as the

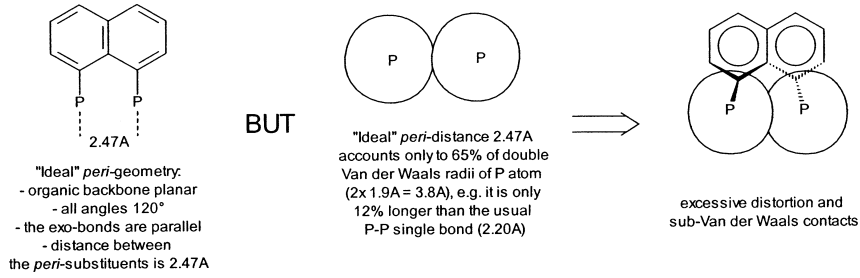

FIGURE 1 Bonding situation in 1,8-diphospha naphthalenes dictated by stiff aromatic backbone.

^{13}C satellites were hidden in the central line. The slow methanolysis rate of Nap[P(NMe_2)$_2$]$_2$, however, allowed ^{31}P NMR detection of intermediate Nap[P(NMe_2)$_2$][P(OMe)(NMe_2)] with two magnetically inequivalent ^{31}P nuclei (AX system), facilitating direct reading of its ^{4}J(PP) 246 Hz. Such a magnitude is comparable with ^{1}J(PP) in systems with a conventional σ^3P–σ^3P bond (the usual range 180–230 Hz).

The monoxidized derivatives **2**–**4** also possess lone pairs available for through-space interaction. Interestingly, the magnitudes of the P···P interaction in compounds **2**–**4** [^{4}J(PP) = 3.0–7.3 Hz], were found to be much smaller than those in the two relatively similar systems Nap[P(E)Ph$_2$](PPh$_2$) [E = S and Se, ^{4}J(PP) = 43 and 53 Hz] [4]and Nap[P(S)Ph(*t*Bu)] [PPh(*t*Bu)] [^{4}J(PP) = 40 and 42 Hz for the two diastereomeric forms].[5] By the way of contrast, the magnitudes of ^{5}J(PSe) are very similar (and extraordinarily high) in both monoseleno derivatives Nap[P(Se)Ph$_2$](PPh$_2$) (54 Hz)[4] and Nap[P(Se)(OMe)$_2$] [P(OMe)$_2$] (**4**, 61.1 Hz). As expected, the usual values of ^{5}J(PSe) < 2 Hz were found in **7**, **9** and **10** as confirmed from both ^{31}P and ^{77}Se NMR spectra.

Based on the data above, we expect that the molecules of Nap[P(E)Ph$_2$](PPh$_2$) (E = S, Se) and of Nap[P(S)Ph(*t*Bu)][PPh(*t*Bu)] in the solution would populate conformation in which the lone pair is positioned inside the peri-space and points towards the P^V atom, whilst in **2**–**4**, the lone pair is rotated slightly off the peri-space, pointing not directly to the P^V atom. In the same manner, the high magnitude of ^{5}J(PSe) would indicate relative proximity of Se and P^{III} atoms' lone pair in **4**. However, a comparison of crystal data of mixed valence P^{III}, P^V systems with their solution NMR data did not give any simple correlations of ^{4}J(PP) to P···P distance or to angular orientation of the P^{III} atoms' lone pair with respect to the P^V atom. For example, in the crystal of **4** the P···P distance identical to that in Nap[P(S)Ph(*t*Bu)][PPh(*t*Bu)] (3.30 Å) was found, yet the contrasting magnitudes ^{4}J(PP) 7 and 40 Hz were found in the solution.[5] In the same manner, nearly identical orientation of phosphorus' lone pair was found in the crystal of **4** and in Nap[P(Se)Ph$_2$](PPh$_2$) (n–P–C···P dihedral angles 8.8 and 7.2°),* yet the corresponding values of ^{4}J(PP) were 7.3 and 53 Hz. This may reflect subtle differences between solid state and solution geometries.

*n = lone pair positioned on respective P atom, its position is calculated by reversing the direction of the vector from the phosphorus atom to the centre of gravity of its methoxy groups.

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