The synthesis of novel main group containing heterocycles is a challenging and demanding area which is in its infancy compared to organic chemistry and is thus capable of delivering complete new classes of materials.

We have set about investigating 1,8-substituted naphthalene derivatives with one of our long term intentions being the formation of P-P and/or S-S containing radicals. We have recently prepared a range of materials including 1-4 which we have characterised spectroscopically and by X-ray crystallography. 1-4 and the related systems which we have made include rare examples of intramolecular P(III)-P(V) adducts as well as a good, high yield synthesis of the *bis*-PCl₂ system (which will be a useful synthon for phosphine chemists) and a simple entry into a *bis* P(II) compound. We have extended this work to test the amount of ring strain that can be induced in the naphtho backbone and examples of recent X-ray structures in this area are shown below.

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**Examples of unusual bonding situations supported by the 1,8-naphthalene backbone which we have in the past year. A simple P(II)-P(II) system, a hypercoordinated P(III)-P(V) system showing...**
“frozen” early stage of electrophile-nucleophile interaction, an intramolecular P(III)-P(V) Lewis acid-base system and an extremely strained repulsively interacting system.

This naphthalene based work has been conducted on the premise that the ‘natural’ E...E in a 1,8-substituted species is ca 2.4 Å and that this distance and a bonding interaction will be favoured over ring strained alternative geometries when heavier elements are placed close to each other using the 1,8 scaffolding. Thus the premise is to take disubstituted but ring strained naphthalene [ie the naphthalene is twisted from ideal aromatic planar geometry or the E groups are pushed apart with non trigonal geometries at carbon] systems and react them to release the ring strain and to form the appropriate E-E bond. The combination of a weak E-E bond coupled with the energy gained from release of ring strain should enable unusual systems to be obtained. This premise is supported by our observations that 2 and 3 have severely distorted naphthalene backbones with P...P distances of 2.80 and 2.77 Å whereas 4 with a formal P-P bond and a P(II) oxidation state has a completely planar C_{10}P_{2} framework and a P-P bond length of 2.22 Å i.e. the P-P bonding also reduces ring strain. As part of our efforts we have already synthesized naphPP [which is not yet fully characterised].

We have also investigated the steric effects in the naph(PR_{2}E)(PR_{2}E) system and have established some basic principles - the referees in Dalton regarded this work as ‘outstanding’ it is currently a ‘Hot Paper’ on the Dalton www site [http://www.rsc.org/]

We have also conducted preliminary work on the naphS_{2} system as well as its sequentially oxidized derivatives, apart from establishing good routes to these compounds (multigram scale) we have obtained simple complexes as well as binuclear systems. The manuscript for the work on NaphS_{2Ox} (x = 0,1,2,3,) was described as a ‘synthetic tour de force’ by the referees of Chemistry a European Journal.

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Recent References


Onset of three-centre, four-electron bonding in peri-substituted acenaphthenes: A structural and computational investigation