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Synthesis of Phosphorus-Centered and Chalcogen-Bridged Concave Molecules: Modulation of Bowl Geometries and Packing Structures by Changing Bridging Atoms

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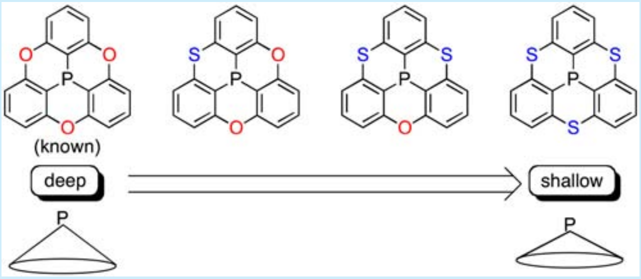
Ⓢ *Supporting Information*

ABSTRACT: A series of phosphorus-centered concave molecules having oxygen and sulfur as bridging atoms, C_{3v}-symmetric **P4** and C_s-symmetric **P2** and **P3**, were newly synthesized. The packing diagrams of the concave molecules **P1**−**P4** are dependent on the bridging atoms, columnar structures for **P1** and **P4**, and zigzag structures for **P2** and **P3**. The bowl depth becomes shallower in the order of **P1**, **P2**, **P3**, and **P4** as the number of bridging sulfur atoms increases.



Significant progress has been made in the research field of curved π-systems because of their unique electronic, photonic, and structural properties.[1] Recently, the self-assembly of curved molecules based on concave/convex interactions has been explored in order to provide stacked materials with properties distinguishable from common planar π-conjugated molecules, for example, pyroelectric,[2] ferroelectric,[3] and circular dichromic properties.[4] The assembled structures of the curved molecules have been extensively investigated in buckybowls, corannulene, and sumanene because control of the packing types is considered to be important regarding the properties of the crystal. The packing structures of buckybowls are classified into three forms; i.e., one-dimensional concave/convex stacks types A and B and the others, type C (Figure 1).[1b] The packing structures are dependent on various factors, such as the substituents, and are difficult to predict.

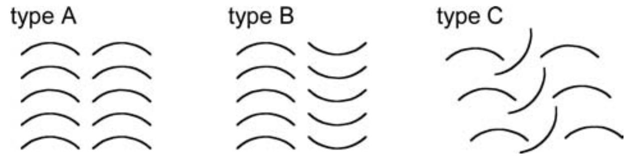


Figure 1. Packing structures of curved molecules. One of the type C examples, noncolumnar structures, is shown.

The phosphorus-centered molecule **P1** (phosphangulene) is a unique concave molecule, which features a type-A columnar packing in the crystal and a pyroelectric property in the crystal.[2] We have developed molecular hosts based on **P1** and their supramolecules based on concave/convex interactions.[5] We have now designed and synthesized concave molecules **P2**−**P4**, which are sulfur analogues of **P1** (Figure 2). Due to the longer C−S bond, **P2**−**P4** should have a longer rim than **P1**.[6] Our objective is to control the bowl geometries and packing structures by changing the bridging atoms, O and S.

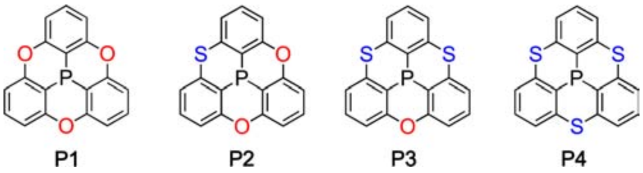


Figure 2. Phosphorus-centered concave molecules (phosphangulenes).

The synthesis of the concave molecule **P4** is depicted in Scheme 1. A key reaction for the synthesis of **P1** is the intramolecular S_{N}Ar reaction of the phenol OH group in **1**. Thus, the thiophenol derivative of **1** is a precursor of choice. The reaction of phosphine **1** with thiocarbamoyl chloride gave **2** in 87% yield, which underwent Newman−Kwart rearrangement to afford **3** in 96% yield.[7] The treatment of **3** with MeONa gave phosphine oxide **P4-o** in 61% yield via decarbonyl and successive intramolecular S_{N}Ar reactions. The reduction of oxide **P4-o**[8] gave **P4** containing three sulfur atoms in 69% yield.

In order to synthesize the less symmetric molecules **P2** and **P3**, the selective functionalization of the three OH groups of **1** is required. We developed a versatile synthetic method for the selected thiocarbamoylated compounds by utilizing the phosphorus(V) compound **4** as the starting material instead of the phosphorus(III) compound **1**. The reaction of **4** with thiocarbamoyl chloride gave **5** in 92% yield, which has one

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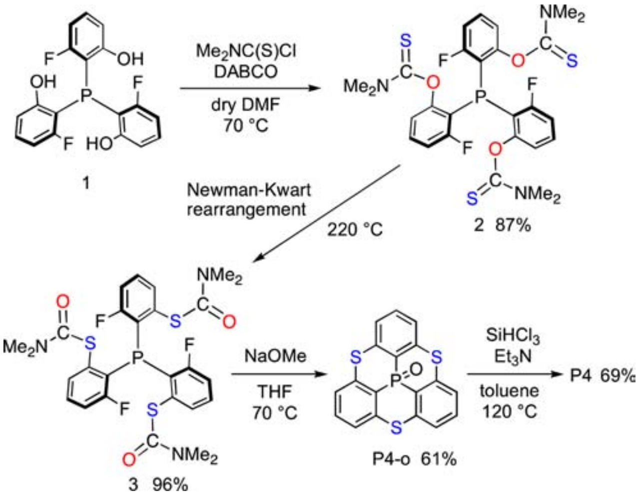
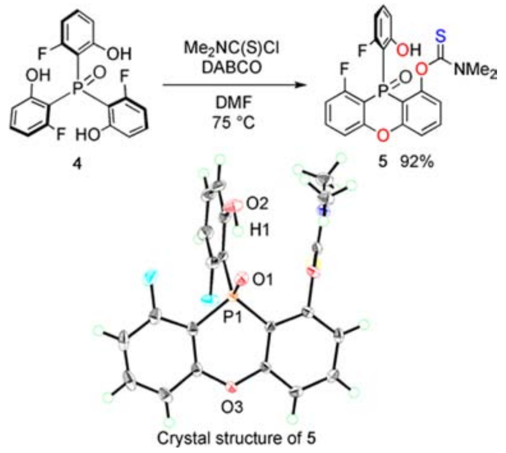
Scheme 1. Synthesis of P4



thiocarbamoyl group and a 9*H*-9-phosphaxanthene skeleton (Scheme 2). It is worth mentioning that this reaction is one of the limited synthetic methods for preparing phosphaxanthene derivatives.[9] The X-ray crystallographic analysis of **5** revealed that the phosphaxanthene moiety of **5** is nearly perpendicular to the 2-fluoro-6-hyroxyphenyl group with a dihedral angle of 89.9°. An intramolecular hydrogen bond is formed between the phenol OH and phosphine oxide groups (H1···O1 and O1···O2 distances: 1.64 and 2.59 Å, respectively). In the ^{1}H NMR spectrum, an OH resonance was observed downfield at 11.67 ppm, which also supports the hydrogen bond. The hydrogen bond should inhibit the further functionalization of the bound hydroxy group.[10]

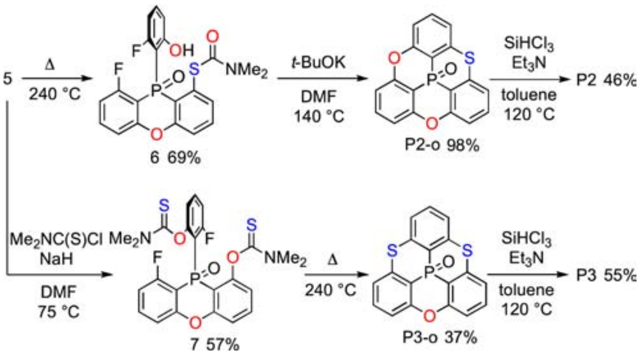
Scheme 2. Selective Thiocarbamoylation of 4



Upon the heating of **5** at 240 °C, the rearranged product **6** was obtained in 69% yield (Scheme 3). The treatment of **6** with *t*-BuOK led to deprotection and cyclization to give the concave molecule **P2-o** in 98% yield, which underwent reduction to form **P2** in 46% yield.

One more thiocarbamoyl group was introduced to **5** by the reaction with thiocarbamoyl chloride in the presence of NaH. The product **7** having two thiocarbamoyl groups underwent rearrangement, deprotection, and cyclization to form the concave molecule **P3-o** in 37% yield. The reduction of **P3-o** furnished **P3** in 55% yield.

Scheme 3. Synthesis of P2 and P3



The single crystals of **P2–P4** suitable for X-ray diffraction were obtained by recrystallization from hexane/chloroform. Although the molecular structures of **P1–P4** are similar, the packing diagrams are different. The crystal of **P4** exhibits a one-dimensional π-stacked structure in type B in which the directional alignment of neighboring columns is diametrically opposed to each other (Figure 3). This result is in contrast to the type A packing of **P1**.[2a] The distance between the stacked **P4** in one column is 3.98 Å, which is shorter than that of **P1**, 4.17 Å. The shallower bowl structure of **P4** should be responsible for the shorter molecular distance. The intermolecular distance between the benzene rings in a column of **P4** is 3.60 Å, which is very similar to that in a column of **P1**, 3.59 Å.

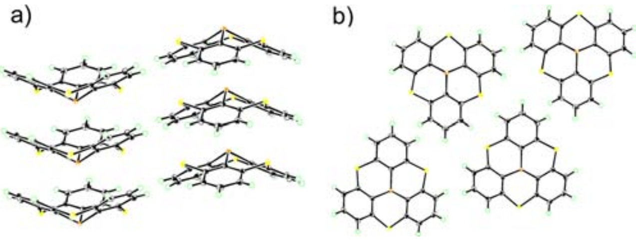


Figure 3. Crystal structure of **P4** with thermal ellipsoids of 50% probability: (a) side and (b) top views.

In contrast to the C_{3v}-symmetric **P1** and **P4**, the C_s-symmetric **P2** and **P3** do not exhibit a columnar packing, but a zigzag packing, type C (Figure 4). Symmetry breaking should be due to the destabilization of the stacked packing. Therefore, the packing structure of the phosphangulenes can be tuned by changing the bridging atoms.

An analysis of the molecular geometries was compared among the bowl structures of **P1–P4**. Two structural parameters, the bowl depth (d) and the cone angle (θ), are

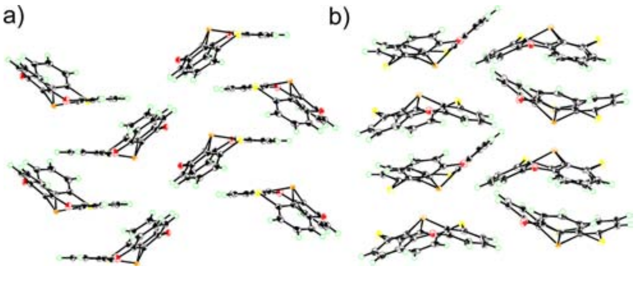


Figure 4. Crystal structure of (a) **P2** and (b) **P3** with thermal ellipsoids of 50% probability.

estimated (Figure 5).[11] The *d* values decreased in the order of **P1** (2.43 Å) > **P2** (2.24 Å) > **P3** (2.11 Å) > **P4** (2.03 Å). In the DFT-optimized structures of **P1**−**P4** in the gas phase at the M062X/6-31G* level, the *d* values are very similar to the experimental values in the order of **P1** (2.45 Å) > **P2** (2.22 Å) > **P3** (2.13 Å) > **P4** (2.01 Å). The *θ* values increased in the same order of **P1** (115.9°)[12,13] < **P2** (121.2°) < **P3** (125.8°) < **P4** (128.0°). Thus, the increase in the number of bridged sulfur atoms makes the bowl geometry shallow.

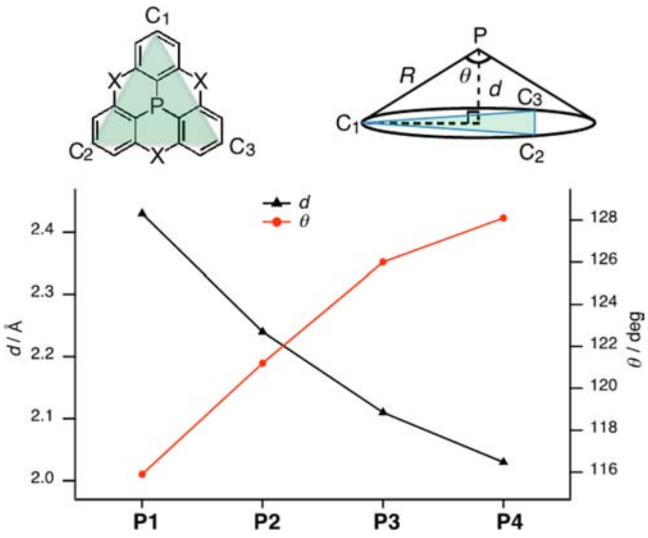


Figure 5. Comparison of the bowl depths (*d*) and cone angles (*θ*) of **P1**−**P4**.

The difference in the bowl geometry is caused by the structural change around the phosphorus atoms; the C−P−C bond angles are 93.1° for **P1**,[2a] 93.78(7)−98.40(7)° (avg 95.4°) for **P2**, 94.78(8)−99.34(8)° (avg 98.0°) for **P3**, and 99.91(7)−100.20(7)° (avg 100.1°) for **P4**.[13,14] The geometries around the phosphorus atom should be important for the bowl geometry in **P1**−**P4**. The bond angles around a phosphorus atom are related to the resonance of the ^{31}P NMR spectra.[13] The phosphorus resonance of **P1** was observed to be significantly upfield at −133 ppm[2a] because the large s-character of the phosphine lone pair leads to a large diamagnetic shift. As the number of bridging sulfur atoms increased, the chemical shift changed downfield, −114 ppm for **P2**, −92 ppm for **P3**, and −69 ppm for **P4**. This significant chemical-shift change should be due to the hybridization change of the phosphorus atom accompanied by the geometry change, suggesting that the difference in the bowl geometries of **P1**−**P4** is maintained in solution.

As seen in phosphines **P1**−**P4**, their oxide analogues **P1-o**−**P4-o** also exhibit a geometrical change dependent on the bridging atom. The *d* values decreased in the order of **P1-o** (2.11 Å) > **P2-o** (1.88 Å) > **P3-o** (1.68 Å) > **P4-o** (1.46 Å), which are much smaller than those of the corresponding phosphines **P1**−**P4** due to the axial substituent at the phosphorus atom contributing to the geometry.[13]

In summary, we have synthesized a series of phosphorus-centered concave molecules having oxygen and sulfur as bridging atoms. The valence of the starting phosphorus compounds plays an important role in the versatile synthesis; the synthesis from the trivalent **1** afforded the C_{3v}-symmetric **P1** and **P4**, while the synthesis from the pentavalent **5** afforded the C_s-symmetric **P2** and **P3**. The bowl geometries and packing diagrams were dependent on the bridging atoms. The packing diagrams are type A for **P1**, type B for **P4**, and type C (zigzag) for **P2** and **P3**. The bowl depth becomes shallower as the number of bridging sulfur atoms increases. We envisioned that the phosphorus-centered concave molecules, whose symmetry and geometry are tunable, could be utilized in various self-assembled materials of the π-conjugated molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00105.

Experimental details, spectral data, and crystallographic information (PDF)
Crystallographic data for **P2** (CIF)
Crystallographic data for **P3** (CIF)
Crystallographic data for **P4** (CIF)
Crystallographic data for **5** (CIF)
Crystallographic data for **P2-o** (CIF)
Crystallographic data for **P3-o** (CIF)
Crystallographic data for **P4-o** (CIF)

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Notes

The authors declare no competing financial interest.

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(11) The depth d is defined on the basis of the basal plane composed of three terminal carbon atoms. The angle θ is defined as $2\cos^{-1}(d/R)$ where R is the length between the phosphorus and terminal carbon atom.

(12) The angle θ of **P1** defined in this paper dose not precisely match with that in the previous paper, 115.8°, because the estimation method is different (ref 11). See reference 13.

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(14) The deviations of the bond angles for **P2** and **P3** are larger because of the lower symmetric geometry. The bond angles for phosphaxanthene skeletons are smaller than those for the phosphathioxanthene skeleton.