

Figure 1. Stereoscopic view of the [16]annulene molecule looking along the *b* axis. Bond distances in ångströms; standard deviation of C–C bond distances lie in range 0.010–0.015 Å.

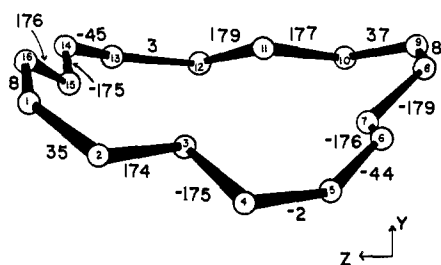


Figure 2. View of the [16]annulene molecule looking along the *a* axis. The dihedral angles along the bonds in the ring are given in degrees. The angle is taken as positive if, when viewed along the bond, the nearer substituent has to be rotated clockwise to eclipse the more distant substituent.

was solved by the symbolic addition method⁷ and has been refined by full-matrix least-squares procedures to an *R* factor of 0.12. All 16 hydrogen atoms have been located.

Views of the molecular structure are shown in Figures 1 and 2. The [16]annulene molecule is seen to contain alternating *cis* and *trans* double bonds, thus confirming the proposals of Sondheimer² and Schröder.³ The maximum distance of a carbon atom from the best plane through C(3), C(7), C(11), and C(15) is 0.57 Å, so that the nonplanarity of the molecule, although *highly significant*, is not exceptionally great. If bond alternation is a reliable indicator of the absence of aromaticity, then there is no evidence from the X-ray analysis for aromatic character in [16]annulene.⁸ The average C(sp²)–C(sp²) distance is 1.46 Å, and the average C(sp²)=C(sp²) distance is 1.34 Å. The C–C–C bond angles (external to the ring) at C(3), C(7), C(11), and C(15) range from 120 to 123°, while the other C–C–C bond angles (internal to the ring) range from 125 to 131°. The nonplanarity of the molecule arises principally from quite large dihedral angles (Figure 2) around four of the eight single bonds (τ 35–45°). The dihedral angles at the other bonds range from 1 to 8° (or the equivalent deviation from 180°). The result of the large twists about four of the single bonds is to force two of the four “inner” protons (*i.e.*, H(3) and H(11)) to one side of the mean molecular

(7) For an authoritative review, see J. Karle and I. L. Karle, *Acta Cryst.*, **21**, 849 (1966).

(8) This is in marked contrast to the result of X-ray analyses on [14]annulene⁹ and [18]annulene,¹⁰ where the molecules occupy positions of site symmetry C_i(1) in the crystal, and in the case of [18]annulene only very small differences in bond distance are observed.

(9) J. Bregman, *Nature*, **194**, 679 (1962).

(10) J. Bregman, F. L. Hirshfeld, D. Rabinovich, and G. M. J. Schmidt, *Acta Cryst.*, **19**, 227 (1965); F. L. Hirshfeld and D. Rabinovich, *ibid.*, **19**, 235 (1965).

plane, and the other two inner protons (*i.e.*, H(7) and H(15)) to the other side of the plane, thus minimizing the internal H–H contacts. In this way, the molecule approaches S₄(4) symmetry.

There is therefore evidence from ground-state geometry to support Longuet-Higgins' explanation⁵ for a large paramagnetic ring current in [16]annulene to account for the differences in nmr behavior between the 4*n* and 4*n* + 2 annulenes.¹¹ At 4° there is no evidence for valence tautomerism or conformational isomerism in the crystal.

Acknowledgment. We thank Dr. Gerhard Schröder for kindly supplying the sample of [16]annulene used in this study.

(11) See also discussions by J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966), and by F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(12) Alfred P. Sloan Foundation Fellow.

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Bis(phosphino)silane and Tris(phosphino)silane¹

Sir:

This communication describes the preparation of two new ternary silicon–phosphorus hydrides, bis(phosphino)silane (SiH₂(PH₂)₂) and tris(phosphino)silane (SiH(PH₂)₃). Although monophosphinosilanes, *i.e.*, SiH₃PH₂^{2,3} and Si₂H₅PH₂,^{4,5} have been reported previously, SiH₂(PH₂)₂ and SiH(PH₂)₃ are the first well-characterized examples of ternary hydrides containing multiple PH₂-group substitution.

Bis(phosphino)silane and SiH(PH₂)₃ were prepared by allowing stirred triglyme (1,2-bis(2-methoxyethoxy)ethane) solutions of LiAl(PH₂)₄⁶ to react at –30° for 15 min with SiH₂Br₂ and SiHBr₃, respectively. The reactions occur as shown below.



The reaction mixtures were separated by high-vacuum

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) G. Fritz, *Z. Anorg. Allgem. Chem.*, **280**, 332 (1955).

(3) J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962).

(4) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).

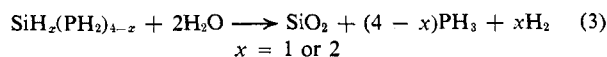
(5) S. D. Gokhale and W. L. Jolly, *ibid.*, **4**, 596 (1965).

(6) The LiAl(PH₂)₄ used in these experiments was prepared essentially as described by A. E. Finholt, C. Helling, V. Imhof, L. Nielsen, and E. Jacobson, *ibid.*, **2**, 504 (1963).

column distillation.⁷ In each reaction small quantities of SiH₄ and PH₃ were formed along with the desired products. Bis(phosphino)silane and SiH(PH₂)₃ were obtained in yields of 30 and 18%, respectively. Bis-(phosphino)silane (mol wt (vapor tension): found, 96.2; calcd, 96.06) has a vapor pressure of 9.0 ± 0.5 mm at 0°. Tris(phosphino)silane has a vapor pressure of ca. 2 mm at room temperature.

Bis(phosphino)silane and SiH(PH₂)₃ were characterized unequivocally on the basis of data obtained from elemental analyses, reactions with HCl, and mass, infrared, and ¹H and ³¹P nmr spectral analyses.

Elemental analysis of the samples was accomplished by hydrolysis in dilute aqueous NaOH. The calculated ratio of SiH_x(PH₂)_{4-x}:PH₃:H₂ (hydrolytic) according to the reaction shown in eq 3 is, for SiH₂(PH₂)₂, 1.00:



2.00:2.00 (found 1.00:1.96:1.98); for SiH(PH₂)₃, 1.00:3.00:1.00 (found 1.00:2.94:0.97). The reactions of SiH₂(PH₂)₂ and SiH(PH₂)₃ with excess HCl resulted in the quantitative formation (>94%) of PH₃, SiH₂Cl₂, and SiHCl₃, respectively.

The monoisotopic mass spectra of SiH₂(PH₂)₂ and SiH(PH₂)₃ contain peaks at (assignments in parentheses) *m/e* 28–34 (SiH_x⁺ and/or PH_x⁺), 59–64 (SiPH_x⁺), and 90–96 (SiP₂H_x⁺) and 28–34 (SiH_x⁺ and/or PH_x⁺), 59–63 (SiPH_x⁺), 90–95 (SiP₂H_x⁺), and 121–128 (SiP₃H_x⁺), respectively. Weak peaks from *m/e* 64–67 assigned to P₂H_x⁺ ions are also observed in the spectrum of SiH(PH₂)₃. The source of these ions has not been determined; however, it appears likely that they arise because of pyrolysis of the sample in the ionization chamber of the spectrometer. The most intense peaks in the spectra of SiH₂(PH₂)₂ and SiH(PH₂)₃ occur at *m/e* 63 and 95, respectively, corresponding in each case to the loss of a neutral PH₂ fragment from the molecular ion.

The gas-phase infrared spectra in the region 4000–400 cm⁻¹ exhibit the following absorptions (in cm⁻¹): for SiH₂(PH₂)₂, 2310 (s), 2160 (vs), 1066 (m), 930 (s), 823 (vs), 738 (w), 688 (w), 586 (w), and 482 (w); for SiH(PH₂)₃, 2308 (vs), 2152 (s), 1062 (m), 810 (s), 786 (m), 755 (w), 697 (w), 567 (m), and 474 (m). The absorptions at 2310 and 2308 cm⁻¹ and 2160 and 2152 cm⁻¹ can be assigned to the Si–H and P–H stretching modes, respectively. A complete analysis and assignment of the remainder of the absorptions is in progress and will be reported later.

The 60-MHz ¹H nmr spectrum of SiH₂(PH₂)₂ is comprised of a low-field resonance (A) at δ -4.32 ppm⁸ of area 2.0, which is assigned to the SiH₂ protons, and a high-field, complex doublet (B) at δ -1.44 ppm of area 4.0, which arises from the PH₂ protons. Resonance A appears as a 1:2:1 triplet (*J* = 18.4 cps, H–P coupling in HSiP) of 1:4:6:4:1 quintets (*J* = 4.9 cps, H–H coupling in HSiPH). Resonance B is a doublet (*J* = 1855 cps, H–P coupling) in which each doublet member is further split in a complex coupling pattern. The coupling exhibited by the PH₂ protons is consistent with that expected for an X₂AM₂A'X₂'

(7) The distillation column is a 30-cm long concentric-tube apparatus of a type designed and used in the laboratories of Professor R. Schaeffer and coworkers, Indiana University, Bloomington, Ind.

(8) Proton chemical shift values are reported relative to internal (CH₃)₄Si. Phosphorus-31 chemical shifts are given relative to external 85% H₃PO₄.

spin-coupling system. The ¹H nmr spectrum of SiH(PH₂)₃ consists of a low-field resonance (C) at δ -4.80 ppm of area 1.0, which is assigned to the SiH proton, and a high-field complex doublet (D) at δ -1.79 ppm of area 6.0, which arises from the PH₂ protons. Resonance C appears as a 1:3:3:1 quartet (*J* = 20.8 cps, H–P coupling in HSiP) of 1:6:15:20:15:6:1 heptets (*J* = 4.9 cps, H–H coupling in HSiPH). Resonance D is a complex doublet (*J* = 189 cps, distance between the two most intense peaks of the doublet) in which each doublet member is split in a complex coupling pattern. A complete analysis of the complex coupling situation which exists for the PH₂ protons of SiH₂(PH₂)₂ and SiH(PH₂)₃ will be reported in detail elsewhere.⁹

The ³¹P nmr spectra of SiH₂(PH₂)₂ and SiH(PH₂)₃ consist of single 1:2:1 triplet resonances (PH coupling) at δ +252 ± 2 and 216 ± 2 ppm, respectively. Because of the second-order spin-spin coupling which exists in these compounds, each member of the triplets shows additional splitting which we have been unable to adequately resolve so far; however, of essential importance is the fact that only one type of phosphorus atom chemical environment is present in each molecule.

Bis(phosphino)silane and SiH(PH₂)₃ are surprisingly stable compounds. Neither compound showed detectable decomposition after periods of ca. 1 hr at 37° in the probe of the nmr spectrometer. The stability of SiH₂(PH₂)₂ is in marked contrast to that reported for the isolectronic phosphorus hydride, P₃H₅, which decomposes rapidly at temperatures above -23°.¹⁰

Further studies of the chemistry of these new ternary silicon-phosphorus hydrides is in progress and will be reported later.

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- (9) R. A. Newmark and A. D. Norman, submitted for publication.
(10) T. P. Fehlner, *J. Am. Chem. Soc.*, **88**, 2613 (1966).

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The Reaction of Dioxygen Difluoride and Perfluoropropene. Preparation of 1-Fluoroperoxyperfluoropropane and 2-Fluoroperoxyperfluoropropane

Sir:

Dioxygen difluoride (O₂F₂) is a very reactive, unstable species. At temperatures above -160°, O₂F₂ decomposes to oxygen and fluorine. The chemistry of O₂F₂ can be explained in two manners. If the reaction is run under conditions causing decomposition of O₂F₂, simple fluorination results. Sulfuryl fluoride (F₂SO₂) is formed in this manner by the reaction of O₂F₂ and sulfur dioxide (SO₂).¹ If this reaction is moderated, the OOF group is transferred from O₂F₂ to form peroxy-sulfuryl difluoride (FSO₂OOF).¹

Jackson² determined the structure of O₂F₂ by micro-

- (1) I. J. Solomon, A. J. Kacmarek, and J. K. Raney, *Inorg. Chem.*, in press.
(2) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).