is 1.6 kcal., the corresponding ethyl and isopropyl groups should have this energy reduced to 0.8 kcal./mole. Qualitatively it is seen that these groups do have smaller energies when axial than does the methyl, but the agreement is not quantitative. Djerassi[11] suggested from a consideration of the rotatory dispersion curves of menthone and isomenthone that the energy of an axial isopropyl adjacent to a carbonyl was less than that of an axial methyl β to a carbonyl (0.9 kcal.), and the present work bears out that suggestion.

The t-butyl case needs to be considered separately from the above since the values for ΔH and ΔS set it apart from the other groups. The enthalpy change of I (X = t-Bu) from the cis to the $trans$ chair would be expected to be essentially the same as that found in the hydrocarbon (5.9 kcal./mole).[12] On the other hand, the enthalpy required to put a cyclohexanone ring in the boat form has been calculated[13] to be only 2.7 kcal./mole. It therefore was predicted that I_t would exist in the boat form, and ΔH is in good agreement with this prediction. It has also been predicted that the boat form of cyclohexane would have a higher entropy than would the chair form.[14] In the only case where this prediction was tested experimentally,[12] it was found to be true. The greater entropy of the I_t form (relative to I_c) when X = t-butyl is therefore expected and found.

(11) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 106, 187.

(12) N. L. Allinger and L. A. Freiberg, J. Am. Chem. Soc., 82, 2393 (1960).

(13) N. L. Allinger, ibid., 81, 5727 (1959).

(14) P. Hazebroek and L. J. Oosterhoff, Discussions Faraday Soc., 10, 87 (1951).

DEPARTMENT OF CHEMISTRY
WAYNE STATE UNIVERSITY   NORMAN L. ALLINGER
DETROIT 2, MICHIGAN   HERBERT M. BLATTER
RECEIVED NOVEMBER 29, 1960

CRYSTAL AND MOLECULAR STRUCTURE OF THE COMPOUND OF TRIETHYLPHOSPHINE AND CARBON DISULFIDE[1]

Sir:

Red monoclinic prismatic crystals are formed when triethylphosphine reacts with carbon disulfide in benzene or other solvents.[2] Analogous compounds are known for several other tertiary phosphines. The conflicting proposals for the molecular structures of these substances are reviewed by Issleib and Brack,[3] who concluded incorrectly that they are loose molecular compounds. We have determined the structure of the triethyl compound by X-ray diffraction and find that there is a chemical bond between phosphorus and the carbon atom of CS_2. The shape of the molecule corresponds to a zwitterion of a quaternary phosphonium derivative of dithioformate as proposed by Jensen,[4] $(CH_3CH_2)_3P^+$—CSS^-.

Single-crystal diffraction patterns were recorded with Cu Kα radiation by Weissenberg and preces-

(1) This work was done under the auspices of the U. S. Atomic Energy Commission.

(2) A. W. Hofmann, Ann. Suppl., 1, 1 (1861).

(3) K. Issleib and A. Brack, Z. anorg. u. allgem. Chem., 277, 271 (1954).
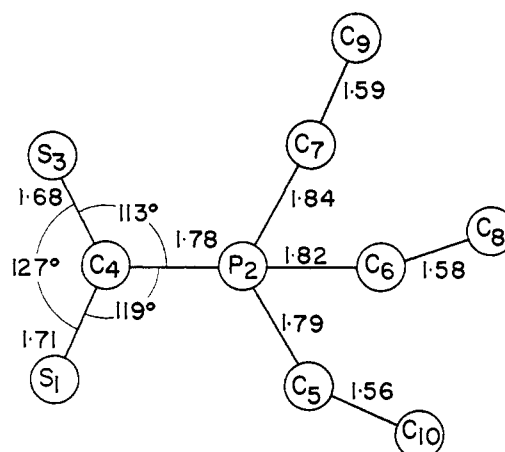
(4) K. A. Jensen, J. prakt. Chem., 148, 101 (1937).

Fig. 1.—Bond distances in Å. and bond angles (not to scale).

sion techniques. The crystals are monoclinic, space group P2₁/c, with 4 molecules in the unit cell of dimensions:

$a = 7.50 \pm 0.02$ Å.
$b = 11.97 \pm 0.02$ Å. $\beta = 123.1° \pm 0.2°$
$c = 13.82 \pm 0.05$ Å.

The density is calculated to be 1.24 g. cm.$^{-3}$.

Atomic coördinates of P and S were found with the three-dimensional Patterson function. Electron density calculations revealed the carbon atoms and accomplished some refinement of the heavy-atom coördinates. Further refinement by full-matrix least squares with isotropic individual temperature parameters and 610 observed independent reflections reduced the conventional unreliability factor R to 0.11. The resulting atomic parameters are listed in Table I. Hydrogen atoms are omitted from these calculations. The phosphorus and sulfur atoms are not clearly distinguished by the X-ray data, but are identified on the basis that phosphorus is the atom bonded to the ethyl groups.

TABLE I

ATOMIC COÖRDINATES AND TEMPERATURE PARAMETERS

Atom	x	y	z	B, Å.²
S₁	0.127	0.114	0.141	6.3
P₂	.132	.244	.329	4.4
S₃	.089	.840	.401	5.7
C₄	.056	.231	.183	5.4
C₅	.104	.751	.169	5.1
C₆	.300	.128	.416	5.6
C₇	.279	.376	.392	5.9
C₈	.348	.372	.042	6.3
C₉	.479	.377	.380	6.7
C₁₀	.249	.645	.218	7.8

The bond distances and some of the bond angles are shown in Fig. 1. Standard deviations are about 0.03 Å. for P–C and S–C bonds and 0.04 Å. for C–C bonds. The thioformate carbon (C₄) is coplanar with its three neighbors, and its bond angles ($\sigma = 1°$) are typical of those of salts of carboxylic acids. The bond angles at the phosphorus atom range from 108° to 111° ($\sigma = 1°$). The bond angles at the methylene carbon atoms (C₅, C₆, C₇) are 115°, 113°, and 109° ($\sigma = 2°$).

We thank Dr. George A. Wiley for preparing the crystals which we used. Further refinement of this structure is in progress.

DEPARTMENT OF CHEMISTRY AND
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA   THOMAS N. MARGULIS
BERKELEY 4, CALIFORNIA   DAVID H. TEMPLETON
          RECEIVED DECEMBER 27, 1960

TRIPTYCH-SILOXAZOLIDINES: PENTACOORDINATE BRIDGEHEAD SILANES RESULTING FROM TRANSANNULAR INTERACTION OF NITROGEN AND SILICON

Sir:

We have found the alcoholysis of trialkoxysilanes by trialkanolamines to lead to the exclusive formation of crystalline monomeric products.[1]

$$ZSi(OR)_3 + (HOCHRCH_2)_3N \longrightarrow$$
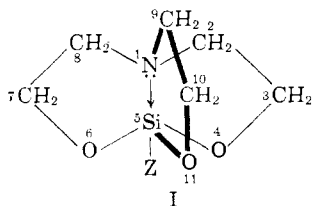$$ZSi(OCHRCH_2)_3N + 3ROH$$
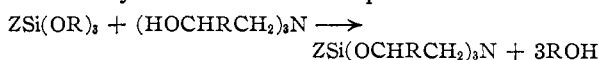
This is in striking contrast to the polymeric products one might reasonably have anticipated from the condensation of such highly functional reactants. A series of such derivatives has been prepared and representative members are shown in Table I.

with the structurally related borates.[4,5] While pentacoördinate complexes of various halosilanes have been reported,[6] the triptych-siloxazolidines herein described are believed to be the first examples of pentacoördinate alkoxysilanes. Their marked stability despite the weakly basic nature of trialkanolamines[7] and the apparent failure of trimethoxysilane to complex with an amine as nucleophilic as piperidine (*vide infra*) underscores the importance of steric factors in such interactions.

Brown[4c] based his assignment of a triptych structure to triethanolamine borate upon the inertness of the nitrogen atom toward methyl chloride and its sluggish neutralization by methanesulfonic acid in nitrobenzene solution. Similarly, we have found that triptych-siloxazolidines are not neutralized immediately by perchloric acid in a glacial acetic acid medium, thereby supporting a structure wherein the nitrogen's basic pair of electrons is not available for immediate protonation.

The silicon system provides the means for a unique test of the triptych model. Smith and Angelotti[8] studied the effect of molecular structure upon the Si–H stretching frequency, showing clearly that

TABLE I
TRIPTYCH-SILOXAZOLIDINES

Substituents	M.p.,[a] °C.	Molecular formula	Silicon, % Calcd.	Found	Neut. equiv. Calcd.	Found
None	253–256	$C_6H_{13}O_3SiN$	16.02	16.23	175	177
5-Methyl[b]	123–125	$C_7H_{15}O_3SiN$	14.84	14.66	189	189
	151–153[c]					
3,5-Dimethyl	95–97	$C_8H_{17}O_3SiN$	13.82	13.60	203	203
5-Octadecyl	85–86	$C_{24}H_{49}O_3SiN$	6.57	6.73	428	428
5-α-Phenethyl	192–194	$C_{14}H_{21}O_3SiN$	10.05	10.16	279	282
5-Vinyl	163–165	$C_8H_{15}O_3SiN$	13.96	14.14	201	202
5-Phenyl	208–209	$C_{12}H_{17}O_3SiN$	11.18	11.24	251	250
3-Methyl-5-phenyl	85–87	$C_{13}H_{19}O_3SiN$	10.58	10.48	265	267
5-Ethoxy[d]	100–102	$C_8H_{17}O_4SiN$	12.81	12.72	219	218
5-(−)-Menthoxy	152–154	$C_{16}H_{31}O_4SiN$	8.52	8.32	330	333

[a] Uncorrected. [b] B.p. 174° (31 mm.). [c] Apparent polymorphism; the lower-melting form was obtained by crystallizing the melt at about 100°. [d] B.p. 180° (0.6 mm.).

That even a fourth substituent on the silicon may be functional is illustrated by the monomeric products derived from such silanes as trimethoxysilane and ethyl orthosilicate. For reasons cited below, these silanes are believed to be pentacoördinate as a result of transannular dative bonding between the nitrogen and silicon atoms (I). They have been

I

designated as triptych-siloxazolidines[2,3] by analogy

increased electron supply at the silicon displaces the absorption to lower energy regions. Although showing some solvent dependency, the position of ν(SiH) for $HSi(OCH_2CH_2)_3N$ was displaced from the region characteristic of silanes bearing three Si–O bonds to a lower energy region wherein silanes

systematic[3] name 4,6,11,1,5-trioxazasila-5-ethoxytricyclo[3.3.3.0^{1,5}]-undecane.

(3) IUPAC 1957 Rules, *J. Am. Chem. Soc.*, **82**, 5573 (1960).

(4) (a) A. A. Schleppnik and C. D. Gutsche, *J. Org. Chem.*, **25**, 1378 (1960); (b) H. Steinberg and D. L. Hunter, *J. Am. Chem. Soc.*, **82**, 853 (1960); (c) H. C. Brown and E. A. Fletcher, *ibid.*, **73**, 2808 (1951); (d) C. A. Rojahn, German Patent 582,149 (*Chem. Zentr.*, **104**, II, 2704 (1933)).

(5) It seems likely that similar compounds containing such elements as Al, Fe, Ti, Sn, Ge, P, etc., might be feasible. In this connection, preliminary studies have shown sublimable material of the anticipated composition to result from the reaction of triisopropanolamine and aluminum isopropylate. The importance of atomic size and/or the presence of relatively low-lying vacant orbitals was demonstrated by the condensation of ethyl orthoformate and triethanolamine to form a cross-linked polymer rather than a monomeric species.

(6) (a) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, 1960, p. 92; (b) F. G. A. Stone and D. Seyferth, *J. Inorg. and Nucl. Chem.*, **1**, 112 (1955).

(7) H. K. Hall, *J. Am. Chem. Soc.*, **79**, 5441 (1957).

(8) A. L. Smith and N. C. Angelotti, *Spectrochim. Acta*, **15**, 412 (1959).

(1) Subsequent to completion of this work, an account of the independent preparation of $C_6H_5Si(OCH_2CH_2)_3N$ and CH_3CH_2OSi-$(OCH_2CH_2)_3N$ appeared in U. S. Patent 2,953,545 granted to Arnold B. Finestone, Sept. 20, 1960. The melting point of the latter compound (35–37°) differs significantly from our value (100–102°).

(2) This nomenclature is best illustrated by a specific example such as the naming of $C_2H_5OSi(OCH_2CH_2)_3N$. Using the numbering scheme shown (I), one obtains the name 5-ethoxytriptych-siloxazolidine. This compares favorably with the precise but unwieldy