

# Nuclear Magnetic Resonance Studies on the Conformation of Five-Membered Ring Phosphites and Related Compounds

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**Abstract:** The temperature and solvent dependence of the nmr spectra of isobutylene phenylphosphonite, isobutylene phenylphosphonate, and the syn and anti isomers of methyl styrene phosphite have been investigated. From changes in the proton-proton and proton-phosphorus coupling constants with the above variables it is concluded that the five-membered ring exists in a twist-envelope conformation. For compounds containing groups on carbon syn to the group on phosphorus, the preferred average conformation is such that these groups are as far apart as possible. In the anti compounds, there appears to be a smaller energy difference between the various conformers resulting from pseudorotation of the five-membered ring such that the preference for one of the possible conformations is not as large as in the case of the syn compounds.

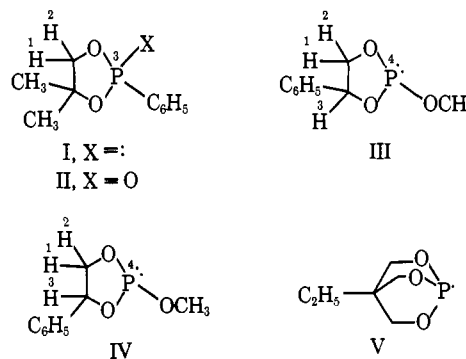
In recent years, the conformation of various six-membered ring compounds containing phosphorus has been the subject of extensive investigation.<sup>1-12</sup> Evidence largely from nmr studies has shown that these molecules usually adopt a chair conformation similar to that of the cyclohexanes with the group on phosphorus being in an axial position. Furthermore, the data indicate that more than one conformer of a single stereoisomer is stable at room temperature in certain cases.<sup>9</sup> Data from the above investigations also suggest that the POCH coupling constant exhibits a dependence on dihedral angle similar to that observed for other vicinal couplings.<sup>10</sup> Thus, for the phosphate esters, the  $\text{POCH}_{\text{trans}}$  ( $\phi = 180$ ) coupling constant is usually  $\sim 20$  Hz while the  $\text{POCH}_{\text{gauche}}$  ( $\phi = 60$ ) coupling constant is  $\sim 3$  Hz.<sup>8-10</sup> Similar data for six-membered ring phosphites yield different values for the POCH coupling constants, possibly due to differences in hybridization and bond angles at phosphorus.<sup>10-12</sup>

While it has been established that there is no inversion at phosphorus in five-membered ring phosphites,<sup>13</sup> there is little information concerning the conformation of the five-membered ring. Two explanations have been offered for the different POCH coupling constants ( $\sim 10$  and  $\sim 2$  Hz) observed in ethylene phosphites: (1) the five-membered ring exists in an envelope conformation with phosphorus in the "flap" position

and the methylene protons on the ring carbons are influenced to different extents by the lone pair on phosphorus,<sup>14</sup> and (2) the five-membered ring exists in a twist-envelope conformation resulting in different P-O-C-H dihedral angles for the methylene protons syn and anti to the group on phosphorus.<sup>15</sup> Our studies of the nmr spectra of isobutylene phosphites and phosphates suggested that the five-membered ring exists in a twist-envelope conformation and that the twist in the five-membered ring was larger in the isobutylene phosphites than in the ethylene phosphites.<sup>16</sup>

In order to obtain further information concerning the conformation of five-membered ring phosphites and related compounds, we have conducted investigations on the effect of both temperature and solvent on the nmr spectra of five-membered ring phosphorus compounds. We wish to report here our investigations of the solvent and temperature dependence of the nmr spectra of isobutylene phenylphosphonite (I), isobutylene phenylphosphonate (II), and the syn and anti isomers of methyl styrene phosphite (III and IV). The results are discussed in relation to the conformation of the five-membered ring in these and related compounds. The numbering scheme used in this paper is given in Chart I.

Chart I. Numbering Scheme Used



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## Experimental Section

**Materials.** The preparation of isobutylene phenylphosphonite (I) and isobutylene phenylphosphonate (II) have been described elsewhere.<sup>16</sup> Methyl styrene phosphite (III and IV) was prepared from styrene glycol and trimethyl phosphite by a modification of the transesterification procedure of Denney, *et al.*<sup>17</sup> Approximately a 2:1 mixture of the anti and syn isomers was obtained from this reaction (bp 88° (0.6 mm)). 4-Ethyl-2,6,7-trioxaphosphabicyclo-[2.2.2]octane (V) was of commercial origin (Frinton Laboratories). Solvents were reagents grade or better. All materials were checked for purity by nmr immediately prior to use. Samples were degassed and sealed in 5-mm, thin-wall Pyrex sample tubes with 3% TMS added as an internal reference and lock signal source. Hexamethyldisiloxane was used as the internal reference in the variable temperature experiments.

**Spectra.** Proton spectra were obtained on a Varian Associates HA-100 spectrometer operating in the field sweep mode with an ambient probe temperature of 29°. Spectra were calibrated by utilizing the frequency difference network. Line positions used in the calculation of the chemical shifts and coupling constants were the average of two upfield and two downfield scans. A sweep width of 50 Hz and a sweep time of 1000 sec were used. Temperatures were calibrated using the methanol and ethylene glycol standards supplied by Varian. Spin-decoupling experiments were performed using a Hewlett-Packard Model 200-AB audio oscillator. Chemical shifts and coupling constants were obtained by utilizing the computer program LAOCN3.<sup>18</sup> The probable error for all parameters was always less than 0.03 Hz and we believe the data to be accurate to within  $\pm 0.1$  Hz.

## Results

**Isobutylene Phenylphosphonite (I).** This compound was examined as a 5 mol % solution in toluene-*d*<sub>8</sub> over a temperature range of 157°. Assignment of the chemical shifts and coupling constants is identical with that given elsewhere.<sup>16</sup> Analysis of the spectra of I was carried out assuming a three-spin system arising from the methylene protons and the phosphorus atom. There is the possibility that the chemical shifts and coupling constants reported for I and II may not be the "correct" values since they were treated as three-spin systems and only the proton spectrum was used in the analysis.<sup>19</sup> However, the reported values are similar to those found when the phosphorus spectrum was included in the analysis and are also similar to those values reported for other isobutylene phosphites and phosphates.<sup>16</sup>

Chemical shifts and coupling constants obtained for I over the above temperature range are given in Table I.

**Table I.** Temperature Dependence of the Nmr Parameters of Isobutylene Phenyl Phosphonite

Temp <sup>a</sup>	$\nu_1^b$	$\nu_2$	$J_{12}^c$	$J_{13}$	$J_{23}$
93	3.227	3.490	-8.73	0.35	13.62
60	3.179	3.461	-8.74	0.33	13.70
29	3.115	3.417	-8.79	0.29	13.91
-5	3.068	3.391	-8.42	0.24	14.10
-43	2.996	3.329	-8.95	0.26	14.34
-64	2.945	3.274	-8.98	0.27	14.48

<sup>a</sup> In degrees centigrade. <sup>b</sup> In ppm downfield from internal TMS. <sup>c</sup> In Hz.

The geminal proton-proton coupling constant  $J_{12}$  varies by 0.25 Hz. The phosphorus coupling to the proton syn to the group on phosphorus,  $J_{13}$ , varies by 0.1 Hz

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and the phosphorus coupling to the proton anti to the group on phosphorus,  $J_{23}$ , increases by 0.86 Hz with decreasing temperature. Chemical shifts of the methylene protons are temperature dependent, moving to lower field with increasing temperature.

The effect of solvent on the nmr parameters of I was examined. In Table II are given the results of examina-

**Table II.** Solvent Dependence of the Nmr Parameters of Isobutylene Phenyl Phosphonite

Solvent	$\epsilon^a$	$\nu_1^b$	$\nu_2$	$J_{12}^c$	$J_{13}$	$J_{23}$
Benzene	2.26	3.228	3.507	-8.83	0.35	13.91
Toluene- <i>d</i> <sub>8</sub>	2.35	3.115	3.417	-8.79	0.29	13.91
Chloroform- <i>d</i>	4.55	3.452	3.863	-8.84	0.16	13.98
Dichloromethane	9.09	3.426	3.848	-8.93	0.16	14.12
Pyridine	12.3	3.443	3.884	-8.90	0.15	14.13
Acetone- <i>d</i> <sub>6</sub>	19.8	3.436	3.934	-9.03	0.12	14.18
Acetonitrile- <i>d</i> <sub>3</sub>	35.1	3.410	3.897	-9.04	0.12	14.17
Dimethyl- <i>d</i> <sub>6</sub> sulfoxide	46	3.371	3.965	-9.04	0.08	14.15

<sup>a</sup> "Table of Dielectric Constants of Pure Liquids," NBS Circular 514, U. S. Government Printing Office, Washington, D. C., 1951.

<sup>b</sup> In ppm downfield from internal TMS. <sup>c</sup> In Hz.

tion of this compound as a 5 mol % solution in eight solvents of varying dielectric constant. Both phosphorus-proton coupling constants,  $J_{13}$  and  $J_{23}$ , vary by 0.27 Hz over this dielectric range. The geminal proton-proton coupling constant  $J_{12}$  varies by 0.12 Hz and the chemical shifts of the methylene protons move to lower field with increasing dielectric constant of the solvent.

**Isobutylene Phenylphosphonate (II).** The effect of temperature on the nmr spectrum of a 5 mol % solution of II in dimethyl sulfoxide was examined over a temperature range of 76°. Results are given in Table III.

**Table III.** Temperature Dependence of the Nmr Parameters of Isobutylene Phenyl Phosphonate

Temp <sup>a</sup>	$\nu_1^b$	$\nu_2$	$J_{12}^c$	$J_{14}$	$J_{23}$
105	4.234	4.398	-9.22	7.41	13.94
70	4.241	4.403	-9.19	7.09	14.23
29	4.249	4.406	-9.26	6.20	14.77

<sup>a</sup> In degrees centigrade. <sup>b</sup> In ppm downfield from internal TMS. <sup>c</sup> In Hz.

There is essentially no change in the geminal proton-proton coupling constant  $J_{12}$  within experimental error. However, both proton-phosphorus coupling constants are temperature dependent. With decreasing temperature,  $J_{13}$  decreases by 1.21 Hz whereas  $J_{23}$  increases by 0.83 Hz. Previous nmr studies on similar compounds have shown that both phosphorus-proton coupling constants have like signs (probably positive).<sup>12,20,21</sup> The fact that the coupling constants in II do not change in the same direction with temperature negates the hypothesis that these changes are due to temperature effects on coupling constants.<sup>22,23</sup> The results are consistent, however, with the changes in the coupling con-

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**Table IV.** Solvent Dependence of the Nmr Parameters of Isobutylene Phenyl Phosphonate

Solvent	$\epsilon$	$\nu_1^a$	$\nu_2$	$J_{12}^b$	$J_{13}$	$J_{23}$
Carbon tetrachloride	2.20	4.244	4.442	-8.98	7.55	13.54
Carbon disulfide	2.64	3.982	4.169	-9.01	7.19	13.91
Chloroform- <i>d</i>	4.55	4.093	4.308	-8.98	8.23	13.10
Dichloromethane	9.09	4.086	4.290	-9.07	7.42	13.73
Pyridine	12.3	4.187	4.362	-9.13	6.59	14.43
Acetone- <i>d</i> <sub>6</sub>	19.8	4.245	4.385	-9.29	6.36	14.61
Acetonitrile- <i>d</i> <sub>3</sub>	35.1	4.162	4.339	-9.28	6.52	14.56
Dimethyl- <i>d</i> <sub>6</sub> sulfoxide	46	4.249	4.406	-9.26	6.20	14.77

<sup>a</sup> In ppm downfield from internal TMS. <sup>b</sup> In Hz.

**Table V.** Nmr Parameters for the Two Isomers of Methyl Styrene Phosphite at Various Temperatures

Isomer	Temp <sup>a</sup>	$\nu_1^b$	$\nu_2$	$\nu_3$	$J_{12}^c$	$J_{13}$	$J_{14}$	$J_{23}$	$J_{24}$	$J_{34}$
III	91	4.069	3.422	5.038	-8.54	6.91	2.92	6.90	7.50	0.59
III	61	4.009	3.359	4.984	-8.55	6.99	3.01	7.00	7.44	0.63
III	29	3.936	3.289	4.919	-8.57	7.00	3.11	7.12	7.29	0.67
III	-6	3.877	3.229	4.871	-8.64	7.08	3.22	7.11	7.16	0.51
III	-36	3.800	3.161	4.802	-8.64	6.98	3.34	7.06	7.14	0.01
IV	91	3.579	3.877	4.684	-8.73	9.92	0.32	6.77	14.23	3.11
IV	61	3.518	3.819	4.620	-8.75	10.13	0.28	6.77	14.30	2.84
IV	29	3.453	3.749	4.542	-8.77	10.25	0.32	6.67	14.34	2.76
IV	-6	3.399	3.696	4.477	-8.89	10.36	0.34	6.66	14.55	2.59
IV	-36	3.340	3.624	4.399	-8.78	10.43	0.36	6.68	14.62	2.47

<sup>a</sup> In degrees centigrade. <sup>b</sup> In ppm downfield from internal TMS. <sup>c</sup> In Hz.

stants being due to a change in conformational equilibria with temperature.

The results of an investigation of the effect of solvent on the nmr parameters of II (examined as a 5 mol % solution) are given in Table IV. The geminal proton-proton coupling constant  $J_{12}$  decreases by 0.2 Hz with increasing dielectric constant of the solvent. This change is in the correct direction in view of the negative sign of  $J_{12}$ .<sup>24</sup> For the phosphorus-proton coupling constants,  $J_{13}$  decreases by 2.03 Hz with increasing dielectric constant whereas  $J_{23}$  increases by 1.67 Hz with increasing dielectric constant of the solvent. Thus, the temperature and solvent dependence of the phosphorus-proton coupling constants are similar in that the coupling constants change in opposite directions in both sets of experiments.<sup>25</sup>

**Methyl Styrene Phosphite (III and IV).** The 2:1 mixture of the anti and syn isomers of this compound was used in this investigation. Assignment of structures to the two isomers was made on the following basis: (1) on the basis of steric arguments, the isomer present in the larger amount should be the isomer which has the phenyl group anti to the group on phosphorus and (2) protons on the five-membered ring which are syn to the group on phosphorus should be deshielded by the -OR group on phosphorus with respect to those protons anti to the group on phosphorus.<sup>17</sup> Considering the proton on the same carbon as the phenyl group with the above arguments, the anti isomer is assigned to II and the syn isomer to IV. This assignment is consistent with data from other five-membered ring phosphites.<sup>14-16</sup> Assignment of the chemical shifts and coupling constants in the individual isomers is then

straightforward with the aid of spin-decoupling experiments.

The results obtained from examination of a sample of III and IV as a 5 mol % solution in toluene-*d*<sub>8</sub> at various temperatures are given in Table V. The geminal proton-proton coupling constant in both III and IV does not vary with temperature within experimental error. For III, the vicinal proton-proton coupling constants,  $J_{13}$  and  $J_{23}$ , are essentially constant. However, the phosphorus-proton coupling constants are temperature dependent. With decreasing temperature,  $J_{14}$  increases by 0.48 Hz,  $J_{24}$  decreases by 0.36 Hz, and the changes in  $J_{34}$  are almost within experimental error.

The syn isomer (IV) exhibits a larger temperature dependence than does III. The trans vicinal proton-proton coupling constant  $J_{13}$  increases with decreasing temperature by 0.51 Hz whereas the change in the cis coupling constant  $J_{23}$  is within experimental error. For the phosphorus-proton coupling constants,  $J_{14}$  is constant within experimental error,  $J_{24}$  increases by 0.39 Hz, and  $J_{34}$  decreases by 0.64 Hz with decreasing temperature.

**4-Ethyl-2,6,7-trioxaphosphabicyclo[2.2.2]octane (V).** This compound was examined as a 5 mol % solution in several solvents of varying dielectric constant. The POCH coupling constant (1.9 Hz) does not change with dielectric constant within experimental error over the dielectric constant range 2-46. Since this is a rigid molecule, it must be concluded that the effect of solvent on POCH coupling constants is within experimental error.

## Discussion

A large body of evidence has been accumulated which suggests that vicinal couplings between hydrogen and an element of the first or second row depend upon the dihedral angle similar to the well-studied vicinal proton-proton coupling constants.<sup>26</sup> Data from a variety of compounds suggest that POCH coupling constants behave similarly.<sup>10</sup> Although the observed values for the maxima and minima in a Karplus type curve<sup>27</sup> for POCH couplings may vary depending on hybridization of phosphorus, angle strain for cyclic systems, substituents, etc., there is no reason to believe that POCH coupling constants in five-membered ring phosphites and related compounds should not depend upon the

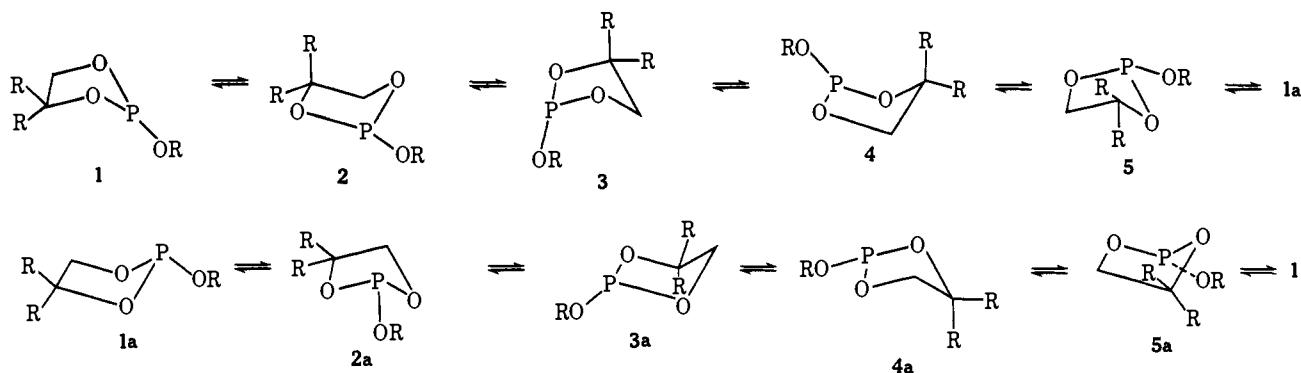
(24) S. L. Smith and R. H. Cox, *J. Chem. Phys.*, 2848 (1966).

(25) H. Finegold, *J. Phys. Chem.*, 73, 4020 (1969), for an example where this is not the case.

(26) A. A. Bothner-By and R. H. Cox, *J. Phys. Chem.*, 73, 1830 (1969).

(27) (a) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959); (b) *J. Amer. Chem. Soc.*, 85, 2870 (1963).

Scheme I. Conformations Due to Pseudorotation around the Five-Membered Ring



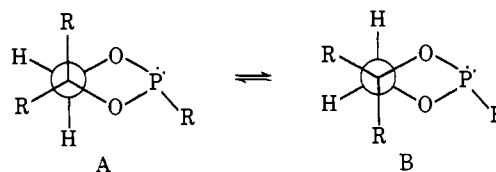
POCH dihedral angle. A recent investigation has shown that the orientation of the lone pair on phosphorus has no influence on POCH couplings.<sup>10</sup> Therefore, we have used the vicinal coupling constants in this investigation as the probe for determining conformational changes.<sup>28</sup>

Since the initial plan of this investigation was to examine the conformational mobility of five-membered ring phosphorus compounds by observing the temperature and medium effects on their vicinal couplings, it is first necessary to establish that temperature and solvent have no effect on these couplings *per se*. Previous investigations have shown that in rigid systems, solvent has no effect on vicinal proton coupling constants.<sup>24</sup> It seems reasonable to suggest that solvent has no effect on POCH coupling constants since this coupling in V does not vary over the dielectric constant range 2–46. Although the effect of temperature on vibrational contributions<sup>22,23</sup> to the coupling constants cannot be assessed with these data, the fact that the POCH coupling constants in II and IV change in opposite directions with either temperature or solvent indicates that the observed changes in the coupling constants cannot be ascribed to vibrational effects. Since it has been shown that inversion at phosphorus does not occur in these compounds,<sup>13,16</sup> a reasonable explanation for the observed changes in the coupling constants is a change in the conformational equilibria of the five-membered ring.

From consideration of the vicinal proton–proton coupling constants in ethylene phosphites and ethylene sulfite, and from comparisons of the ir spectra of ethylene phosphites with that for ethylene sulfite, it was concluded that the five-membered phosphite ring exists in a twist-envelope conformation.<sup>15</sup> Furthermore, it was suggested that the group on phosphorus occupies an axial position similar to that recently found for six-membered ring phosphites.<sup>9</sup> From analogy with the cyclopentane system, the following conformations are considered as possibilities for the five-membered phosphite ring system: planar, envelope, and half-chair.<sup>29</sup> The planar ring system is not considered for reasons similar to those invoked for cyclopentane.<sup>29</sup> In the envelope conformation (four atoms in a plane) with phosphorus in the “flap” position (1 and 1a in Scheme I), eclipsing occurs with substituents on carbons 4 and 5. Furthermore, comparison of the nmr data for

ethylene phosphites and propylene phosphites also suggests that this is not a major contributor since in the anti propylene phosphites, different POCH coupling constants are observed for the two syn protons. Part of the eclipsing interaction may be relieved by pseudorotation around the ring (Scheme I) which would place an atom other than phosphorus in the “flap” position. However, based on models, this relief of eclipsing interaction would not be large enough to account for the vicinal proton–proton couplings observed<sup>15</sup> in unsubstituted ethylene phosphites. The eclipsing interaction between substituents on carbons 4 and 5 may be relieved further by the ring adopting a conformation with two of the five atoms out of the plane formed by the three remaining atoms, similar to the half-chair conformation of cyclopentane. This has been referred to as the twist envelope conformation<sup>15</sup> (Scheme II). Only

Scheme II. Newman Projections of the Five-Membered Ring



with this conformation, or a time average of other conformations yielding the same effect, can a consistent explanation for all the nmr data on five-membered ring phosphites be derived (see later discussion).

Examination of a model of 1 in conformer A (Scheme II) shows the POCH<sub>2</sub> dihedral angle to be ~170° whereas the dihedral angle for the POCH<sub>1</sub> fragment is ~90°. In conformer B, the POCH dihedral angles are ~170 and ~90°, respectively, for protons 1 and 2. Therefore, if the two conformations were equally populated, identical POCH coupling constants should be observed for proton 1 and 2 assuming no influence from the lone pair on phosphorus.<sup>10</sup> The fact that proton 2 has a much larger coupling with phosphorus than proton 1 indicates that conformer A is lower in energy than is conformer B. As the population of A increases,  $J_{\text{POCH}_2}$  will increase due to a larger contribution from  $J_{\text{trans}}$ . The results of the solvent dependence of the POCH coupling constants (Table II) show that solvent has a smaller effect on the coupling constants than does temperature. This is reasonable since there should be little difference in the dipole moments of A and B. The fact that  $J_{\text{POCH}_2}$  increases with increasing dielectric constants of the solvent indicates that conformer A has the larger dipole moment.<sup>30</sup> Both the temperature and

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(29) E. Eliel, “Stereochemistry of Carbon Compounds,” McGraw-Hill, New York, N. Y., 1962.

solvent dependence of the nmr parameters of I are consistent with a rapid equilibrium between two or more conformations of the five-membered ring and with conformers like 3A being more populated than those like 3B.

The POCH coupling constants observed for the syn isomer of methyl styrene phosphite (IV) are similar to those observed in I. However, an added advantage of IV is that vicinal proton-proton couplings can be observed in IV along with the phosphorus-proton couplings for information concerning the conformation of the five-membered ring. Considering the two twist-envelope conformations of IV (Scheme II), in A the POCH dihedral angles are  $\sim 90^\circ$ ,  $\sim 170^\circ$ , and  $\sim 90^\circ$ , respectively, for protons 1, 2, and 3 while the angles in B are  $\sim 170^\circ$ ,  $\sim 90^\circ$ , and  $\sim 170^\circ$ . In view of the differences in the POCH coupling constants observed in IV, it appears that conformer A is more populated than B. Furthermore, the increase in  $J_{24}$  and the decrease in  $J_{34}$  with decreasing temperature indicate that A is the lower energy conformation. The vicinal proton-proton coupling constants also support this view. The gauche coupling  $J_{23}$  is essentially constant over the temperature range while the trans coupling  $J_{13}$  increases with decreasing temperature. The  $H_2CCH_3$  dihedral angles are identical in IVA and B and, hence, no change in  $J_{23}$  is expected with temperature, as is observed. Since the  $H_1CCH_3$  dihedral angles are  $180^\circ$  and  $60^\circ$ , respectively, for IVA and B, the large value of  $J_{13}$  and its increase with decreasing temperature indicate that conformation A is lower in energy and more populated than B.<sup>30</sup> By using the equations of Haake, *et al.*,<sup>15</sup> with the proton-proton coupling constants of IV, a value of  $34^\circ$  is calculated for the twist in the five-membered ring.

That IVA is more populated and lower in energy than IVB is not surprising in view of the isomer ratios ( $\sim 2:1$  for anti to syn) found by Denney, *et al.*,<sup>17</sup> for some five-membered ring phosphites. In each case reported, the anti isomer was more abundant than the syn isomer. Clearly, the major difference in the two isomers is the steric interactions between groups on carbon and the group on phosphorus in the syn isomer. In conformer IVA the phenyl group is directed as far away as possible from the group on phosphorus whereas in IVB the phenyl group is as close as possible to the group on phosphorus. Therefore, it seems reasonable that IVA should be lower in energy and more populated than IVB.

A somewhat different situation exists for the anti isomer of methyl styrene phosphite (III) in that both the phosphorus-proton and proton-proton coupling constants are more similar to those observed for ethylene phosphites<sup>14,15</sup> than for the isobutylene phosphites.<sup>16</sup> Dihedral angles for the POCH fragments in III  $\sim 90^\circ$ ,  $\sim 170^\circ$ , and  $\sim 170^\circ$ , respectively, for protons 1, 2, and 3 in IIIA and  $\sim 170^\circ$ ,  $\sim 90^\circ$ , and  $\sim 90^\circ$  for IIIB. For the POCH coupling constants, an increase is observed for  $J_{14}$ , a decrease is observed for  $J_{24}$ , and  $J_{34}$  remains essentially constant with a decrease in temperature. This observation seems to indicate that IIIB is the lower energy conformation although the results are not entirely consistent. If IIIB were the lower energy conforma-

tion, then one should observe a decrease in  $J_{13}$  similar to that observed for  $J_{23}$  with decreasing temperature.<sup>30</sup>

The dihedral angles given above for III are based on a twist in the five-membered ring of approximately  $30^\circ$  according to the suggestion of Haake, *et al.*<sup>15</sup> If this were the case for III, then approximately identical POCH couplings should be observed for protons 2 and 3 since their POCH dihedral angles are equal. Furthermore, for the vicinal proton-proton couplings,  $J_{23}$  should be larger than  $J_{13}$  if IIIB is populated to any extent. Clearly the results for III are not consistent with either of these expectations. The results are consistent, however, with a smaller energy barrier to pseudorotation around the five-membered ring due to the absence of the steric interactions which are present in I, II, and IV.

The data for isobutylene phenylphosphonate (II) are similar to those observed for I with a few exceptions. By applying arguments similar to those used for I, the variable temperature data (Table III) indicate that IIA (Scheme II) is the lower energy conformer and is populated to a greater extent than is IIB. In this case both POCH coupling constants change with temperature (in the opposite direction) with  $J_{13}$  exhibiting a much larger change compared to  $J_{12}$ . The solvent dependence data (Table IV) show that the POCH coupling constants of II are more sensitive to solvent than are those of I. Again the two coupling constants,  $J_{13}$  and  $J_{23}$ , change in opposite directions with a change in dielectric constant of the solvent. In the hydrogen bonding solvents, chloroform and dichloromethane, deviations to the trends in the coupling constants with dielectric constant are observed. This is probably a result of specific solvent-solute interactions, possible hydrogen bonding with the phosphoryl oxygen. Considering the direction of change of the POCH coupling constants with dielectric constant, it appears that IIA is the more polar conformer.<sup>30</sup>

The data from this investigation clearly show that some five-membered ring phosphites and phosphonates have a preferred conformation in solution. Based on the coupling constants observed in these systems, there appears to be two different preferred average conformations of the ring which depends upon the substituents attached to the ring carbons. Thus in molecules containing groups syn to the substituent on phosphorus (I, II, and IV), both the proton-phosphorus and pro-

Table VI.  $J_{POCH}$  for Some Five-Membered Ring Phosphites

	$J_{15}$	$J_{25}$
$R_1, R_2, R_3, R_4 = H$	2	9
$R_1, R_2, R_3 = H; R_4 = CH_3$	2	8
$R_1, R_2, R_3 = H; R_4 = C_6H_5$	3.0	7.5
$R_1, R_2, R_4 = H; R_3 = C_6H_5$	0.3	14.3
$R_1, R_2 = H; R_3, R_4 = CH_3$	0.3	13-14
$R_1, R_3 = H; R_2, R_4 = CH_3$	2	
$R_2, R_4 = H; R_1, R_3 = CH_3$		9
$R_1, R_4 = H; R_2, R_3 = CH_3$	4.2	0
$R_1, R_3 = 4; R_2, R_4 = C_6H_5$	2.0	

(30) R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 471 (1966).

ton-proton coupling constants suggest that the five-membered ring exists in a twist-envelope conformation with an OCCO dihedral angle of  $\sim 30^\circ$  and that the preferred conformation is the one in which the group on carbon and the group on phosphorus are as far apart as possible. Calculations<sup>31</sup> based on equations similar to that given in ref 30 indicate that the populations of conformers like A in I and IV are 87 and 90%, respectively. In molecules with groups anti to the substituent on phosphorus (III and the propylene phosphites), the phosphorus-proton and proton-proton coupling constants suggest that the energy difference between the various conformers resulting from pseudorotation of five-membered ring is much smaller than in the anti isomers and the preference for one conformation is not

(31) Values of POCH coupling constants at dihedral angles of  $170^\circ$  and  $90^\circ$  were taken to be 16.0 and 0.5 Hz, respectively.<sup>10</sup> If values other than these are used, slightly different values of  $p$  will be obtained.

as large as in the case of the anti isomers. This allows a consistent explanation for all nmr data on five-membered ring phosphites (Table IV). In each case where there is a group syn to the group on phosphorus, the data are consistent with the twist-envelope conformation with a preference for conformations like 3A whereas the data for the examples with groups anti to the group on phosphorus are consistent with a more equal population of conformers like 3A and 3B. Not only does this allow a consistent explanation for all the five-membered phosphites, but this is also consistent with the recent data for six-membered ring phosphites,<sup>9</sup> 1,3-dioxalanes,<sup>32</sup> 1,3-oxathiolanes,<sup>33</sup> and ethylene sulfites.<sup>15</sup>

(32) W. E. Willy, G. Binsch, and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 5394 (1970), and references therein.

(33) G. E. Wilson, Jr., M. G. Huang, and F. A. Bovey, *ibid.*, **92**, 5907 (1970).

## Stereochemistry of Asymmetric Silicon. XXI. Optical Rotary Dispersion and Circular Dichroism of Asymmetric Disilanes $\text{Ph}_3\text{SiSi}^*\text{X}(\text{Ph})(\text{Me})$ and a Case of Aberrant Cotton Effect Behavior<sup>1,2</sup>

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**Abstract:** Ultraviolet (uv), optical rotatory dispersion (ORD), and circular dichroism (CD) spectra are reported for eight optically active  $\text{Ph}_3\text{SiSi}^*\text{X}(\text{Ph})(\text{Me})$  compounds in which X = H, F, OH,  $\text{OCH}_3$ , Cl, Br, and (-)-OMen. The uv spectrum of each of these compounds displays a primary absorption maximum in the wavelength range 236–242 nm which is attributable to the chromophoric Ph-Si-Si grouping. The corresponding ORD and CD spectra give sizable Cotton effects in the vicinity of this absorption maximum and are considered to be closely associated with it. These interesting Cotton effects are discussed with respect to the assigned relative configurations of the compounds. This reveals that one of the compounds (X = H) displays striking aberrant Cotton effect sign behavior relative to the collective and internally consistent Cotton effect sign behavior of all of the other compounds. This aberration provides a clear example of the extraordinary sensitivity of ORD and CD spectra to subtle structural changes and advises only circumspect use of such spectra for configurational assignments of  $\text{Ph}_3\text{SiSi}^*\text{X}(\text{Ph})(\text{Me})$  and similar structures.

A previous paper<sup>3</sup> in this series reported the preparation of a family of optically active 1,2,2,2-tetra-phenyl-1-methyldisilanes,  $\text{Ph}_3\text{SiSi}^*\text{X}(\text{Ph})(\text{Me})$ , which permitted study of the dynamic stereochemistry of a silicon center bonded to a second silicon atom.<sup>3</sup> For optically active  $\text{Ph}_3\text{SiSi}^*\text{X}(\text{Ph})(\text{Me})$  structures in which X = H, F, OH,  $\text{OCH}_3$ , Cl, Br, and (-)-OMen, firm assignments of relative configuration were achieved<sup>3</sup> by means of stereochemical principles and reasoning based on the known stereochemical behavior of monosilicon centers.<sup>4</sup> These studies revealed that for a wide variety of substitution reactions the dynamic stereochem-

istry of the asymmetric disilicon center is identical with that of monosilicon centers.

Concurrent with our interest in the stereochemistry of disilanes, there has developed an interest on the part of other investigators in the electronic nature of the silicon-silicon bond.<sup>5</sup> Work on compounds containing silicon-silicon bonds has led to the conclusion that such bonds have conjugating properties and are capable of giving absorption in the ultraviolet.<sup>5</sup> In the case of phenyl-substituted disilanes, Hague and Prince<sup>6</sup> were able to show that the Ph-Si-Si grouping is responsible for the intense uv absorption of such compounds near 245 nm. Simple Hückel MO treatment of the uv absorption spectra of phenyl- and vinyl-substituted polysilanes indicates that the data can best be accommodated

(1) For the preceding paper in this series, see L. H. Sommer, L. Arlie Ulland, and G. A. Parker, *J. Amer. Chem. Soc.*, **94**, 3469 (1972).

(2) We are grateful to the National Science Foundation for support of this work.

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