until the last traces of ammonia were removed. The residue was dissolved in 100 ml of water; the pH was adjusted to pH 5 with acetic acid, and the solution was put on a column of Dowex 50 (H^+) 100–200 mesh (previously washed free of ultraviolet-absorbing contaminants). The column was washed with water until the washings were free of absorbing material, then the product was eluted with 1 *N* ammonium hydroxide. The combined fractions were evaporated rapidly under high vacuum with a bath temperature <40°, and the residual syrup was reconcentrated with ethanol until a white glass resulted. The glass was dissolved in hot ethanol which on cooling deposited a crystalline product, 1.0 g, mp 195–197°, $[\alpha]^{25}\text{D}$ −62° (*c* 2.73, water). A mixture melting point with **12** gave 174–185°; ultraviolet absorption in water: maxima at 213 and 291 mμ (ε 11,300 and 12,280, respectively), minimum at 247 mμ (ε 1315).

Anal. Calcd for $C_9H_{12}FN_3O_4$: C, 44.08; H, 4.93; N, 17.14; F, 7.75. Found: C, 44.09; H, 4.94; N, 17.14; F, 7.72.

The synthesis of **13** by another route has been reported.[39] The product has a reported mp 186–187° and $[\alpha]^{25}\text{D}$ −92°. A private communication from one of the authors has corrected their rotation value to −59°.

1-(Tri-*O*-acetyl-α-D-arabinofuranosyl)-5-fluorouracil. (Tri-*O*-acetyl-19). A solution of 500 mg of 1-α-D-arabinofuranosyl-5-fluorocytosine (**17**) in 25 ml of 1 *N* NaOH was heated 30 min at 120°. The solution was cooled to room temperature and passed through a column of 15 g of Dowex 50 (H^+) resin. The resulting solution was evaporated under vacuum to about 5 ml, decolorized with Norit, filtered through a pad of Celite, and evaporated under vacuum to yield 386 mg of **19** (77%) as an amber syrup, λ_{max} 265 mμ in ethanol.

The syrup did not crystallize and was acetylated with 1.0 ml of acetic anhydride (10.6 mequiv) in 2.5 ml of pyridine. The mixture was heated (bath temperature = 130°) until the syrup was dissolved and then placed in the refrigerator for 22 hr. Water (5 ml) was added, and after 0.5 hr the solution was evaporated to dryness to yield an amber syrup. Tlc showed a slight impurity was present. The syrup was placed on a column of silica gel G (1 × 21 mm) and eluted with 5% methanol–chloroform. Fractions (2 ml) were collected and fractions 2–11 gave, upon evaporation of solvents, a slightly yellow syrup (138 mg, 25%) of the tri-*O*-acetyl derivative of **19**. Tlc (silica gel GF_{254}) in 5% MeOH–$CHCl_3$ showed one spot, R_f 0.61; in 5% MeOH–benzene (three times) one spot showed, R_f 0.25. The spots were developed using uv and a 10% H_2SO_4 spray. The tlc and uv data for tri-*O*-acetyl **19** were identical with that for tri-*O*-acetyl **18**, the β anomer of **19**.

Anal. Calcd for $C_{15}H_{17}FN_2O_9$: C, 46.40; H, 4.42. Found: C, 46.69; H, 4.62.

Acknowledgment. The authors are indebted to Mr. M. J. Olsen for determining the pmr spectra and Dr. L. D. Hall, University of British Columbia, for determining the ^{19}F spectra, and to Dr. K. A. Watanabe for helpful discussions. The authors should like to thank the following for their generous supply of compounds: Dr. T. Y. Shen, Merck and Co., **10**; and from Hoffmann-La Roche (Nutley, N. J.): Dr. A. Nussbaum, **39**; Mr. T. Gabriel, 2,4-dimethoxy-5-fluorouracil; and Dr. M. Hoffer, **17** and 1-(2′-deoxy-3′,5′-di-*O*-*p*-toluyl-α-D-ribofuranosyl)-5-fluorouracil.

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Proton Magnetic Resonance Spectra of Ethylene Phosphites and Ethylene Sulfite[1]

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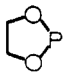
Contribution No. 2144 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received May 20, 1967*

Abstract: Complete analyses of proton magnetic resonance spectra are reported for three ethylene phosphites and for ethylene sulfite neat, in benzene, and in chloroform. The vicinal H–C–C–H and P–O–C–H coupling constants indicate that the ethylene phosphites appear to prefer twist–envelope conformations. This result may be generally applicable to the conformation of five-membered rings.

Our interest in the chemistry presented in this paper was aroused by the unusual properties of 1,3,2-dioxaphospholane rings (**1**). Ethylene phosphates[4] (**2**), intermediates in the alkaline hydrolysis of ribonucleic acid,[5] have been shown to undergo very rapid hydrolysis relative to their acyclic analogs.[6] These results prompted structural analysis studies of the cyclic phosphates: methyl ethylene phosphate[7] and methyl pinacol phosphate.[8]



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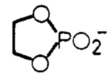

2

Complex pmr spectra have been obtained for compounds related to **1**, including phosphites (**3**),[9,10] sulfites (**4**),[11] and dioxolanes (**5**).[12] The spectra

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[2] Alfred P. Sloan Research Fellow, 1964–1967.

[3] National Science Foundation Undergraduate Research Participant.

[4] Although Ring Index nomenclature has been employed for these cyclic compounds, we believe that they are best named as derivatives of the appropriate phosphorus acids. The fact that the acid form of 2 is a cyclic ester of phosphoric acid is not readily apparent from the Ring Index name, 2-hydroxy-2-oxo-1,3,2-dioxaphospholane, and 2 is not readily and clearly named as an anion. The same argument holds for other compounds considered in this paper.

[5] H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," John Wiley and Sons, Inc., New York, N. Y., 1961.

[6] J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956); P. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

[7] D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965); T. A. Steitz and W. N. Lipscomb, *ibid.*, **87**, 2488 (1965).

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[9] (a) H. Goldwhite, *Chem. Ind.* (London), 494 (1964); (b) B. Fontal and H. Goldwhite, *Tetrahedron*, 22, 3275 (1966).

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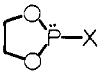
indicate pyramidal sulfur and phosphorus atoms, but to our knowledge the spectra of the sulfites and phosphites unsubstituted at carbon have not been analyzed by computer methods. The phosphite spectra are of particular interest since there should be two P-O-C-H coupling constants, which should give considerable information about the preferred conformations in **3** and indirectly about five-membered rings in general.



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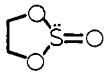

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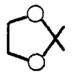


5

Experimental Section

Preparation of Materials. Ethylene Sulfite (Glycol Sulfite). A commercial sample of ethylene sulfite was obtained from Aldrich Chemical Company.

Ethylene chlorophosphite was prepared according to the method of Lucas, *et al.*[13] Improved yields are obtained by conducting distillation at moderate temperatures (70–90°, pot temperature). Redistillation of crude material through a Teflon spinning-band column resulted in pure ethylene chlorophosphite, bp 49.5° (20 mm) (lit. 45.5–47° (15 mm),[13] 41.5° (10 mm),[14] 65–66° (42 mm)[15]). For this work, degassed fractions were sealed in ampoules immediately following distillation and stored at 5°. Aliquots were removed when needed. Infrared spectrum (neat film) included a P–O band at 1005 cm^{-1}.

Methyl ethylene phosphite was prepared by a modification of the procedures reported by Arbuzov.[14] A 500-ml, three-necked flask was fitted with two pressure-equalizing addition funnels, mechanical stirrer, and calcium chloride drying tube. Dry hexane (200 cc) was added, followed by 38.4 g (0.3035 mole) of ethylene chlorophosphite. This solution was stirred and cooled with an ice bath. Triethylamine (0.41 mole distilled from acetic anhydride and then from KOH under N_2) was added from a dropping funnel; a thick white precipitate formed. Dry, freshly distilled (from Mg turnings) methanol (0.30 mole) was dissolved in 12 cc of dry hexane and added very slowly from a dropping funnel to the thick white precipitate. About 50 cc more hexane was added to increase mobility of the suspension, and the thick white mixture was stirred overnight at room temperature. Following filtration, the filtrate was distilled under water vacuum pressure on the steam bath to remove hexane. The residue contained impure methyl ethylene phosphite as indicated by nmr spectra. Attempts at slow and careful distillation apparently caused decomposition; however, simple distillation through a micro Claisen head yielded a small forerun followed by methyl ethylene phosphite, bp 44° (16 mm) (pot temperature 130°) (lit. 60–62° (35 mm),[13] 55–56° (23 mm)[14]). Integration of methyl and ethylene peaks in the ratio 3:4 in the nmr spectrum confirmed the identity. Degassed fractions were sealed in ampoules immediately following distillation and stored at 5°. The infrared spectrum of a neat film gives two bands in the P–O stretching region: 1035 and 1000 cm^{-1}.

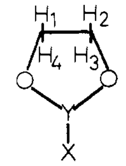
Phenyl ethylene phosphite was prepared by the method described by Ayres and Rydon.[16] Attempted careful purification on a Teflon spinning-band column resulted in continuous distillation of phenol. A fast distillation through a small Claisen head gave pure phenyl ethylene phosphite, bp 67° (0.3 mm) (lit. 70–76° (0.2 mm),[16] 75° (0.5 mm)[17]). No trace of ethylene phosphite or of phenol was observed. Degassed fractions were sealed in ampoules immediately following distillation and were stored at 5°. The infrared spectrum of a neat film shows two bands in the P–O stretching region: 1064 and 1005 cm^{-1}.

Spectra. The pmr spectra were measured at 60 Mc (Varian A-60) and at 100 Mc (Varian HA-100) with sweep rates of 0.1 to 0.4 cps/sec. Variable-temperature studies were performed on a Varian A-60 equipped with a variable-temperature probe. Except where noted that neat solutions were employed, 5–20% solutions of compounds in appropriate solvents were prepared, degassed, and sealed under vacuum. Spectra were calibrated relative to an internal standard of tetramethylsilane. Line positions were obtained by averaging the results of three or more spectra. Infrared spectra were taken on Perkin-Elmer Infracord and Model 221 instruments.

Spectral Analysis. Ethylene sulfite was treated as an AA'BB' system. Ethylene phosphites were treated as AA'BB'X systems. All spectra were analyzed using described procedures[18] with the aid of an iterative least-squares computer program, LAOCOON II.[19] Observed frequency transitions were correlated with line values calculated from specific parameters; iterations were performed to give the best fit. Tables of calculated and observed line positions are available from the authors on request.

Results

Numbering of the ring protons corresponds to[18]



1,2 = A protons; 3,4 = B protons

$\delta_A > \delta_B$

6, Y = S; X = O
7, Y = P; X = OCH_3
8, Y = P; X = OC_6H_5
9, Y = P; X = Cl

Ethylene Sulfite. Chemical shifts and coupling constants for ethylene sulfite (**6**) are given in Table I, together with root mean square errors for these parameters; neat preparations and 20% solutions in chloroform and benzene are reported. Chemical shifts in a nonpolar hydrocarbon solvent, *cis*-decalin, are intermediate between chloroform and benzene; the spectrum in this solvent has not been completely analyzed. The shift to higher field in benzene is expected, due to diamagnetic anisotropic effects.[20] The shift to lower field in chloroform may reflect the formation of intermolecular hydrogen bonds between the solvent and three oxygens and/or the sulfur atom in the molecule.[18a]

The final calculated spectra agree very closely with the observed spectra. Maximum line errors were less than ±0.08 cps.

The pmr spectrum of **6** in *cis*-decalin was examined at various temperatures up to 190°. No significant changes in the multiplicity of the spectrum were observed, indicating that there is no observable low-temperature exchange process for ethylene sulfite such as inversion at sulfur.[21]

The closeness of $J_{1,2}$ and $J_{3,4}$ in benzene and chloroform indicates that $J_{1,2} = J_{3,4}$ is a reasonable assump-

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[19] Program originally written by S. Castellano and A. A. Bothner-By. A description of the program can be found: *J. Chem. Phys.*, **42**, 3863 (1964). The program used in this work included modifications by Drs. M. Maddox and J. Sudmeier.

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Table I. Summary of Coupling Constants and Chemical Shifts

		Chemical shift[a]			Coupling constants, cps					
Compound	Solvent	Proton A	Proton B	Root mean square error	$J_{1,2}$	$J_{3,4}$	$J_{1,3} = J_{2,4}$	$J_{1,4} = J_{2,3}$	$J_{1,5} = J_{2,5}$	$J_{3,5} = J_{4,5}$
Ethylene sulfite (**6**)	Neat	275.63	258.60	0.040	6.93	6.93	6.66	−8.59		
	Benzene[b]	247.34	217.39	0.040	6.89	6.84	6.67	−8.40		
	Chloroform[b]	280.40	260.02	0.040	7.16	6.95	6.70	−8.57		
Ethylene chlorophosphite (**9**)	Benzene[c,e]	226.20	202.98	0.070	8.11	8.11	6.96	−8.79	1.62	10.0
Methyl ethylene phosphite (**7**)	Benzene[c,e]	219.38	204.34	0.072	7.08	7.08	6.59	−8.44	1.87	8.97
Phenyl ethylene phosphite (**8**)	Cyclohexane[d,e]	241.07	230.93	0.077	7.78	7.78	6.01	−8.20	1.53	9.11

[a] Cycles downfield from tetramethylsilane; 60-Mc spectrum. [b] 20% solution. [c] 10% solution. [d] 5% solution. [e] $J_{1,2}$ assumed equal to $J_{3,4}$.

tion in the other analyses although not demanded by symmetry.

Calibrated infrared spectra of ethylene sulfite exhibited S=O stretching as follows in the indicated solvents: 1193 cm^{-1} (neat), 1198 cm^{-1} (CH_3CN), 1203 cm^{-1} (CS_2), 1205 cm^{-1} (CCl_4), 1210 cm^{-1} (benzene), 1214 cm^{-1} (cyclohexane).

Methyl Ethylene Phosphite. Chemical shifts and coupling constants for **7** in benzene are given in Table I. These parameters yield the calculated line frequencies which are compared with the observed in Figure 1. The average line error was 0.072 cps. No change in spectrum was observed at temperatures up to 190°.

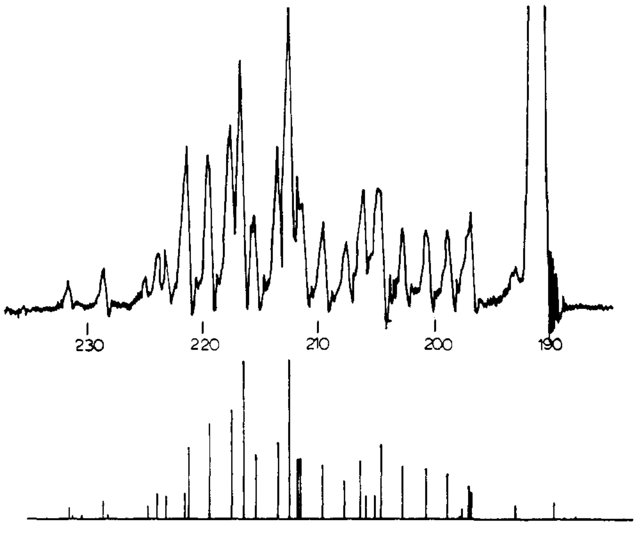


Figure 1. Pmr spectrum of methyl ethylene phosphite. Upper: observed spectrum in benzene at 60 Mc; numbers represent cps downfield from TMS (internal standard); methyl resonance appears around 192 cps and obscures the most upfield part of the ethylene resonance. Lower: line spectrum calculated from parameters in Table I.

The splitting of the methyl resonance by phosphorus is 10.5 ± 0.2 cps. Spectra were run in both benzene and cyclohexane. As noted with ethylene sulfite, spectra in benzene have somewhat larger chemical shifts than those determined in hydrocarbon solvents, making peaks easier to identify. However, in the benzene spectrum, a small part of the *upfield* part of the ethylene spectrum falls under one of the methyl peaks as can be seen in Figure 1.

Phenyl Ethylene Phosphite. Magnetic parameters for **8** in cyclohexane are given in Table I; Figure 2 presents the observed spectrum and calculated line values. The average line error was 0.07 cps. Heating a sealed nmr tube containing 3% phenyl ethylene phosphite in cyclohexane at temperatures up to 100° produced no major change in the spectrum. Therefore, the rather broad bands in this spectrum cannot be due to slow inversion at room temperature.

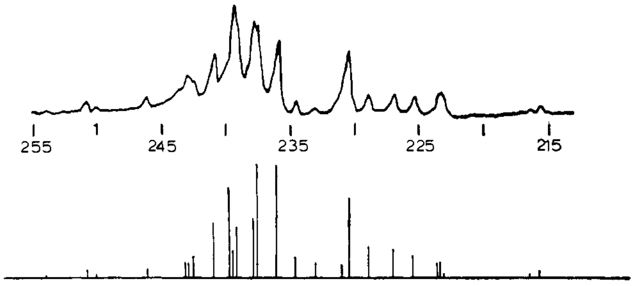


Figure 2. Pmr spectrum of phenyl ethylene phosphite. Upper: observed spectrum in cyclohexane at 60 Mc; numbers represent cps downfield from TMS (internal standard). Lower: line spectrum calculated from parameters listed in Table I.

The change in chemical shift toward higher field relative to **7** and **9** is probably an anisotropic effect due to the phenyl substituent.[20]

Ethylene Chlorophosphite. Coupling constants and chemical shifts for **9** (10% in benzene) are given in Table I. The average line error is 0.047 cps. The observed spectrum and calculated line positions are displayed in Figure 3.

The nmr spectrum of a neat sample of ethylene chlorophosphite is a singlet at room temperature. This peak broadens and splits into two peaks if the temperature is lowered. Dilution with an inert solvent produced a complex spectrum, similar to those found for **6**, **7**, and **8**. Fontal and Goldwhite[9b] report similar observations on the tetramethyl derivative of **9**. They conclude that there is a chloro-exchange process resulting in inversion at phosphorus.[22]

(22) Independent analyses of the spectra of some ethylene phosphites have been published in an article called to the authors' attention after completion and submission of this manuscript: D. Gagnaire, J.-B. Robert, J. Verrier, and R. Wolf, *Bull. Soc. Chim. France*, 3719 (1966). Their results are in reasonable agreement with Table I; we observed a spectrum similar to theirs for neat ethylene chlorophosphite, but in benzene (Figure 3) the line separation is better.

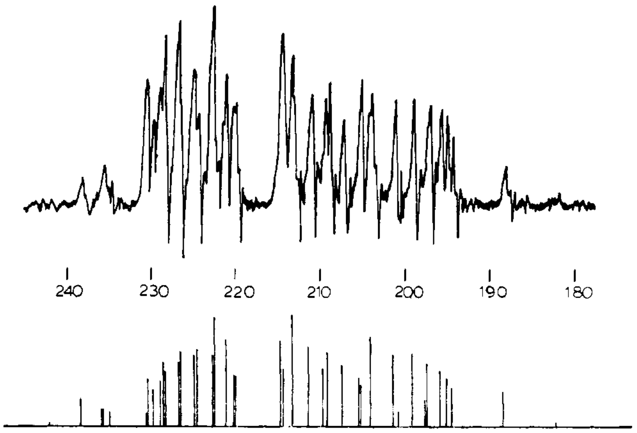
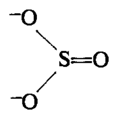


Figure 3. Pmr spectrum of ethylene chlorophosphite. Upper: observed spectrum in benzene at 60 Mc. Numbers represent cps downfield from TMS (internal standard). Lower: line spectrum calculated from parameters listed in Table I.

Discussion

The geminal coupling constants we have found agree with the one reported for isobutylene sulfite: ±8.5 cps.[11] All the H-H coupling constants are in the range found in 1,3-dioxolanes.[23,24] Abraham's[24] approximated parameters for ethylene sulfite agree well with our computer-calculated results.

Structure of Ethylene Sulfite. Pritchard and Lauterbur[11] assumed a planar ethylene sulfite ring and then assigned H_A (Table I) to the protons *cis* to the S=O bond. However, the dipole moment of **6** has been explained[25] by an envelope conformation with the S atom above the plane of the ring. A calculation assuming an envelope conformation resulted in the assignment of H_A to the protons *trans* to the S=O bond.[26] Recently, the S=O bond anisotropy has been considered to be like that of a C≡C bond.[27] This gives a good explanation of chemical shifts in some six-membered ring sulfoxides.[27] A reliable prediction of chemical shifts in ethylene sulfite would require knowledge of conformational equilibria and the nature of bonding and anisotropy in sulfites. Half-chair as well as envelope conformations may contribute to the structure, and the entire



system should be included in calculations of anisotropy effects.

In trimethylene sulfites, the sulfite oxygen prefers to be axial.[28] The same conformational preference is found in six-membered ring sulfoxides.[27,29] Assignment of axial and equatorial sulfite oxygens has been made[28] on the basis of the position of the S=O stretching band in trimethylene sulfites: 1190 cm^{-1} for an axial oxygen and 1230 cm^{-1} for an equatorial oxygen. If this can be extended to ethylene sulfite, and assuming an equilibrium between pseudo-axial and pseudo-equatorial conformers (*e.g.*, the oversimplified **10** ⇌ **11**), the position of the S=O stretching band, 1193 cm^{-1} (neat) to 1214 cm^{-1} (cyclohexane) would indicate predominance of pseudo-axial conformers (*e.g.*, **11**), especially if one includes a correction from five- to six-membered rings (about 25 cm^{-1} for carbonyl groups). The position of the S=O bond in ethylene sulfite is considerably more dependent on solvent than in trimethylene sulfite.[30] This may indicate a more variable conformational equilibrium in the five-membered ring.

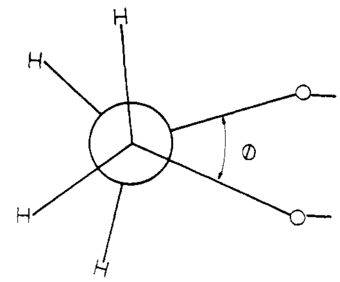
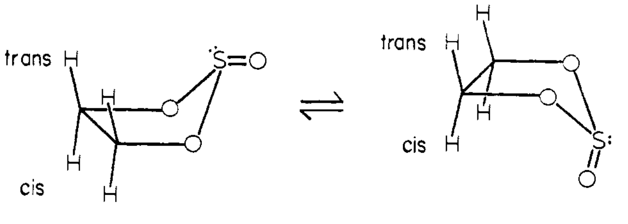


Figure 4. A Newman projection down the C–C bond of 1,3-dioxolanes.



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Geminal Coupling Constants. There is a significant increase in the geminal coupling constants observed here compared to that for methane.[31] This increase is apparently due to a combination of: (1) widening the H–C–H angle, (2) electron withdrawal by oxygen, (3) back donation of electrons from the oxygen lone pairs.[31]

Vicinal Proton–Proton Coupling Constants. Use of the $\cos^2 \phi$ relation[32] led Lemieux, Stevens, and Fraser to conclude that 2,2-dimethyl-1,3-dioxolane (**12**) had a dihedral angle, ϕ, of 41° (Figure 4).[23c] This approach was examined more closely by Abraham and applied to 2-methyl-1,3-dioxolane (**13**) resulting in a dihedral angle of about 38°.[24] However, the $\cos^2 \phi$ approach did not fit the data exactly, leading Abraham to conclude, in agreement with Karplus,[32] that other factors must be involved.

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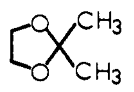

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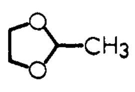

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Vicinal coupling constants have also been correlated with dihedral angle through the relation $J = A + B \cos \phi + C \cos 2\phi$.[31,32b] Our data on ethylene sulfite and on three ethylene phosphites offer the opportunity to correlate a number of vicinal hydrogen–hydrogen couplings in closely related systems. Assuming approximately normal bond angles at the carbon atoms,[33] the $A + B \cos \phi + C \cos 2\phi$ relation leads to

$$J_{cis} = A + B \cos \phi + C \cos 2\phi \tag{1}$$

$$J_{trans} = A + (B/2)[\cos (120 + \phi) + \cos (120 - \phi)] + (C/2)[\cos 2(120 + \phi) + \cos 2(120 - \phi)] \tag{2}$$

Since we have four sets of *cis* and *trans* coupling constants (eight J's), it might appear that one could solve for seven unknowns: values of A, B, and C applicable to all four compounds and a dihedral angle, ϕ, for each compound (four ϕ's). However, it can be shown that $\cos X = -[\cos (120 + X) + \cos (120 - X)]$, so that there is really only one equation for each set of J_{cis} and J_{trans}. It is therefore impossible to fit unique values of A, B, C, ϕ_1, ϕ_2, ϕ_3, and ϕ_4 to the data.

However, the $\cos^2 \phi$ relation gives reasonable correlation of experimental results using $J = k_1 \cos^2 \phi$ for $0 \leq \phi < 90°$ and $J = k_2 \cos^2 \phi$ for $90° < \phi \leq 180°$. The best correlation involves omission of the data for ethylene chlorophosphite. The equations are[34]

$$J_{cis} = k_1 \cos^2 \phi \tag{3}$$

$$J_{trans} = {}^1\!/_2[k_2 \cos^2 (120 + \phi) + k_1 \cos^2 (120 - \phi)] \tag{4}$$

Since the $\cos^2 (120 - \phi)$ term is quite small, these equations may be simplified by selecting the proper Taylor's expansion so that all terms after the first two may be neglected. This gives eq 5 and 6 with ϕ in radians. These equations are excellent approximations

$$\cos^2 \phi \cong 1.203 - 0.866\phi \tag{5}$$

$$\cos^2 (120 + \phi) \cong 0.297 + 0.866\phi \tag{6}$$

for $\phi = 30 \pm 10°$. Using J_{cis} and J_{trans} values for methyl ethylene phosphite and phenyl ethylene phosphite, and average J_{cis} and J_{trans} values for ethylene sulfite, there are six equations in five unknowns: k_1, k_2, and a ϕ for each compound. Elimination of ϕ from each set of J_{cis}, J_{trans} gives three equations in k_1 and k_2. Application of the method of least squares yields $k_1 = 9.90$ and $k_2 = 16.87$. These values then enable determination of ϕ's: methyl ethylene phosphite, 32°; phenyl ethylene phosphite, 27°; and ethylene sulfite, 33°. Table II compares calculated and observed values.

We find poor application to ethylene chlorophosphite: the best ϕ is 30° giving $J_{cis}(\text{calcd}) = 7.42$ (obsd $J = 8.1$) and $J_{trans}(\text{calcd}) = 6.33$ (obsd $J = 7.0$). Assuming that the agreement in Table II is not completely fortuitous,[32b] we conclude that there must be a factor in ethylene chlorophosphite which increases the vicinal coupling constants.[35]

Table II. Comparison of Observed Vicinal Couplings with Those Calculated by the $\cos^2 \phi$ Relation[a]

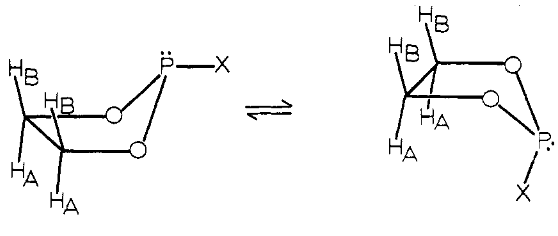
Compound	Dihedral angle ϕ, deg,	J_{cis}, cps		J_{trans}, cps	
		Obsd	Calcd	Obsd	Calcd
Methyl ethylene phosphite	32	7.1	7.12	6.6	6.58
Phenyl ethylene phosphite	27	7.8	7.86	6.0	5.97
Ethylene sulfite	33	6.95	6.96	6.68	6.70

[a] Using eq 3 and 4 and $k_1 = 9.90$, $k_2 = 16.87$.

Using eq 1 and 2, we could not, by trial and error, find a set of A, B, C, and four ϕ values which gave calculated coupling constants comparable to those found in Table II. Because of the approximate nature of eq 3 and 4,[32] we do not wish to claim that the ϕ values in Table II are exact. The reasonable conclusions are that the dihedral angle is about 30° for these compounds and that the dihedral angle in phenyl ethylene phosphite is probably smaller than in methyl ethylene phosphite or ethylene sulfite.

Vicinal Phosphorus–Proton Coupling Constants. Relatively little data are available on the dependence of P–O–C–H couplings on dihedral angle. However, Verkade's work indicates a 3:1 value for $J_{trans}:J_{gauche}$ in six-membered ring compounds.[36] In steroidal phosphonates, P–C–C–H couplings are: $J_{gauche}(60°) = 10$ cps, $J_{trans}(180°) = 35$ cps, $J(90°) \sim 2.6$ cps.[37] Therefore, the different P–O–C–H$_A$ and –H$_B$ couplings in ethylene phosphites (Table I) indicate markedly different dihedral angles in the two P–O–C–H systems. This necessitates an important contribution of the envelope conformation to the structure of ethylene phosphites. In **15**, ϕ(P–O–C–H$_B$) is near 180° and ϕ(P–O–C–H$_A$) is near 90°. Assuming that our infrared data on ethylene sulfite and the conformational data on sulfoxides and sulfites can be applied to phosphites, **15** would be the favored envelope conformation and

	$J_{gauche}(60°)$	$J_{trans}(180°)$
phosphite	2 cps	6 cps
phosphate	7 cps	20 cps



14

15

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(33) Not completely justified, of course, in view of the known strain in such rings.[7,8]

(34) Since ϕ turns out to be about 30° in these compounds, k_1 in the equation for J_{trans} must be replaced by k_2 if $\phi > 90°$.

(35) An attractive speculation would center about the chlorine atom in **9**.

(36) J. G. Verkade and R. W. King, *Inorg. Chem.*, 1, 948 (1962); J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, 3, 884 (1964); J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *ibid.*, 4, 83 (1965).

(37) C. Benezra and G. Ourisson, *Bull. Soc. Chim. France*, 1825 (1966).

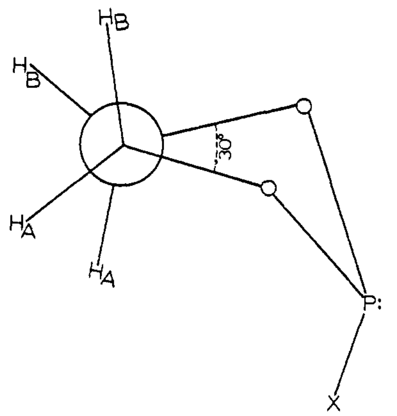

Figure 5. Twist–envelope conformation for ethylene phosphites; Newman projection down C–C bond.

we can then assign H_A (downfield, $J_{PH_A} \sim 2$ cps) as *cis* to X and H_B (upfield, $J_{PH_B} \sim 9$ cps) as *trans* to X. However, the uncertainty about the conformational size of S and P lone pairs makes this a tentative conclusion. If **14** were favored rather than **15**, the reverse assignment would be required.

Structure of Ethylene Phosphites. The vicinal hydrogen–hydrogen coupling constants are not in agreement with a simple envelope conformation (**15**). Instead, **14** and/or **15** must be twisted to yield an H–C–C–H dihedral angle of about 30°. Therefore, taking **15** to be the favored envelope form, *ethylene phosphites appear to prefer two equivalent twist–envelope forms*, one of which is approximately shown in Figure 5. A time average of other conformations yielding the same effect as H–C–C–H dihedral angles of about 30° and very different P–O–C–H dihedral angles would, of course, also satisfy the results found here. However, it seems quite reasonable that the nonbonded interactions in ethylene phosphites and ethylene sulfite should result in the twist–envelope conformation being favored.

This conformational result was obtainable because both H–C–C–H and P–O–C–H couplings could be observed. However, the twist–envelope conformation may well have applicability to other five-membered rings.

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A Kinetic Study of Double-Bond Migration in Allyloxy Polyether Alkoxides

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Abstract: The rates of rearrangement of $CH_2{=}CHCH_2(OC_3H_6)_nO^-M^+$ to *cis*-$CH_3CH{=}CH(OC_3H_6)_nO^-M^+$ have been studied kinetically at 30° in tetrahydrofuran solution. The rates are cation dependent. The Cs^+ compounds react about 60 times as fast as the K^+ compounds; the Na^+ compounds do not rearrange under the conditions used. The rates depend on the value of n, being maximum when $n = 3$ in the K^+ series and when $n = 3$ or 4 in the Cs^+ series. Chelation of cation by the polyether chain is adduced as the cause of this dependence. Addition of fluorenylpotassium or potassium dodecylbenzenesulfonate greatly reduces the rearrangement rates, suggesting that mixed ion pair aggregation is occurring in these systems.

There has been considerable interest in the last few years in elucidating the details of the mechanism of base-catalyzed double-bond migration reactions. An excellent review of the subject is given by Cram,[1] who points out many of the subtleties of the reaction, including the effects of the solvent, the type of base catalyst, and the associated cation on the course of the reaction. During our study of the base-catalyzed polymerization of propylene oxide (PO),[2] we have had the occasion to study the rates of rearrangement of a series of allyl ethers to the corresponding propenyl ethers and have found some interesting results which we would like to report here.

The polymerization of propylene oxide is ordinarily carried out at elevated temperatures using basic catalysts and mono- or polyhydroxylic compounds as initiators. Price and St. Pierre,[3] however, found that the polymerization could be accomplished at room temperature with anhydrous KOH as the catalyst and with no added hydroxylic initiators. The products of the polymerization under the latter conditions comprised mainly compounds of the type

$$CH_2{=}CHCH_2O(C_3H_6O)_nH \qquad AO(PO)_nH$$

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[1] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965.

[2] E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *J. Amer. Chem. Soc.*, **86**, 4678 (1964).

[3] L. E. St. Pierre and C. C. Price, *ibid.*, **78**, 2432 (1956).