# Conformational Studies of Acyclic Organophosphate Esters using Nuclear Magnetic Resonance Spectroscopy<sup>1</sup>

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The vicinal <sup>31</sup>P $-O-C^{-1}$ H couplings of a series of acyclic phosphate esters have been measured and rationalized in terms of varying populations of individual rotamers. Variable temperature measurements have been interpreted in terms of the enthalpy and entropy differences between *gauche* and *trans* rotational isomers.

Les couplages vicinaux <sup>31</sup>P—O—C—<sup>1</sup>H d'une série de phosphate esters acyliques ont été mesurés et rationalisés en termes de populations variables pour des rotomères donnés. Les mesures à températures variables ont été interprétées en termes de différences d'enthalpie et d'entropie entre les isomères de rotation gauche et trans.

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#### Introduction

Previous studies from this (1, 3) and other (4, 8) laboratories have recognized the potential of *vicinal*<sup>31</sup>P—O—C—<sup>1</sup>H couplings as a basis for conformational studies of organophosphate esters. Many such studies have made the *a priori* assumption that cyclic systems such as the 2-oxo-1,3,2-dioxaphosphorinanes (Scheme 1) can serve as acceptable models for acyclic phosphates (Scheme 2). The experimental data available in the literature clearly indicates that there is indeed a semi-quantitative relationship between the coupling constants of these two systems; however the data also imply that a simple quantitative relationship does not exist.

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In the present paper we review briefly the coupling constants available in the literature for derivatives of the 2-oxo-1,3,2-dioxaphosphorinane system, and compare these with data from series of specifically prepared acyclic phosphates. The couplings observed for the acyclic compounds are interpreted in terms of the populations of the gauche (A and B) and trans (C) rotational isomers, and in terms of the free energy differences between these isomers. The changes in the observed coupling with temperature for selected representatives of these compounds are studied and interpreted in terms of the enthalpy and entropy differences between the rotational isomers. Since this study was completed another group has published n.m.r.

<sup>1</sup>Part 3 of a series "Studies of Organophosphorus Derivatives". For part 2 see ref. 1.

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SCHEME 1. Conformational isomers of 2-oxo-1,3,2-dioxaphosphorinane.



SCHEME 2. Rotational isomerism in acyclic phosphates.

data for some acyclic phosphates (5); we shall discuss their work later on in this paper because we disagree with some of their interpretations.

#### **Results and Discussion**

The vicinal <sup>31</sup>P—O—C—<sup>1</sup>H coupling data for three series of acyclic phosphotriester derivatives are shown in Table 1. The monotonic decrease in these values with increasing size of the alkyl group R is attributed to an increasing population of the rotational isomer having the R group *trans* to the phosphate moiety (as in C, Scheme 2).

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	Compound									
-	$K = CH_2 U = P = (UPh)_2$	$(R - CH_2 O)_2 - P - OPh$	$(R - CH_2O)_3 - P = O$							
R	Set 1	Set 2	Set 3							
Н	11.5	11.3	11.0							
Me	8.7	8.4	8.1							
Et	7.8	7.6	7.4							
iso-Pr	6.6	6.5	6.4							
tert-Bu	5.1	5.0	4.85							

TABLE 1. Observed couplings (Hz) for acyclic phosphate rotamers

TABLE 2. <sup>31</sup>P—O—C—<sup>1</sup>H couplings (Hz) and percentage time-averaging in 2-oxo-1,3,2-dioxaphosphorinane systems

F

R4	~
4	
R1	.0~pi
	ÓR

Compound					Experimental values			Calculat	ed values	97.41.4		Ď - C	
No.	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Jg	$J_{i}$	J <sub>sum</sub>	$J_{g}$ real	$J_{g}$ real $J_{t}$ real averaging $\Delta G$ (ca	$\Delta G$ (cal)	) ence	
1	Ph	Н	н	Ph	Н	1.4	22.8	24.2	1.4	22.8	0.0		*
2	Ph	Н	Н	н	Н	2.8	21.3	24.1	1.35	22.7	6.9	1570	1.2
3	Ph	н	Н	CH <sub>3</sub>	CH <sub>1</sub>	1.7	22.5	24.2	1.38	22.8	1.4	3945	1, 2
4	Ph	н	н	Н	Ph	3.8	20.2	24.0	1.4	22.6	11.7	1215	*
5	Н	н	н	CH <sub>1</sub>	CH <sub>2</sub>	12.0	12.0	24.0	1.4	22.6	50.0	0.0	4h
6	н	н	н	н	Ph	5.6	17.9	23.5	1.3	22.2	21.3	787	*
7	К	н	Ph	н	н	1.9	22.3	24.2	1.36	22.9	2.3	2240	4 <i>d</i>
8	CH3	Н	Н	Bu <sup>t</sup>	н	1.2	22.8	24.0	1.2	22.8	-0.5	œ	10

\*Private communication. J. Campbell of this laboratory.

In order to place these observations on a quantitative basis it is necessary to know the magnitudes of the couplings corresponding to dihedral angles between the P—O and C—H bonds, of 180 and 60° ( $J_{180^\circ}$  and  $J_{60^\circ}$ , respectively). These two values, or an estimate thereof, may be obtained from the *vicinal* <sup>31</sup>P—O—C—<sup>1</sup>H couplings of derivatives of the 2-oxo-1,3,2-dioxaphosphorinane system; a summary of the data available in the literature for such derivatives is given in Table 2.

It is evident that although there is a considerable spread in the values for  $J_{trans}(J_1)$  and  $J_{gauche}(J_g)$ , the sum of the couplings is nearly constant. This suggests that the variations in the observed values are due to averaging of the couplings arising from varying populations of the different conformations of the phosphorinane ring. Assuming that only chair conformations are involved, a conformational inversion process will cause the observed *trans* coupling value,  $J_t$  (obs), to be lower than the true value  $J_t$  (real) and the observed *gauche* coupling value,  $J_g$  (obs), to be larger than the true value  $J_g$  (real).

These values are related to the extent of population time averaging by the expressions

$$\alpha J_t$$
 (real) +  $(1 - \alpha) J_s$  (real) =  $J_t$  (obs)

 $\alpha J_{g}$  (real) +  $(1 - \alpha)J_{t}$  (real) =  $J_{g}$  (obs)

where  $\alpha$  is the population of one conformer and  $(1 - \alpha)$  the population of the other. This process would however leave the sum of the two observed couplings unchanged.

We believe that compound 1 undergoes only a very small amount of conformational inversion because it contains both the axial electronegative substituent on the phosphorous atom (such a substituent favours an axial configuration, with a  $\Delta G$  of *ca*. 1500 cal (compound 2, Table 2;

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see also X-ray data ref. 6) and the equatorial substituent on C-5. Hence the experimental values of  $J_t$  22.8 and  $J_g$  1.4 Hz from this compound approximate  $J_t$  (real) and  $J_g$  (real).<sup>3</sup> These values in conjunction with the observed couplings can therefore be used to calculate the extent of time-averaging  $(100 - \alpha)$  and hence the free energy difference ( $\Delta G$ ) between the two conformers: all of these data are listed in Table 2.

Using the percentage time-averaging we have approximated what the couplings would be for these compounds if no time-averaging were to occur. These calculated, non time-averaged couplings are seen to differ from those for compound 1 only in so far as their  $J_{sum}$  values differ; and thus support our premise that <sup>31</sup>P—O—C— <sup>1</sup>H couplings in 2-oxo-1,3,2-dioxaphosphorinanes are largely independent of the ring substituents, but vary mainly as a function of conformational time-averaging.

It now remains to take these values of  $J_t$  (real) and  $J_g$  (real) and relate them to the required couplings  $J_{180^\circ}$  and  $J_{60^\circ}$ .

X-Ray studies on compound 1 (6) have shown that the P—O—C<sub>6</sub>—C<sub>5</sub> and P—O—C<sub>4</sub>—C<sub>5</sub> dihedral angles are 54° rather than the 60° that would occur for an "ideal" cyclohexane geometry. Assuming that C-6 and -4 are tetrahedral centers, the P—O—C—H dihedral angles become  $120^\circ - 54^\circ = 66^\circ$  for the axial proton and  $120^\circ + 54^\circ = 174^\circ$  for the equatorial proton (Scheme 3).

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It is well established that the  $\cos^2 \phi$  relationship between the magnitude of the vicinal



SCHEME 3. P—O—C—H dihedral angles in 2-oxo-1,3,2dioxaphosphorinane.

<sup>3</sup>Compound 8 in Table 2 of Bentrude and Hargis (10) has slightly more extreme couplings, however we calculate that compound 8 time averages to an extent only 0.5% less than compound 3 and it may therefore be taken as good supporting evidence for our choice of  $J_t$  and  $J_g$ . 
$$J_{180^\circ} = J_t \text{ (real } \times \cos^2 180/\cos^2 174 = 22.9 \text{ Hz}$$
  
 $J_{60^\circ} = J_c \text{ (real) } \times \cos^2 60/\cos^2 66 = 2.1 \text{ Hz}$ 

Using these data, and assuming that they are applicable to acyclic phosphate rotamers we can calculate the coupling exhibited by methyl phosphates.

$$J_{av} = 1/3(J_{180^\circ} + 2J_{60^\circ}) = 9.0 \text{ Hz}$$

The observed values, however, lie in the range 11.0 to 11.5 Hz.

Thus it is not possible to compare directly data from cyclic phosphates with that from acyclic phosphates. Several possible reasons for this lack of quantitative agreement have been considered:

(a) That the phosphorinane ring system is flatter in solution than in the crystalline phase. The P—O—C—H<sub>ax</sub> dihedral angle would thus be increased, causing the calculated  $J_{60^{\circ}}$  to be increased; the P—O—C—H<sub>eq</sub> dihedral angle would decrease causing the calculated  $J_{180^{\circ}}$  to increase; thus  $J_{av}$  would increase. However, the calculated  $J_{av}$  for methyl rotamers is still less than the observed value when  $J_{60^{\circ}}$  (the more rapidly changing quantity) reaches the lowest observed coupling for the acyclic rotamers (trineopentyl phosphate 4.05 Hz at 185 °K) a coupling that still contains some *trans* contribution. This value therefore acts as a maximum limit for  $J_{60^{\circ}}$ .

(b) That the energy minima for the acyclic rotamers do not occur at P—O—C—H dihedral angles of 60 and 180°, but at  $(60 + \phi)^\circ$  and  $(60 - \phi)^\circ$  and at  $(180 \mp \phi)^\circ$ . The observed coupling  $J_{\rm obs}$  is then given by  $1/3(J_t + 2J_g)$ , where

$$J_{t} = J_{180^{\circ}} \times \cos^{2} (180 \pm \phi)^{\circ} / \cos^{2} 180^{\circ}$$
  
$$2J_{g} = J_{60^{\circ}} \times \cos^{2} (60 + \phi)^{\circ} / \cos^{2} 60^{\circ}$$
  
$$+ (J_{60^{\circ}} \times \cos^{2} (60 - \phi)^{\circ} / \cos^{2} 60^{\circ}$$

From which it follows that  $J_t$  is less than  $J_{180^{\circ}}$ and  $J_g$  is less than  $J_{60^{\circ}}$ , and hence that  $J_{obs}$  is less than  $J_{av}$ . The  $J_{obs}$  in the phosphorinanes 11–11.5

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Hz is in fact more than the calculated 9.0 Hz and indicates that such asymmetric rotational isomers are not the cause of the inconsistency in the data.

(c) That the electronegative phosphoryl oxygen selectively reduces the coupling into the equatorial proton by 8–10 Hz due to the all *trans* transmission pathway; no similar effect being operable for the axial proton. If this effect were to operate, conformers with an axial phosphoryl oxygen would have to show a  $J_t$  of ca. 30 Hz. The axial preference of OR substituents on phosphorus precludes direct observation of these conformers; however any phosphorinane which significantly time-averages should show an increase in both  $J_t$  and  $J_{sum}$ . Inspection of the data in Table 2 shows no evidence of such an effect.

(d) That a significant amount of twist conformation is present in the phosphorinane ring; in this case both dihedral angles are 120° and exhibit small vicinal couplings. The presence of twist conformations would thus produce a decrease in  $J_{sum}$ . The observed constancy of  $J_{sum}$ indicates that the population of twist conformers either is constant for all the compounds studied or more reasonably that it is zero.

None of these approaches is able to account for the only semi-quantitative agreement between the data obtained from the two sources. The only obvious difference between these systems is that free rotation about the P—O bond can occur in the acyclic rotors but not in the phosphorinanes; it seems likely that this is in some way responsible for the discrepancy.

We have therefore calculated the populations of the *trans* rotational isomers of the compounds in Table 1 using, first the derived values for  $J_{180^{\circ}}$  and  $J_{60^{\circ}}$  (lines A<sub>1</sub>, A<sub>2</sub>, and A<sub>3</sub>, Fig. 1) and second using the ratio of  $J_{180^{\circ}}/J_{60^{\circ}}$  and the observed coupling value for the methyl representative of each set of compounds. In this case a different set of  $J_t$  and  $J_g$  values,  $J_T$  and  $J_G$ , have been derived for each set of compounds. These normalized data which all fall very close to line B, are given in Table 3.

Assuming that a  $\cos^2$  relationship exists between dihedral angle and *vicinal* coupling, the rate of change of the coupling with angle will be greatest for the *gauche* angle of 60°. Thus  $J_g$ , the parameter upon which the calculated rotamer







(compound set 2, (RCH<sub>2</sub>O)<sub>2</sub>P—OPh), and line A<sub>3</sub> (compound set 3 (RCH<sub>2</sub>O)<sub>3</sub>P=O) obtained using  $J_{180}$  and  $J_{60}$  values derived from the 2-oxo-1,3,2-dioxaphosphorinane system. Line B using  $J_T$  and  $J_G$  values normalized to give a 33.3% rotameric population for the methyl phosphate of each compound set; set 1,  $J_T$  29.0,  $J_G$  2.7; set 2,  $J_T$ 28.6,  $J_G$  2.6; set 3,  $J_T$  27.9,  $J_G$  2.55. Lines C and D for compounds of set 2. Using the likely extreme values of  $J_G$ ; C,  $J_T$  +28.6,  $J_G$  2.1; D,  $J_T$  +28.6,  $T_G$  3.1.

populations are most sensitive, is the one with the greatest uncertainty. The lines C and D in Fig. 1 represent the calculated *trans* rotamer populations for the likely extremes of  $J_g$ ( $\pm 0.5$  Hz). The uncertainties in  $J_T$  and the sensitivity of the populations toward it are considerably smaller and are ignored. The derivation of the relationships that we have used to calculate the *trans* rotamer population and the equilibrium constants are given in the Appendix.

Regardless of the  $J_t$  and  $J_g$  values used, the observed monotonic decrease in  $J_{obs}$  with increasing bulkiness of the substituent R is reflected in a considerable increase of the *trans* rotamer population. We would point out that the differences between the rotamer populations calculated using the normalized and unnormalized data decreases with increasing population of the *trans* rotamer, thus in studying systems of potential biochemical interest for which this

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 TABLE 3.
 Thermodynamic properties of acyclic rotamers

Compound		% population of	Equilibrium constant	Free energy differences			
R	*	R trans C	interconversions	states (cal)			
н	I	33.3	1.0	0.0			
	II	33.3	1.0	0.0			
	III	33.3	1.0	0.0			
Me	I	54.3	2.38	512			
	II	55.5	2.50	541			
	III	56.3	2.57	557			
Et	I	61.2	3.16	678			
	II	61.6	3.21	688			
	III	61.7	3.23	692			
<i>iso-</i> Pr	I	70.2	4.72	915			
	II	70.1	4.69	<b>91</b> 1			
	III	69.9	4.66	908			
<i>tert-</i> Bu	I	81.6	8.97	1295			
	II	81.6	8.97	1295			
	Ш	81.8	9.02	1300			

\*I, ROP (OPh)<sub>2</sub>,  $J_T$  29.0,  $J_G$  2.67; II, (RO)<sub>2</sub>POPh,  $J_T$  28.6,  $J_G$  2.62; III, (RO)<sub>3</sub>P=O,  $J_T$  27,9,  $J_G$  2.56.

present work acts as a model study, the R groups encountered are usually large enough to give *trans* rotamer populations not seriously altered in a semi-quantitative way by the choice of  $J_t$ and  $J_g$ .

The data represented by line **B**, Fig. 1 are, we believe, the best available at present. Using these parameters we have calculated the *trans*gauche interconversion equilibrium constants and also the free energy differences between the gauche and trans rotational isomers (Table 3).

The quantitative agreement between the data from the three sets of acylic rotamers is excellent and exemplifies the independence of  $J^{31}P-O-C-^{1}H$  upon phosphorus substituents in phosphotriesters. Thus we discount the rationale of Axtmann *et al.* (11) that decreases in couplings arise from electronegativity effects. We also discount the attempt by Katritsky *et al.* (8) to rationalize the data from cyclic and acyclic compounds by assuming that the steric effect of the R group is zero and hence that no nonequivalent rotational isomers occur.

## Temperature Studies

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Invariance of  $J_{obs}$  with temperature, observed for methyl diphenyl phosphate is the behavior expected from the assumption of the equivalence of the rotational isomers in methyl phosphates. The decrease of  $J_{obs}$  with decreasing temperature observed for the ethyl and neopentyl derivatives arises from an increasing proportion of the *trans* rotamer at lower temperatures. (Table 4, columns 1 and 2).

It is convenient to express the  $J_{obs}$  temperature relationship as a plot of  $J_{obs}$  vs. 1/T (Fig. 2). Over the temperature range experimentally accessible the relationship between  $J_{obs}$  and 1/T appears linear, and has been so reported (5). However, from the expression for the equilibrium constant K derived in the Appendix to this paper it can be seen that at very high temperatures when the rotational isomers tend to equivalence and Kapproaches unity,  $J_{obs}$  approaches  $J_{av}$ . At low temperatures when the trans rotamer becomes populated exclusively K becomes very large and then  $J_{obs}$  asymptotically approaches  $J_g$ . Combining the expression for K and the expression relating the equilibrium constant with temperature it can be seen that the relationship between  $J_{obs}$  and 1/T is indeed non-linear except when  $J_{obs}$  is equal to  $J_{av}$ . The conclusions drawn by the workers in ref. 5, that with increasing temperature compounds such as tri-neopentyl phosphate will never attain equal populations of the rotational isomers, are based on a linear relation-

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Temperature (°K)		0    MeO—P—(0	OPh)2			O ∥ (EtO)₂P-	-OPh		O    neo-Pentyl OP(OPh)2			
	J <sub>abs</sub> (Hz)	Population trans (%)	K	ΔG (cal)	J <sub>obs</sub> (Hz)	Population trans (%)	K	ΔG (cal)	J <sub>obs</sub> (Hz)	Population trans (%)	K	Δ <i>G</i> (cal)
185				-					4.05	89.8	17.5	1050
193									4.15	89.0	16.2	1063
203									4.3	87.9	14.5	1095
233	11.5	33.3	1.0	0.0	7.7	61.0	3.13	528	4.6	85.6	11.9	1145
253					7.95	59.0	2.88	532				
273					8.15	57.3	2.69	536	4.9	83.3	9.9	1240
298	11.5	33.3	1.0	0.0	8.4	55.4	2.49	540	5.1	81.8	9.0	1308
335	11.5	33.3	1.0	0.0	8.65	53.5	2.30	553	5.45	78.2	7.9	1370
370	11.5	33.3	1.0	0.0	8.9	51.6	2.13	555				
393	11.5	33.3	1.0	0.0	9.0	50.7	2.05	560	5.7	77.3	6.85	1500

TABLE 4. Thermodynamic parameters as a function of temperature for acyclic phosphate esters



FIG. 2. Variation of the observed rotamer coupling  $J_{obs}$  with 1000/T for (A) methyl diphenyl phosphate, (B) diethyl phenyl phosphate, (C) *neo*-pentyl diphenyl phosphate. The dashed straight lines passing through the data points of B and C represent interpretation of similar data made in the study, ref. 5.

ship between  $J_{obs}$  and 1/T, and are therefore incorrect.

By plotting ln K vs. 1/T and  $\Delta G$  vs. T (Figs. 3 and 4) we have estimated the enthalpy and entropy differences between the rotational states about the O—C bond. The ln K vs. 1/T plots have correlations greater than 0.996 and yield values of  $\Delta H$  of 650 cal for neopentyl diphenyl phosphate and 500 cal for diethyl phenyl phosphate. The plots  $\Delta G$  vs. T have correlations of 0.999 for neopentyl diphenyl phosphate, 0.988 for diethyl phenyl phosphate and >0.999 for





methyl diphenyl phosphate yielding values of 650, 480, and 0 cal respectively for  $\Delta H$  and 2.2, 0.2 and 0 cal/degree mol for the entropies.

In summary then, we have confirmed that a qualitative relationship exists between the *trans* and *gauche* <sup>31</sup>P—O—C—<sup>1</sup>H couplings of derivatives of the 2-oxo-1,3,2-dioxaphosphorinane system and the couplings of acyclic phosphate esters. This relationship accords with variations of rotamer populations which follow conven-

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FIG. 4. Plot of the free energy differences between rotameric states,  $\Delta G$  as a function of the absolute temperature *T*. (A) *neo*-Pentyl diphenyl phosphate, (B) diethyl phenyl phosphate, (C) methyl diphenyl phosphate.

tional conformational tenets. However, it must be emphasized that a precise quantitative relationship does not exist and we can at present offer no acceptable reason as to why this should be.

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# Experimental

The following general method was used for the preparation of the acyclic phosphate esters. Phosphorus oxychloride, phenylphosphorodichloridate, or diphenylphosphorochloridate as appropriate (1 equiv) was added slowly to a solution of the alcohol (1.2 equiv) in pyridine solvent, the rate of addition being adjusted to keep the temperature below 40°. After standing for 2 h, unreacted phosphorochloridate was destroyed by the addition of 5 volumes of water. After a further 30 min the mixture was extracted into chloroform and evaporated to a small volume and traces of pyridine were removed as the toluene azeotrope. The crude alkyl phosphate was purified by vacuum distillation (180-220° at 0.1 mm). Yields of crude product in excess of 80% were obtained. Compounds in set 1 (Table 1) were characterized by elemental micro-analysis in addition to the n.m.r. measurements. The remaining compounds were shown to be pure by t.l.c. and were characterized by comparison of the n.m.r. spectra with the appropriate compound of set 1.

Room temperature n.m.r. spectra were run on ca. 15% solutions in CDCl<sub>3</sub> using a Varian HA 100 spectrometer in the frequency sweep mode. Spectral assignment was simplified by means of phosphorus decoupling experiments (9) and true couplings obtained using the LA $\varphi C \varphi \varphi N$ -3 iterative computer programme. Variable temperature studies were conducted in ca. 5% solutions in CH<sub>2</sub>Cl<sub>2</sub> for tempera-

tures below 25° and on neat oils at high temperatures using a Varian XL-100 spectrometer.

The t.l.c. experiments were on silica gel G plates in 5% methanol in chloroform solvent.

Measurements were not made with diethyl phosphate below 233  $^{\circ}$ K because the magnitude of the phosphorus coupling approached that of the proton vicinal coupling.

The plots shown in Figs. 3 and 4 are least squares analyses made with a Hewlett Packard model 9100 programmed calculator and model 9125A plotter.

#### Appendix

This gives the derivation of expressions for the *trans* population and the *trans*-gauche rotamer equilibrium constants in terms of  $J_{180^\circ}$  and  $J_{60^\circ}$ .

The observed coupling for the rotational isomers shown in Scheme 2 which interconvert rapidly on the n.m.r. time scale is given by the weighted sum of the coupling occurring in each isomer:

$$J_{\rm obs} = J_{\rm C}[{\rm C}] + J_{\rm A}[{\rm A}] + J_{\rm B}[{\rm B}]$$

where [C] is the concentration of the *trans* rotamer (C); [B] = [A] concentrations of the *gauche* rotamers (A and B); and [C] + [B] + [A] = 1.

The couplings occurring in each rotational isomer are given by:

$$J_{\rm C} = \frac{J_{\rm G} + J_{\rm G}}{2}$$
  $J_{\rm A} = J_{\rm B} = \frac{J_{\rm G} + J_{\rm T}}{2}$ 

thus

$$J_{\rm obs} = J_{\rm G}[{\rm C}] + (J_{\rm G} + J_{\rm T})[{\rm A}]$$

and hence

$$J_{obs} = J_{G}[C] + (J_{G} + J_{T}) \left(\frac{1 - [C]}{2}\right)$$

Rearranging this equation yields the percentage concentration of the *trans* rotamer:

$$[C] = \frac{J_{\rm T} + J_{\rm G} - 2J_{\rm obs}}{J_{\rm T} - J_{\rm G}} \times 100$$

The equilibrium constant is given by:

$$\frac{[C]}{[A]} = \frac{2[C]}{1 - [C]}$$

Yielding

$$K = \left[\frac{J_{\rm T} - J_{\rm obs}}{J_{\rm obs} - J_{\rm G}}\right] - 1$$

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- 1. L. D. HALL and R. B. MALCOLM. Can. J. Chem. This issue.
- 2. L. D. HALL and R. B. MALCOLM. Can. J. Chem. This issue.
- 3. L. D. HALL and R. B. MALCOLM. Chem. Ind. (London), 92, (1968).
- 4. For detailed list of references see those quoted in ref. 1 above: a selected list is given here. (a) D. W. WHITE, G. K. MCEWEN, R. D. BERTRAND, and J. G. VERKADE. J. Mag. Res. 4, 123 (1971). (b) D. W. WHITE and J. G. VERKADE. J. Mag. Res. 3, 111 (1970). (c) R. D. BERTRAND, J. G. VERKADE, D. W. WHITE, D. GAGNAIRE, J. B. ROBERT, and J. VERRIER. J. Mag. Res. 3, 494 (1970). (d) M. KAINOSHO and A. NAKAMURA. Tetrahedron, 25, 4071 (1969). (e) M. TSUBOI, S. TAKAHASHI, Y. KYOGOKU, H. HAYATSU and T. UKITA. Science, 166, 1504 (1969). (f) R. S. EDMUNDSON and E. W. MITCHELL, J. Chem. Soc. C, 752 (1970). (g) D. W. WHITE, G. MCEWEN, R. O. BERTRAND, and J. G. VERKERDE.

J. Chem. Soc. B, 1454 (1971). (h) M. KAINOSHO, A. NAKAMURA, and M. TSUBOI. Bull. Chem. Soc. Jap. 42, 1713 (1969).

- 5. A. A. BOTHNER-BY and W. P. TRAUTWEIN. J. Am. Chem. Soc. 93, 2189 (1971).
- 6. H. J. GIESE. Rec. Trav. Chim. 86, 362 (1967).
- M. KARPLUS. J. Chem. Phys. 30, 11 (1959). J. Phys. Chem. 64, 1793 (1961). J. Am. Chem. Soc. 85, 2870 (1963).
- 8. A. R. KATRITSKY, M. R. NESBIT, J. MICHALSKY, Z. TUMILOWSKI, and A. ZWIENZAK. J. Chem. Soc. B, 140 (1970).
- 9. R. BURTON and L. D. HALL. Can. J. Chem. 49, 59 (1970).
- 10. W. G. BENTRUDE and J. H. HARGIS. Chem. Commun. 1113 (1969).
- 11. R. C. AXTMANN, W. E. SHULER and J. H. EBERLY, J. Chem. Phys. 31, 850 (1959).

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