dard rather than Me_4Si. With Me_4Si taken as zero, a downfield shift is then added if given a positive sign and an upfield shift added if it is given a negative sign.
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Elucidation of the Conformational Equilibria for the *cis*-8-Oxabicyclo[4.3.0]non-3-ene Series

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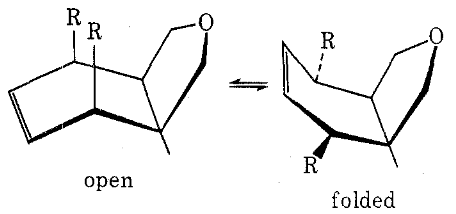
A method for quantitatively determining the solution equilibrium for conformers in a conformationally mobile system by computer analysis of LIS spectra is developed. The relative population of the two major conformations of *cis*-8-oxabicyclo[4.3.0]non-3-ene and *cis*-2,5-dimethyl-*cis*-8-oxabicyclo[4.3.0]non-3-ene have been determined. A second, independent conformational analysis of these molecules supports the use of this method. Some limitations of shift reagents, as applied to conformational analysis, are examined.

There has been considerable interest in utilizing lanthanide shift reagents to deduce conformations of molecules in solution. Until recently, however, very little quantitative work has been attempted owing to the uncertain and tedious nature of the calculations involved. We became interested in lanthanide induced shift (LIS) studies as a tool to probe the subtle effects of a heteroatom on conformation, and, as a result, have taken an active interest in the development of LIS techniques. As part of this effort, we report on the conformational equilibria of the *cis*-8-oxabicyclo[4.3.0]non-3-ene series.

Results and Discussion

Dreiding models clearly demonstrate that there are two major conformations for members of the *cis*-8-oxabicyclo[4.3.0]non-3-ene series, *"open"* and *"folded"* (Chart I).

Chart I
Major Conformations of the 8-Oxabicyclo[4.3.0]non-3-enes



1a, R = H
b, R = Me

Based on NMR spectral analysis, we have previously suggested that the preferred conformation of *cis*-8-oxabicyclo[4.3.0]non-3-ene (**1a**) is *"open"*.[1] At that time we had no quantitative data on this preference, and we undertook a systematic analysis of LIS data.

In all cases the necessary LIS data were obtained by adding aliquots of a carbon tetrachloride solution of $Eu(fod)_3$ to a precisely weighed amount of substrate, also in carbon tetrachloride.[2] For each proton the induced shift was plotted against the ratio of $Eu(fod)_3$ to substrate and the slope determined (Table I). These slopes are the necessary input data for PDIGM, a program designed by Davis and Wilcott.[3]

For a given set of molecular coordinates, PDIGM systematically varies the lanthanide position over a series of spheres of increasing radius. The coordinates for the heteroatom are taken as the center of the sphere and a theoretical shift for each proton, as given by the McConnell–Robertson equation, is calculated and compared with the experimentally determined values. The position of best fit for each radial increment, accompanied by an agreement factor, is given by means of two defining angles, ρ and ϕ. The agreement factor is expressed as a standard deviation

$$R = \left[\frac{\sum \omega_j(\text{obsd}_j - \text{calcd}_j)^2}{\sum \omega_j(\text{obsd}_j)}\right]^{1/2}$$

where ω_j is the weight associated with jth observation. For a given conformation, the lanthanide position is taken to be that at which the best agreement factor occurs.

PDIGM may be used for a qualitative analysis of conformational equilibria by comparing the R values obtained for the various stable conformations and choosing the lowest value among them. That PDIGM may also be used for quantitative work can be inferred from magnetic resonance theory. Specifically, a proton signal appearing in the NMR spectrum will be a time average of the signal for this proton in its various environments, providing that the interconversion of the conformers is fast relative to the NMR time scale.[4] It follows that the signal appearing on the NMR spectrum is representative of a molecule of "intermediate conformation". It is also known that the observed shift in the presence of a lanthanide shift reagent is a linear combination of the induced shifts of the extremes[5]

$$\delta_{\text{obsd}} = n\delta_1 + (1 - n)\delta_2$$

where δ_1 = shift for proton in conformation 1 and δ_2 = shift for proton in conformation 2. From the McConnell–Robertson equation

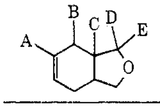
$$\delta_1 = f(r_1, \theta_1)$$

$$\delta_2 = f(r_2, \theta_2)$$

and hence

$$\delta_{\text{obsd}} = nf(r_1, \theta_1) + (1 - n)f(r_2, \theta_2).$$

Table I
Slopes for the Plots Δδ vs. Eu(fod)$_3$/Sub

	1a	1b	2	3
Slope A	0.514	0.820	0.198	3.695
B	0.988	0.900	0.454	3.002
C	1.371	2.200	0.745	5.273
D	3.425	4.08	Me: 0.694	12.663
E	4.00	4.48		12.663
		Me: 0.739		

The question, then, becomes whether δ_{obsd} can be expressed as eq 1. This can be restated in another form: does the average value of the pseudocontact shifts for the stable conformers equal the pseudocontact shift for the average values of r and θ?

$$\delta_{\text{obsd}} = f[n(r_1, \theta_1) + (1 - n)\ (r_2, \theta_2)] = f(r_{\text{obsd}}, \theta_{\text{obsd}}) \quad (1)$$

A rigorous proof of this relationship has been attempted,[6] but difficulties in integrating the expressions

$$\langle \cos^2 \theta - 1/r^3 \rangle$$

and

$$\cos^2 \langle \theta \rangle - 1/\langle r^3 \rangle$$

caused inconclusive, although favorable, results.

Lacking concrete mathematical proof, we attempted to establish the relationship by direct comparison of the two methods of averaging. If $(\cos^2 \phi - 1)/r^3$ (del) is calculated for all protons in a molecule and then plotted against the observed shift for these protons, a straight line results. Further, if

$$(\cos^2 \phi - 1)/r^3 = (\cos^2 \langle \phi \rangle^{-1})/\langle r \rangle^3$$

the slope of the line obtained by averaging the del values for the two conformers should be identical with the slope of the line obtained by averaging the coordinates of the two conformers and then calculating the del values. Compound **1b** was examined in this manner at a conformational weighting of 1:1 using the program BODEL.[7] The least-squares slope for the average of the del values is found to be 0.533, with a standard deviation of 0.048; while that for the del values of the averaged coordinates is 0.519, with a standard deviation of 0.052. Variances obtained are 0.963 and 0.960, respectively. Although this does not constitute a rigorous proof of eq 1, the results are strongly supportive of its use.

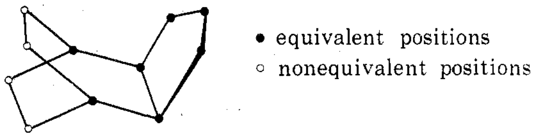
Despite the lack of solid theory, the relationships above are exceedingly useful and have been utilized to good advantage.[8] If then we can accept eq 1, it follows that the set of theoretical calculations which will most closely approximate the experimentally obtained values will be found at the weighted average of the coordinates for the stable conformations which represent the "intermediate conformation". If the sum of the conformers present is unity, the weights placed on the coordinates of the stable conformations at the point of best fit will be identical with the amount of that conformer in solution.

Consequently, a program for averaging the coordinates for the two stable conformers was developed and merged into the existing PDIGM system. It should be noted at this point that the atom positions for the various conformations should overlap in every possible respect, and in the system 1 requires superimposing the furan rings before the averaging process.[9] Neglect of this factor would cause identical atom positions to be averaged (Chart II).

Table II
Agreement Factors for Weighted Averages of Conformation

% open conformation	R values, %, at 2.2 Å (**1b**)	R values, %, at 2.9 Å (**1a**)
100	10.1 (3.81 at 2.9 Å)	1.98
95		1.91
94		1.90
93		1.91
92		1.92
90	3.93 (3.55 at 2.3 Å)	1.96
85		2.17
80		2.50
75	2.37	2.93
70	2.16	
65	2.03	
63	2.01	
62	2.00	
61	1.99	
60	1.99	
55	2.05	
50		5.66
35	3.36 (3.29 at 2.3 Å)	7.19
20	3.59	8.16
0	5.94 (5.23 at 2.9 Å)	5.75 (4.74 at 3.3 Å)

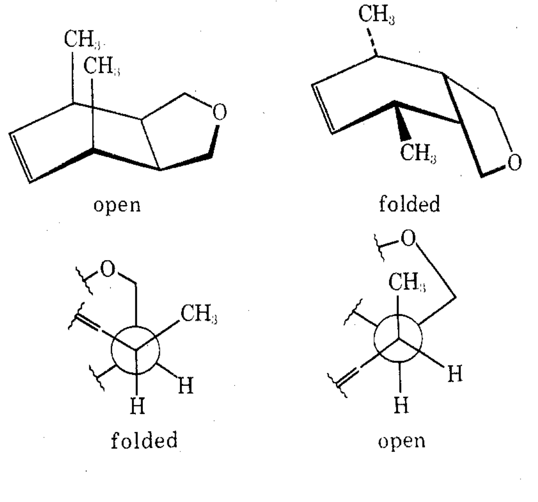
Chart II
Relationships of Folded to Open Coordinates



The data obtained are presented in Table II and Figure 1. The result for **1a**, a 94:6 preference for the *open* conformation, substantiates our earlier views of its preferred conformation. It may be argued that the difference in agreement factors is small in the immediate vicinity of the minimum and that a range rather than an absolute number should be specified. Although the method of reporting the data is immaterial for our purposes, the symmetry of the curve encourages our belief in its accuracy.[10]

The analysis of one other system, *cis*-2,5-dimethylbicyclo[4.3.0]non-3-ene (**1b**), seemed potentially fruitful since, a priori, it could be assumed to exist largely in the folded form. This assumed preference for the folded form is attributed to the 1,4-dimethyl interaction which exists in the open conformer. However, allylic strain[13] in the folded form, plus increased gauche interactions,[14] might tend to counteract the dimethyl interaction so that the exact extent of folding is obscure (Chart III).

Chart III
Steric Interactions of
cis-2,5-Dimethylbicyclo[4.3.0]non-3-ene



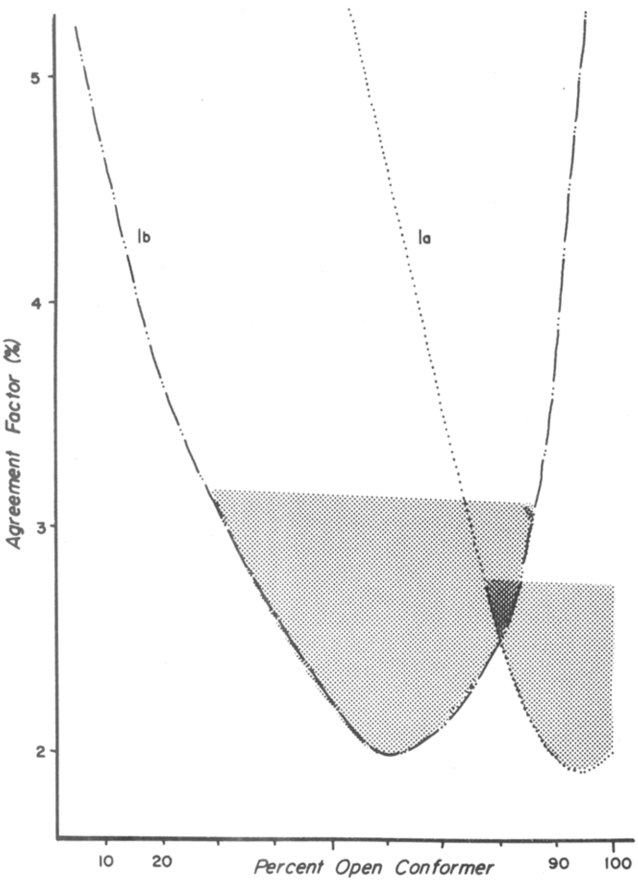


Figure 1. Graph of R value vs. percent *open* conformer.

The results obtained from PDIGM for the various weighted averages are displayed in Table II and Figure 1 with the best agreement of theory to experiment ($R = 1.99$) found at 60% *open* conformer and 40% *folded.*[15]

Several interesting artifacts of PDIĜM may be noted. One is the observation that the lanthanide–substrate bond distance changes for the two conformations, the minimum for the open form being found at 2.9 Å, while the partially closed exists at 2.2 Å. At present we have no reasonable rationalization for this; however, differences in lanthanide–substrate distances for rigid exo/endo isomers has been previously observed.[16]

Another notable observation is the deviation, at extreme conformations, of the lanthanide–substrate bond distance at which the best agreement (minimum R) is found. These "numeric" R minima are very erratic in their positioning of the lanthanide and often place the lanthanide in physically improbable environments. A numeric minimum is a minimum only once. For example, if there is a numeric minimum at 3.0 Å in a 90:10 *open/closed* equilibrium calculation, a minimum will not exist at 3.0 Å in the 80:20 calculation. Consequently, it may be asserted that these numeric minima are fortuitous, the result of forcing a fit of theoretical and experimental data to a conformation that, for NMR, does not exist.

Recently, Servis and co-workers examined the conformational equilibria of some 2-alkylcyclohexanones using lanthanide shift reagents.[17] An extension of this work provides a convenient check on our calculations. Basically, Servis has assumed that the observed shift for any proton in the presence of a shift reagent ($\delta_{\text{obsd}}^{H_a}$) will be the sum of the shift for the uncomplexed molecule ($\delta_0^{H_a}$) and the induced shift for the complexed form (Δ^{H_a}) multiplied by the fraction of molecules complexed (F).

$$\delta_{\text{obsd}}^{H_a} = \delta_0^{H_a} + F\Delta^{H_a}$$

If two conformations exist for the molecule (i.e., if the proton occupies two different regions of space) then the observed shift can be expressed as the weighted averages of the shifts for the two conformations (eq 2)

$$\delta_{\text{obsd}}^{H_a} = n_1\delta_0^{H_{1a}} + n_2\delta_0^{H_{2a}} + F(n'_1\Delta^{H_{1a}} + n'_2\Delta^{H_{2a}}) \quad (2)$$

where $\Delta^{H_{1a}}$ is the bound shift of proton H_a in environment 1 and $\Delta^{H_{2a}}$ is the bound shift of proton H_a in environment 2. Similarly, for any other proton in the molecule, H_b,

$$\delta_{\text{obsd}}^{H_b} = n_1\delta_0^{H_{1b}} + n_2\delta_0^{H_{2b}} + F(n'_1\Delta^{H_{1b}} + n'_2\Delta^{H_{2b}}) \quad (3)$$

Simultaneous solution of these two equations (2 and 3) and subsequent simplifications yields eq 4

$$\frac{\Delta^{H_a}}{\Delta^{H_a} + \Delta^{H_b}} = n'_1\frac{\Delta^{H_{1a}}}{\Delta^{H_{1a}} + \Delta^{H_{2b}}} + n'_2\frac{\Delta^{H_{2b}}}{\Delta^{H_{1a}} + \Delta^{H_{2b}}} \quad (4)$$

where $\Delta^{H_a}/\Delta^{H_a} + \Delta^{H_b}$, the relative induced shift, may be shown to equal the slope of the plot of $\delta_{\text{obsd}}^{H_a}$ vs. $\delta_{\text{obsd}}^{H_a} + \delta_{\text{obsd}}^{H_b}$.[12]

A characteristic relative induced shift is obtained from a rigid model system and the conformational equilibria of its nonrigid cousins ascertained by comparison of the relative induced chemical shifts with the characteristic relative induced shift of the model system. Owing to the unique relationship of axial and equatorial protons in cyclohexanes, only one model is needed for complete analysis of the system. However, for any system in which proton H_a in conformation 1 does not occupy the same space as proton H_b in conformation 2, a two-model system is needed.

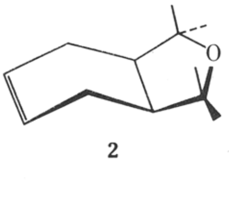
The mathematical relationships for the two-model system may be derived in exactly the same manner as done by Servis and Bowler with the end result displayed in eq 5.

$$\begin{aligned} &\text{relative induced shift} = \\ &\quad n_0\,(\text{characteristic relative induced shift 1}) + \\ &\quad (1 - n_0)\,(\text{characteristic relative induced shift 2}) \end{aligned}$$

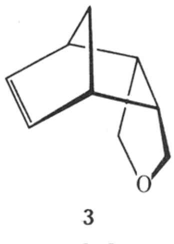
or

$$\begin{aligned} &\text{obsd slope } (\delta_{\text{obsd}}^{H_a} \text{ vs. } \delta_{\text{obsd}}^{H_a} + \delta_{\text{obsd}}^{H_b}) = \\ &\quad n_0\,(\text{standard slope 1}) + (1 - n_0)\,(\text{standard slope 2}) \quad (5) \end{aligned}$$

We chose for our open model *cis*-7,7,9,9-tetramethylbicyclo[4.3.0]non-3-ene (**2**)[18] and for our folded model *endo*-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene (**3**).[19] Examination of Drieding models revealed that **2** should exist entirely in the *open* form owing to the prohibitive bulk of the four methyl groups. Nevertheless, **2** was examined using PDIGM and found to have an agreement (R) factor of 1.43% for the *open* conformer while the corresponding factor for the *folded* conformer was 6.32%. Since this difference is significant to the 99.5% level, we feel justified in stating that **2** exists exclusively in the *open* form.[20] For **3**, rigid covalent bonds, not assumptions, hold it in the *folded* form!



2



3

For convenience in the analysis, we needed two protons whose signals in the NMR were free of interference, at least one of which changed significantly with a conformation change. The vinyl protons (H_v) and the ring juncture protons (H_j) satisfied these specifications. The shift data ob-

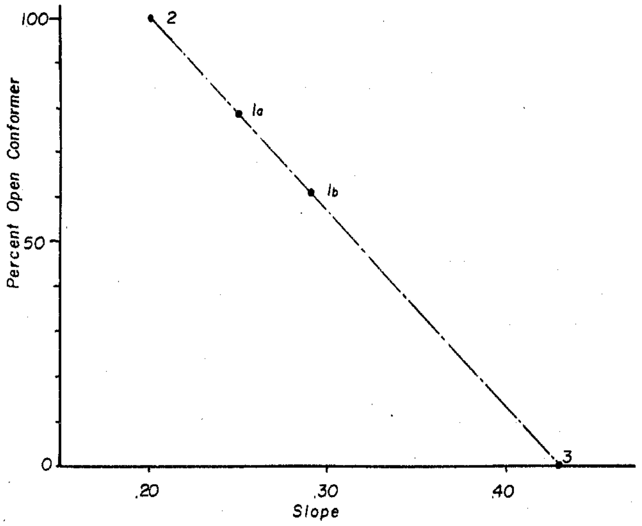


Figure 2. Graphical determination of conformational equilibria of *cis*-8-oxabicyclo[4.3.0]non-3-enes.

tained at various concentrations of $Eu(fod)_3$ with the slopes of the graphs (δ^{H_v} vs. $\delta^{H_v} + \delta^{H_j}$) are displayed in Table III. Figure 2 represents the graphical interpretation of the linear combination, eq 5, and gives a value of 78% *open* for **1a** and 60% *open* for **1b.**

In view of the assumptions and simplifications involved these figures are in good agreement with those obtained from the computer analysis.

If one considers the McConnell–Robertson equation

$$\Psi\text{-contact shift} = K\left[\frac{3\cos^2\theta - 1}{r^3}\right]$$

a direct comparison of the induced shifts for one molecule with those for another may be made only if the distance from the lanthanide to any specific proton, r, and θ, the angle generated by r, and the lanthanide–substrate bond axis, are constant. This is rarely, if ever, the case. A method is needed whereby differences in r and θ "factor out". The procedure of Servis and Bowler is such a method.

Given r and r', the lanthanide–proton distances for two conformers, a relationship may always be derived whereby

$$r = kr'$$

and it follows that

$$r^3 = k^3r'^3$$

or, redefining the constant,

$$r^3 = kr'^3$$

It is this constant, K, which prevents direct comparison of the shift data. However, when $\delta_{\text{obsd}}{}^{H_a}$, which is a function of Kr'^3, is plotted against another value also designed to vary as Kr'^3 ($\delta_{\text{obsd}}{}^{H_a} + \delta_{\text{obsd}}{}^{H_b}$) the deviation is constant along both the absicca and the ordinate. The slope of the plot $\delta_{\text{obsd}}{}^{H_a}$ vs. ($\delta_{\text{obsd}}{}^{H_a} + \delta_{\text{obsd}}{}^{H_b}$) is, therefore, independent of the constant. Unfortunately, this simple relationship does not hold for the ($\cos^2\theta - 1$) term, since it may not be deduced from an equation of the form

$$a = kb$$

that

$$a - 1 = k(b - 1)$$

If the change in θ is less than 20° the change in the Ψ-contact shift is not large and the errors introduced by assuming $\cos^2\theta$ constant are acceptable. It must be noted, however, that preferential binding of the lanthanide to one orbital over another, a consideration of much import in heterocyclic chemistry,[21] would be manifest in this term and may result in larger errors than expected.

Table III
Shift of Vinyl and Juncture Protons with $Eu(fod)_3$

Compd	δ_{H_V}	$Eu(fod)_3$/ substrate	$\delta_{H_V} + \delta_{H_j}$	δ_{H_j}	Slope[a]
1a	5.64		8.02	2.38	
	5.73	0.176	8.28	2.55	
	5.82	0.352	8.63	2.81	
	5.92	0.528	9.05	3.13	
	5.99	0.704	9.40	3.41	0.25
3	6.01		8.77	2.76	
	6.18	0.203	9.19	3.01	
	6.36	0.407	9.59	3.23	
	6.62	0.815	10.19	3.57	
	7.05	1.22	11.18	4.13	0.43
2	5.67		7.76	2.09	
	5.72	0.373	7.95	2.23	
	5.81	0.747	8.44	2.63	
	5.89	1.12	8.82	2.93	
	5.94	1.49	9.11	3.17	0.20
1b	5.58		8.13	2.55	
	5.76	0.216	8.76	3.00	
	5.93	0.431	9.36	3.43	
	6.11	0.647	9.96	3.85	
	6.29	0.863	10.57	4.28	0.29

[a] r^2 for each of these values exceeds 0.99.

A further source of error in this method lies in the suitability of the model compounds. It is essential to choose the model systems carefully and, for the case in hand, to keep in mind that the protons of the models, particularly the folded model, will not have the same chemical shifts as the protons of the molecules of interest, and that considerable error may result from this.

In this paper we have demonstrated the utility of lanthanide shift reagents for conformational analysis, in solution, of mobile systems and have provided a convenient method for quantifying the results. This method, although used to examine the equilibrium between only two conformers, may be applied to any number of species in equilibrium.

Experimental Section[22]

The NMR spectra were recorded on a Varian A-60 instrument using tetramethylsilane as the internal standard. Chemical shifts were measured from Me_4Si.

Typical Procedure. A solution of **1a** (0.140 g, 1.117×10^{-3} mol) and reagent grade carbon tetrachloride with 1% Me_4Si to bring the total volume to 250 µl was placed in an NMR tube and the spectrum was recorded. To this sample tube were then added 100-µl aliquots of a 0.198 *M* $Eu(fod)_3$ solution in carbon tetrachloride. The spectrum was again recorded. This procedure was repeated from five to ten times. The shift data were collected and analyzed.

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Registry No.—**1a,** 50305-98-1; **1b,** 57346-34-6; **2,** 57346-35-7; **3,** 43187-61-7; $Eu(fod)_3$, 17631-68-4.

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(7) Program written by G. D. Smith, Montana State University.

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(9) For all PDIGM calculations, coordinates of all conformations were taken so that the oxygen atom and the four carbon atoms of the tetrahydrofuran ring were superposed in all conformations. Comparison of any two R factors is a comparison of the goodness of fit for two different positions for the substituents on the four nonfused carbon atoms of the six-membered ring.

(10) We applied the Hamilton R-ratio tests[11] to observed R factors in the following way. The conformation or mix of conformations with the lowest R factor was deemed the "best fit conformation". Any other conformation or mix of conformations was considered a "restrained conformation" with the number of protons unable to assume the "best fit conformation" defining the number of restrained parameters (b). Further, the number of experimental observations (n) was taken as the number of observed NMR peaks used in the calculation of slopes and the number of parameters (p) was taken as the number of protons in the molecule. The observed R-ratio, $R_{\text{rest}}/R_{\text{best fit}}$, was compared to the calculated R-ratio values, $R_{b,n-p,\alpha}$, which have to be exceeded to reject the hypothesis that the two conformations are indistinguishable. The confidence level at which the hypothesis is rejected is $(1 - \alpha) \times 100\%$. Values of $R_{b,n-p,\alpha}$, were taken from Hamilton[12] or calculated by the relation

$$R_{b,n-p,\alpha} = [(b/n - p)F_\alpha + 1]^{1/2}$$

as given by Hamilton.[11]

For **1a**, $n = 25$, $p = 12$, $b = 6$. The conformational mix of 94% *open*, 16% *folded* with the lowest R factor is not significantly different from the totally *open* conformation but is significantly different from any conformational mix of 75% or less *open* form at the 90% confidence level. The stipled area in Figure 1 shows the limits of the 90% level.

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Crystal and Molecular Structure of a Spirobicyclic Pentaoxyphosphorane, $(PO_5)(C_6H_4)_2(C_6H_5)$

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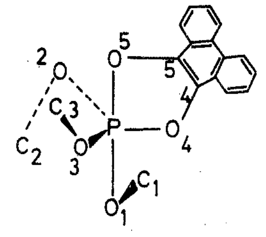
The crystal and molecular structure of a monoclinic form of spirodicatecholphenoxyphosphorane was determined by single-crystal x-ray diffraction techniques. The space group is $P2_{1/c}$ with four molecules in a unit cell of dimensions $a = 6.910$ Å, $b = 15.305$ Å, $c = 14.779$ Å, $\beta = 88.5°$. The final R factor for 2840 independent reflections is 8.7%. The molecular structure does not correspond to an ideal or a "slightly distorted" trigonal bipyramid or tetragonal (square) pyramid. It is suggested that the phosphorus and its five oxygen ligands have the skeletal geometry of a 15°-turnstile rotation configuration.

Compounds with five oxygen ligands covalently bonded to phosphorus, e.g., the trimethyl phosphite–phenanthrenequinone adduct **1**, have been extensively studied from structural[2] and synthetic[3] points of view. The geometry around the phosphorus in the analogous pentaoxyphosphorane **2** is TBP,[4] as established by x-ray crystallography,[5] which revealed also the existence of severe crowding around the central atom. It was suggested[5] that the relatively planar ring minimizes the crowding and contributes to the stability of this type of compound.

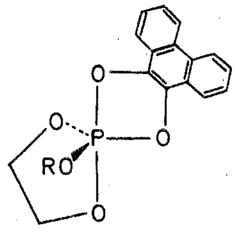


1 $C_1,C_2C_3 \equiv CH_3$; $\delta^{31}P = +44.7$ ppm

2 $C_1,C_2,C_3 \equiv$ iso-C_3H_7; $\delta^{31}P = +48.6$ ppm

3 $C_1,C_2,C_3 \equiv C_6H_5$; $\delta^{31}P = +58.6$ ppm

Spirobicyclic pentaoxyphosphoranes, e.g., **4** and **5**, are also known, and are relatively stable.[6] The introduction of an additional five-membered ring into the monocyclic pentaoxyphosphoranes is accompanied by a significant displacement of the ^{31}P NMR chemical shift toward lower magnetic field, i.e., by a decrease in the shielding of the P nucleus by electrons, cf. **4** vs. **1** and **5** vs. **3**. This effect could reflect significant differences in molecular structure between spirobicyclic and monocyclic pentaoxyphosphoranes, but there are no x-ray data on the molecular structure of **4** and **5**. Six-membered rings do not cause this effect.[6,7]



4 $R = CH_3$; $\delta^{31}P = +23.0$ ppm

5 $R = C_6H_5$; $\delta^{31}P = +27.0$ ppm