Determination of Conformational Free Energies for Phosphorus Functions by ^{31}P Nuclear Magnetic Resonance Spectroscopy

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Summary Direct measurements at 183 K of the conformers of *cis*-4-methylcyclohexylphosphine and its *P*-dimethyl and *P*-dichloro derivatives by ^{31}P n.m.r. spectroscopy, and comparison of the averaged ^{31}P shifts at 300 K with the shifts for t-butylcyclohexyl compounds, have been used to determine the first conformational free energies for phosphorus functions.

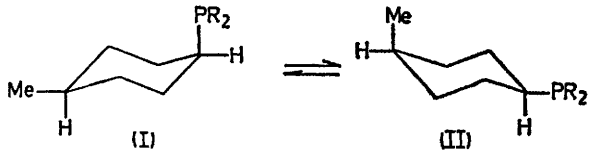
PHOSPHORUS chemical shifts are known to be sensitive to the steric environment of the phosphorus function.[1] We have found that two of the conventional methods of conformational analysis of cyclohexanes that depend on n.m.r. differences between conformers can be performed with proton-decoupled ^{31}P n.m.r. spectroscopy, and we have obtained the first values for the conformational free energies of phosphorus functions when present on the cyclohexane ring.

TABLE 1

^{31}P n.m.r. shifts for 4-*R*-cyclohexyl compounds

R	Temp/K	-PH_2	-PMe_2	-PCl_2
H	300	+111·8	+42·7	−195·0
trans-Bu^t ..	300	+111·6	+42·5	−194·6
trans-Me ..	300	+111·8	+42·5	−194·9
trans-Me ..	183	+111·0	+43·7	−194·6
cis-Bu^t ..	300	+131·3	+54·8	−208·9
cis-Me ..	300	+122·5	+49·0	−199·8
cis-Me(II) ..	183	+110·2	+44·2	−194·1
cis-Me(I) ..	183	+133·4	+57·2	−210·4

(a) *Direct measurement of conformers at low temperature.* The phosphorus functions had sufficiently large 1,3-nonbonded interactions that a ^{31}P signal for only the equatorial conformer of the cyclohexyl derivatives could be observed on reducing the temperature from 300 K to 183 K. The *trans*-4-methyl derivatives had very similar shifts (Table 1), since here too the equatorial disposition of the *P*-function is highly favoured. However, the *cis*-4-methyl compounds had shifts that were dramatically affected by temperature.



On reducing the temperature to about 240 K, the signal became very broad, and nearly vanished into the baseline.† At 183 K, however, two quite sharp ^{31}P signals were present, one in nearly the same position as the *trans*-isomer. This signal is therefore assigned to the conformer with the equatorial *P*-function (II), and the other signal to that with the axial *P*-function (I). The peak heights provided K_{equil}, and hence $\Delta G°$. Since free energy differences for 1,4-disubstituted cyclohexanes in general are additive, the value for $\Delta G°_{Me}$ (−1·7 kcal mol^{-1} [2]) is added to the observed $\Delta G°$ to provide $\Delta G°_{PR_2}$, presented as *A* values ($-\Delta G°$) in Table 2.

(b) *Chemical shift method.* The room-temperature ^{31}P spectra for the *cis*- and *trans*-4-t-butyl derivatives were obtained to provide shifts characteristic of the fixed axial and equatorial *P*-functions (Table 1). Assuming no effect on the shifts by the 4-t-butyl group, the Eliel equation[3] can be used to determine K_{equil} for the mobile *cis*-4-methylcyclohexyl system, and this leads to the *A* values (Table 2)

† This effect provides a simple method for the assignment of *cis*-structure to a pair of *cis*, *trans* isomers.

TABLE 2

Thermodynamic values

	(a) 183 K			(b) 300 K		
	K_{equil}	$\Delta G°_{cis\text{-}4\text{-}Me}$	A_{PR_2}	K_{equil}	$\Delta G°_{cis\text{-}4\text{-}Me}$	A_{PR_2}
$-PH_2$	0·68	+0·14	1·6	0·81	+0·13	1·6
$-PMe_2$	0·54	+0·22	1·5	0·89	+0·07	1·6
$-PCl_2$	1·72	−0·20	1·9	1·75	−0·33	2·0

as in (a). The values obtained by the two methods are quite consistent. We note that replacement of hydrogen by methyl does not have an effect on the *A* values; possibly increased nonbonded interaction between axial $-PMe_2$ and protons at C-3, C-5 is accompanied by increased interaction between equatorial-PMe_2 and protons at C-2, C-6 as has been discussed for methylation of the amino group.[4]

The data in Table 1 also show that the increased steric crowding when the *P*-function is axial causes relative shielding at phosphorus in the PH_2 and PMe_2 cases, but relative deshielding for PCl_2.

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