the latter pathway for Cr(phen)$_3^{3+}$. Back intersystem crossing will be associated with an activation energy equal to the energy gap between the two states. From a temperature dependence study of photoracemization at 457.9 nm we find that while the nonquenchable or quartet component has an activation energy of 2.2 kcal mol^{-1}, the corresponding value for the quenchable reaction component is 10.1 kcal mol^{-1}. This latter value suggests that radiationless deactivation is a major relaxation mode of the doublet, since experimentally no activation energy would be observed for racemization *via* thermal return if the latter process were the sole fate of the doublet molecules. (Total return would mask the energy requirement for return.) The relatively high efficiency of $^2E_g \rightarrow {}^4A_{2g}$ deactivation may also be inferred from the anomalously low activation energy reported for the phosphorescence intensity of Cr(phen)$_3^{3+}$.[5]

Studies on $(-)_{589}$Cr(phen)$_2$oxCl provide further support for these conclusions. For this system corrections for photoaquation and thermal racemization[7] are again negligible. In aqueous solution at 25° a value of ϕ_{rac} of 0.21 is obtained at the wavelengths 350 and 501.7 nm, *i.e.*, a yield 13 times greater than that for Cr(phen)$_3^{3+}$ and in the range[1,2] normally found for Cr(III) photosubstitutions. The very weak emission from this complex precludes a phosphorescence quenching study. However, iodide has no observable effect on ϕ_{rac}. It appears quite probable then that racemization occurs predominantly through the lowest excited quartet state prior to intersystem crossing. This is in accord with the value of 1.4 kcal mol^{-1} found for the activation energy for this reaction.

The generality of the approach suggested in this communication is illustrated by evidence from OH$^-$ doublet quenching which does not match reaction quenching in the photosubstitution of Cr(NH$_3$)$_6^{3+}$. These results will be reported elsewhere.[8]

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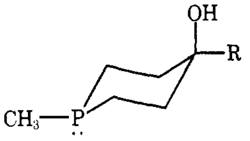
Received November 9, 1971

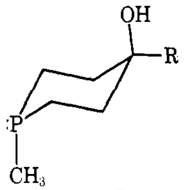
Assignment of Configuration to *cis,trans*-4-Phosphorinanols. X-Ray Analysis of *trans*-1-Methyl-4-*tert*-butyl-4-phosphorinanol[1]

Sir:

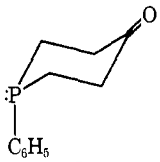
From the beginning[2] of conformational study of six-membered cyclic phosphines (phosphorinanes), it was apparent that the system possessed some unique properties. Cis,trans isomers of 1-methyl-4-alkyl-4-phosphorinanols (I) were given tentative structure assignments from nmr spectral differences which suggested that they differed in configuration at phosphorus in their preferred conformations. Further study[3] has not modified this view, but has shown that even in secondary phosphorinanols little preference is expressed by *P*-methyl for either equatorial or axial orientation. That other unusual properties may prevail in this ring system has been made clear from X-ray analysis of some *P*-phenylphosphorinanes (II[4] and III[5]) which were found to have axially oriented phenyl.



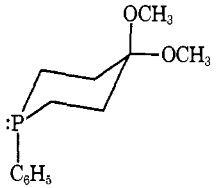
cis-I



trans-I

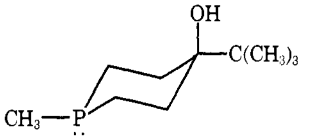


II

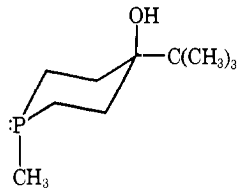


III

It is a matter of considerable importance to the further development of stereochemical understanding of phosphorinanes that unequivocal structural assignments be made among isomer pairs, thus permitting the confident use of spectral differences between isomers for more routine assignments. We here provide unambiguous proof from a single-crystal X-ray analysis for the structure of one of the isomers of IV, both of which are crystalline solids.[3]



cis-IV



trans-IV

The solid which formed in the receiver on distillation of a mixture with composition *ca.* 70% *cis*–30% *trans*-IV had two distinctly different crystalline forms present, and single crystals of each isomer could be identified and separated by microscope examination. One of the isomers crystallizes as well-developed prisms with mp 84–85°, whereas the other forms as thin plates with mp 103–104°. Separation of the isomer mixture by gas chromatography provided specimens with identical melting points. As in earlier studies,[2] the trans structure was assigned to the lower melting isomer, based on the upfield position (δ 0.89) and larger coupling constant (J_{PCH} = 4 Hz) of the PCH$_3$ group relative to the signal from the cis isomer (δ 0.95, J_{PCH} = 2.1 Hz).

A crystal of the more suitable lower melting isomer was selected for X-ray analysis and mounted in a thin-walled capillary under a nitrogen atmosphere. These crystals are monoclinic, space group $P2_1/c$, with eight molecules of C$_{10}$H$_{21}$OP in a unit cell of dimensions a

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[1] Supported in part by Public Health Service Research Grant No. CA-05507, National Cancer Institute.

[2] H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967).

[3] L. D. Quin and J. H. Somers, *J. Org. Chem.*, in press.

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[5] A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *J. Chem. Soc. D*, 1020 (1971).

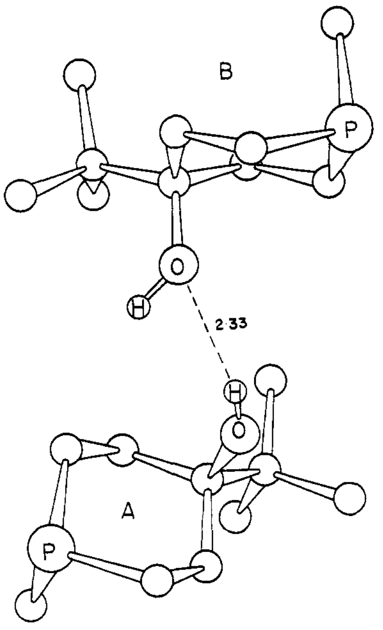
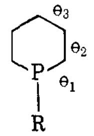


Figure 1. Conformation of the hydrogen-bonded molecules in the asymmetric crystal unit.

= 12.32, b = 10.55, and c = 17.68 Å and β = 93.1°. Three-dimensional intensity data were recorded photographically by the equiinclination multiple-film Weissenberg method and estimated visually. The structure was solved by the heavy-atom method and the positional and thermal (anisotropic P, O, C; isotropic H) parameters were refined by full-matrix least-squares calculations to R = 0.089 over 3153 reflections.

This X-ray analysis establishes unequivocally that the isomer of mp 84–85° has the trans structure in accord with the assignment from nmr data.[3] With eight molecules in the $P2_1/c$ unit cell, two crystallographically independent estimates of the molecular dimensions are derived from the analysis, and any conformational differences due to inter- or intramolecular forces should be evident. Both of the phosphorinane rings in the asymmetric crystal unit have slightly flattened chair conformations with torsion angles (Table I) not significantly different from those observed previously[5] for III which also has an axially oriented P substituent. Bond angles about phosphorus in III and *trans*-IV are also similar.

Table I. Average Ring Torsion Angles and Bond Angles (Degrees) in *trans*-IV and III Assuming C_s Symmetry



	trans-IV	III
θ_1	45.3	45.2
θ_2	57.7	57.1
θ_3	59.7	61.5
C–P–C (internal)	97.7	97.7
C–P–C (external)	101.9	102.3

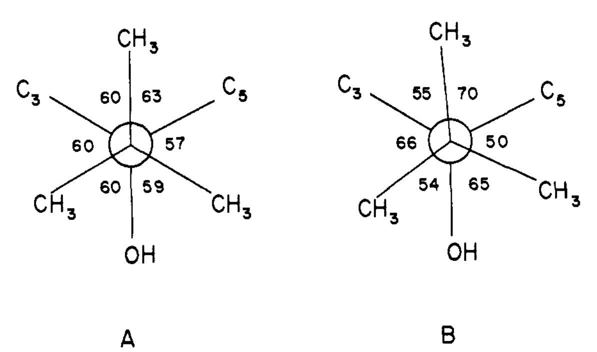


Figure 2. Torsion angles (degrees) at the *tert*-butyl groups of A and B molecules as viewed in projection along the quaternary carbon–ring carbon bonds.

Noteworthy is the average ring carbon–quaternary carbon bond length of 1.583 (6) Å which is significantly greater than the average of the other sp^3–sp^3 carbon distances, 1.535 Å. Longer than normal carbon–carbon single bond lengths at *tert*-butyl groups of substituted cyclohexane rings have been predicted by valence-force energy calculations[6] and they have been observed recently in X-ray studies of these[6] and other overcrowded molecules.[7] The nonbonded strain is also reflected in the bond angles at the *tert*-butyl carbon atoms of *trans*-IV where the average C(ring)–C(quaternary)–C(Me) angle is 111.2° while the C(Me)–C(quaternary)–C(Me) angles average 107.3°.

In the crystal the molecules of *trans*-IV are held in pairs by O–H···O hydrogen bonds with H···O = 2.33 Å (Figure 1). This bond involves the hydroxyl hydrogen atom of A molecules, and the different orientations of the hydroxyl hydrogen atoms in A and B molecules result in dissimilar torsion angles at the *tert*-butyl groups (Figure 2). In A molecules the *tert*-butyl carbon atoms are almost perfectly staggered with respect to the ring carbon atoms and the hydroxyl oxygen atom, whereas in B molecules these groups are rotated by an average of 6° from the completely staggered conformation in order to gain relief from nonbonded interactions between the hydroxyl and *tert*-butyl hydrogen atoms.

With this assignment of trans structure to one of the isomers of IV, the assignments given[2] on the basis of nmr parameters to the isomers of other *tert-P*-methylphosphorinanols need no longer be considered tentative.[8,9]

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(6) D. H. Faber and C. Altona, *J. Chem. Soc. D*, 1210 (1971).

(7) T. Brennan, E. F. Putkey, and M. Sundaralingam, *ibid.*, 1490 (1971); G. J. Visser and A. Vos, *Acta Cyrstallogr., Sect. B*, 27, 1793 (1971); G. J. Visser and A. Vos, *ibid.*, 27, 1802 (1971).

(8) The isomers of IV differ in their ^{31}P chemical shifts by 10 ppm when measured in admixture in benzene,[3] with the trans isomer more shielded (+67.3 ppm). With further examples, this may prove to be another device for the assignment of cis,trans structure to I.

(9) A table of observed ($|F_o|$) and calculated ($|F_c|$) structure factors (×10) for *trans*-1-methyl-4-*tert*-butyl-4-phosphorinanol will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code JACS-72-2126. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

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Received January 6, 1972