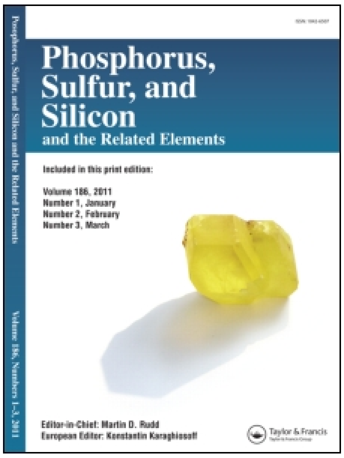

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A CONFORMATIONAL STUDY OF TETRAALKYLDIPHOSPHINES

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A CONFORMATIONAL STUDY OF TETRAALKYLDIPHOSPHINES

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The Extended Huckel (EH) method has been applied to study rotational conformers of symmetrically substituted tetraalkyldiphosphine molecules (R_4P_2, R = methyl, ethyl, isopropyl, t-butyl). Our results predict a preference of the gauche conformers in these molecules although stable trans conformers are observed in the case of tetramethyl and tetra-t-butyl compounds. A possible stable cis conformer is also observed in the case of tetraisopropyldiphosphine.

INTRODUCTION

Since the introduction of computational methods to chemical problems, the study of different geometrical conformers and barriers to rotation has been of special interest. In small molecules, ab initio methods with an extended basis set have been applied successfully. However, limited availability of computer time has deterred many researchers from studying larger molecules. The diphosphine molecule (P_2H_4), however, has been studied by ab initio and semi-empirical methods. In the former case, Cowley *et al.*[1] and Van Wazer *et al.*[2] have determined the gauche and trans rotamers to be the most stable conformers with a probable free rotation around the P—P bond via the trans barrier. In these studies an extended basis set around the P atoms were used. Extended Huckel calculations of diphosphine have also been reported by Cowley *et al.*[3] whereas Frenking and collaborators[4] have studied the diphosphine molecule by the MINDO/3 method. In agreement with ab initio calculations, both these semi-empirical methods reported a preference of the gauche and trans forms. Experimental work, however, seems to be rather ambiguous in the prediction of the more stable conformers[5] although studies by Beagley *et al.*[6] and Frankiss[7] seem to suggest stable gauche and trans configurations. It seems, therefore, that semi-empirical methods can, at least qualitatively, explain the energy differences as a molecule is made to rotate around a fixed axis. The present study introduces an inexpensive computational procedure for the determination of stable conformers of a class of tetraalkyldiphosphines by using the Extended Huckel (EH) method. In the case of tetramethyldiphosphine, for example, our results seem to agree nicely with experimental work obtained by McAdam *et al.*[8] and Ames and Turner.[9] In both experimental studies, the trans and the gauche forms have been observed to be the more stable conformers in parallel with our theoretical investigation. Our results also seem to agree with data obtained by experimentalists[10,11] regarding the tetra-t-butyldiphosphine which was found to favour a gauche and a trans configuration.

Unfortunately, there is no ab initio study of tetraalkyldiphosphines so that a justification of our results might be made. However, with such large molecules, ab initio calculations can only be done sensibly with a small basis set, which may give less reliable results than semi-empirical techniques.[12] However, various authors have reported failure of the EH method for somewhat polar compounds.[13,14] Consequently, it is only because there is strong experimental support of our results that we have actually indulged in pursuing our work.

METHOD

In this work, the EH method has been applied to four tetraalkyldiphosphine molecules, namely, tetramethyl, tetraethyl, tetraisopropyl, and tetra-t-butyl diphosphine. The work is mainly centered on the determination of molecular geometries and the equilibrium values for the different parameters were used. In the alkyl groups, the C—H and C—C bond lengths were chosen to be 1.109 and 1.510 angstroms respectively whereas a tetrahedral angle was assumed around each C atom. The C—P and P—P bond lengths are based on gas phase electron diffraction studies which reports the equilibrium distances in tetramethyldiphosphine as 1.854 and 2.192 angstrom respectively.[8] The C—P—C angle was fixed at 101.9° for all the analogous molecules and pyramidal inversion around the P atoms was studied by varying the C—P—P angle. The CPC angle, however, was not chosen arbitrarily. In fact it was optimized by first fixing the CPP angle and therefrom incrementing the CPC angle by 2°. The starting CPP and CPC angles were chosen to be 90° and 95° respectively. The optimized C—P—C angle was found to vary from 100.6° in the tetramethyl compound to 101.2° in the tetra-t-butyl analogue. Internal rotations around the P—P bond were studied by increasing the dihedral angle from 0° (the cis rotamer) to 180° (the trans rotamer) in increments of 5 degrees. The basis set used in the calculations consisted of one 1s STO of H, one 2s and three 2p STOs of C and one 3s, three 3p and five 3d STOs of P. The off-diagonal Huckel energy matrix elements were calculated by using a mixing factor of 1.75[15] whereas the self energy diagonal elements were set equal to the negative of the ionization potential of the respective orbitals. The program used is that developed by Hoffman[16,17] and an algorithm has been developed in our laboratory in order to calculate the coordinates of the different configurations and link them directly to the input stream of the main program.*

RESULTS

In all the analogous series of the diphosphine molecules studied, the cis conformer with C_{2v} symmetry was first considered. Pyramidal inversion on this rotamer was performed and it was observed that the C—P—P angle increased with the bulk of the alkyl substituent from 96.1 degrees in the case of the tetramethyl substituent to 125.1 degrees in the case of the t-butyl analogue. The experimental CPP angle reported by McAdam *et al.* for tetramethyldiphosphine is 101.1° which is close to our optimized value. MINDO/3 results obtained by Frenking and collaborators,

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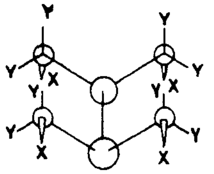
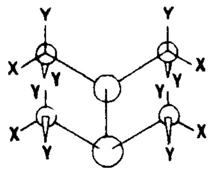
*A copy of this algorithm may be obtained from the authors on magnetic tape.

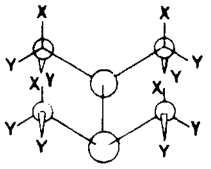
however, give an overestimated angle of 114.4°. The molecules were then rotated around the P—P bond until the trans rotamer with C_{2h} symmetry was realized. In the case of the tetraethyl compound, configurations resulting from different orientations of the ethyl groups relative to each other had to be considered. Three of these configurations are symmetrical around the P—P bond and have the following structure where Y=H and X=CH_3:



a

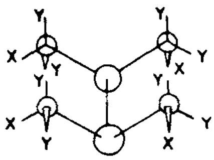


b

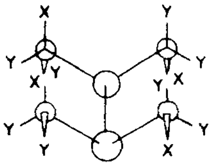


c

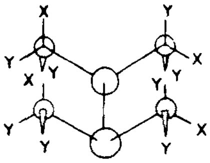
with C_{2v} symmetry while the other three correspond to the C_s symmetry group having a plane of symmetry perpendicular to the P—P bond. These have the structure:



d



e



f

Of course, one can envisage other configurations, but as will be discussed later on, the general trend of the variation of the total energy as the molecule is rotated around the P—P bond is retained for the above six conformers. That is, although concerted rotations around the P—P and C—P bonds will be the prevalent case, yet rotations around the latter bonds will not seem to be of such a nature as to effect the general trend of energy variation as the molecule is rotated around the P—P bond. Structures such as the above, however, are expected to be unstable in the case of tetraisopropyldiphosphine because of interactions between the methyl groups. Only one conformer of each of the tetramethyl and tetra-t-butyldiphosphine compounds was studied; these being (X = Y = H) in the former and (X = Y = CH_3) in the latter. Internal rotation around the C—P bond was only considered for the isopropyl and ethyl analogues. Following the optimization of the geometry of the cis compounds, rotations around the P—P bond were effected in increments of 5 degrees and the most stable rotamer was determined by studying plots of the difference in the electronic energy vs the dihedral angle.

In the case of the tetramethyldiphosphine molecule, two stable rotamers were observed, one occurring at a dihedral angle of 65 degrees (henceforth identified as the "gauche" rotamer) and the other one being the trans (dihedral angle = 180 degrees). Figure 1 shows a plot of the difference in the electronic energy against

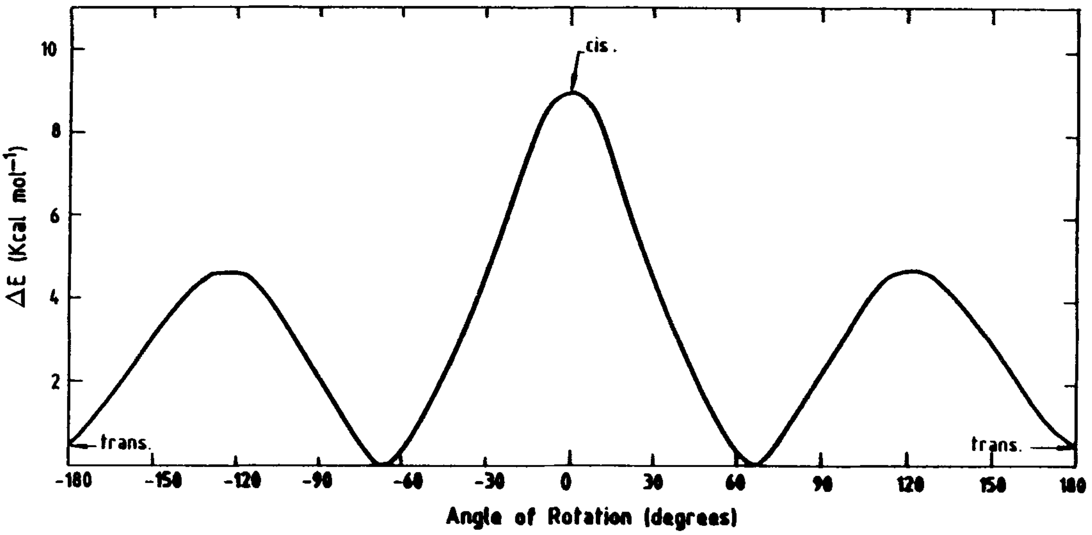
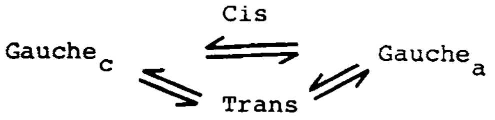


FIGURE 1 Energy difference in Kcal mol^{-1} vs. angle of rotation around the P—P bond for tetramethyldiphosphine. Most stable rotamer occurs at a gauche angle of 65°.

clockwise rotation (0° to 180°) and anticlockwise rotation (0° to $-180°$) of the dihedral angle. There are two possible gauche forms (gauche$_c$ and gauche$_a$), the first resulting from clockwise and the other anticlockwise rotations relative to the cis conformer. The energy barrier of the gauche/cis and gauche/trans transitions are found to be 9.0 and 5.0 kcal mol^{-1} respectively. Thus the equilibrium processes governing these rotamers is thought to be of the form:



This result is in line with some experimental work that has reported the presence of a trans form.[8] In addition to this conformer, we have been able to observe a stable gauche form in agreement with MINDO/3 results[4] that have predicted the presence of this rotamer at 59°. Other experimental work conducted by Albrand *et al.*[18] and Durig and DiYorio,[19] however, seems to support our findings regarding the presence of almost equal amounts of the trans and gauche conformers. We contend, therefore, that the gauche$_c$ ⇌ trans ⇌ gauche$_a$ is a reversible process and predominates over the gauche$_a$ ⇌ gauche$_c$ process that occurs via the cis energy barrier.

Six different conformers were studied in the case of tetraethyldiphosphine ($Y = H, X = CH_3$) and structure (a) was found to be most stable although the difference in energy between structures (a) and (b) on the one hand and structures (a) and (c) on the other were found to be 1.0 kcal mol^{-1} and 1.5 kcal mol^{-1} respectively. The other three structures (d, e and f) were found to be relatively unstable mainly due to steric effects. Figure 2 shows a plot of the energy difference against rotations around the P—P bond for the tetraethyldiphosphine molecule. Rotations around the P—P

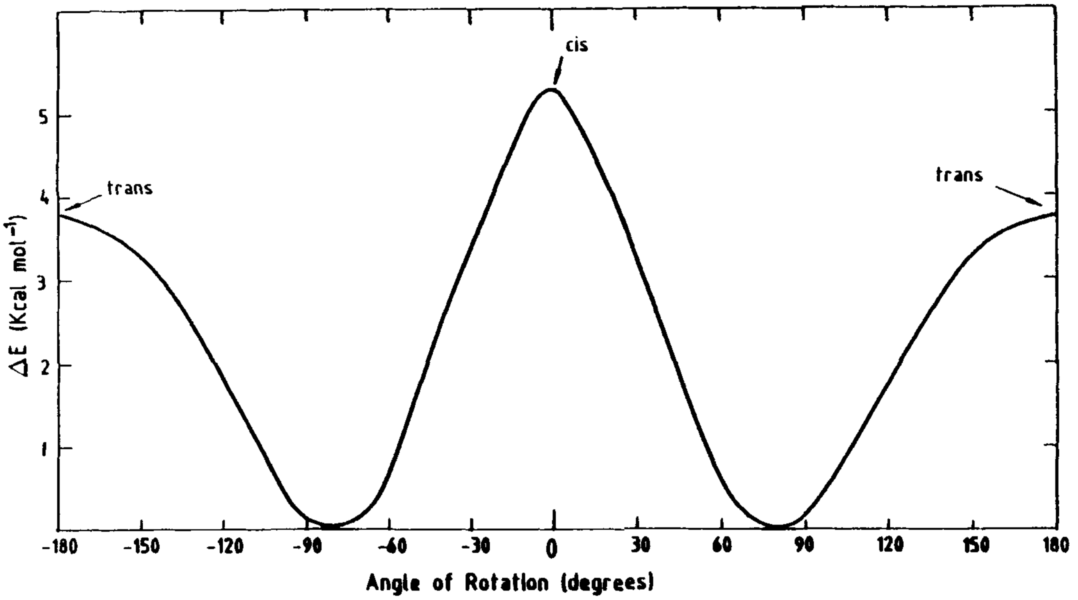


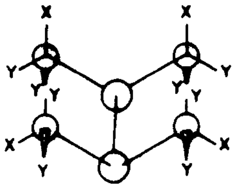
FIGURE 2 Energy difference in Kcal mol^{-1} vs. angle of rotation around the P—P bond for tetraethyldiphosphine. Most stable rotamer occurs at a gauche angle of 80°.

bond were also performed on structures (b) and (c) and curves similar to those appearing in Figure 2 were obtained although the "gauche" angle was found to be slightly different from the 80° angle found for structure (a). Relative to the gauche rotamer, the trans rotamer was found to be unstable but not to the extent of the cis counterpart.[18] Moreover, the cis/trans energy barrier was found to be 3.8 kcal mol^{-1} which is lower than the 4.8 kcal mol^{-1} barrier found in the gauche/cis transition. The reversible equilibrium processes are thus thought to pass through either the cis or the trans barrier, i.e.

$$\text{Gauche}_c \overset{\text{Trans}}{\rightleftharpoons} \text{Gauche}_a \overset{\text{Cis}}{\rightleftharpoons} \text{Gauche}_c$$

where as usual, the a and c subscripts refer to clockwise and anticlockwise rotation relative to the cis conformer. The above argument was based on structure (a) as it is expected that the methyl groups would tend to stay as farther apart as possible from each other. Dynamic NMR studies of this compound reveal a probable gauche form at low temperatures in very good agreement with our results.[18]

The tetraisopropyldiphosphine molecule ($X = H, Y = CH_3$) showed marked steric hindrance effects apparently due to the proximity of the methyl groups on the opposite sides of the P atoms. The optimum C—P—P angle was found to be 122.2° and the total energy was quite sensitive to variation of this angle. Structures (a) and (d) proved to be unstable mainly due to steric effects. An attempt was made to study structures (e) and (c) by rotating the molecule around the P—P bond but the variation in energy was highly exaggerated. Other configurations therefore had to be studied and the following one having a plane of symmetry coincident with the P—P axis was found to be more stable than the previous structures by about 4 kcal mol^{-1}:



(g)

Energy variations of structure (g) as a result of rotating the molecule around the P—P bond are in good agreement with steric hindrance effects. Figure 3 shows a plot of the energy change against the dihedral angle of rotation (structure (g)). The cis rotamer of this structure was found to be quite stable. Initial rotation around the P—P bond would bring a methyl group on one side of P in proximity with another methyl group on the other P. Energy destabilization is a direct consequence of the repulsion between the methyl groups. A certain point is reached, however, when these effects are made minimum and a stable rotamer is attained at a gauche angle of 90°. Moreover, further rotations around the P—P bond would bring two other methyl groups in proximity with each other and thus resulting in steric destabilization effects. Finally, a stable trans rotamer is obtained. It seems, therefore, that in the case of tetraisopropyldiphosphine, two stable conformers are equally likely with a possible preference of the cis configuration. It is also evident, at least qualitatively, that the repulsion between the lone pair of electrons around each of the P atoms is comparable with the steric hindrance effects.[20] This apparently results in a relatively stable cis conformer where electron–electron repulsions between the lone pairs are expected to be maximum. Our results agree with Dynamic NMR studies of tetraisopropyldiphosphine conducted by Albrand and collaborators[18] where a stable gauche

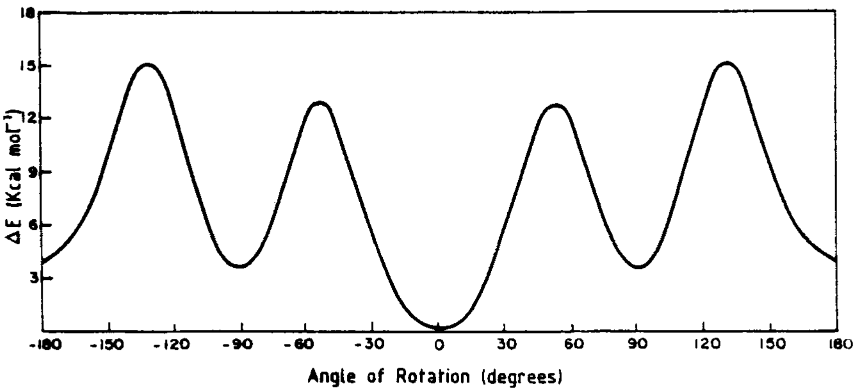
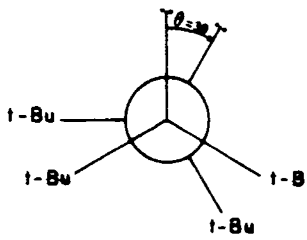


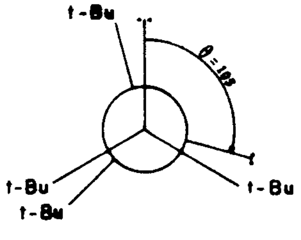
FIGURE 3 Energy difference in Kcal mol^{-1} vs. angle of rotation around the P—P bond for tetraisopropyldiphosphine. Three stable structures are present for the cis, gauche and trans conformers.

conformer was suggested. These results, however, are inconclusive with respect to the stability of the cis conformer.

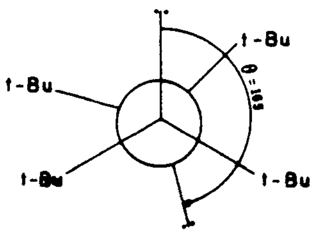
Only one conformer was studied in the case of tetra-t-butyldiphosphine ($X = Y = CH_3$), the different structures (a through d) being equivalent. No attempt was made to rotate the t-butyl groups around the P—C bond and thus breaking the C_{2v} symmetry of the cis conformer. Optimization of the C—P—P angle resulted in a value of 125.1°, somewhat greater than that found in tetraisopropyldiphosphine. An analogous conformer of the t-butyl compound having D_{2h} symmetry (i.e. a C—P—P angle equal to (180 − (C—P—C/2)) was also considered but was found to be highly unstable. This molecule exhibited three relatively stable rotamers occurring at dihedral angles of 30°, 105°, and 165° and herefrom identified as I, II and III respectively with structure I being the most stable:



I



II



III

Figure 4 shows a plot of the energy difference against the dihedral angle. The energy barrier for the interconversion of I_a to I_c via the cis path or to conformer II_a is found to be around 17.1 kcal mol^{-1} and 12.3 kcal mol^{-1} respectively. Moreover,

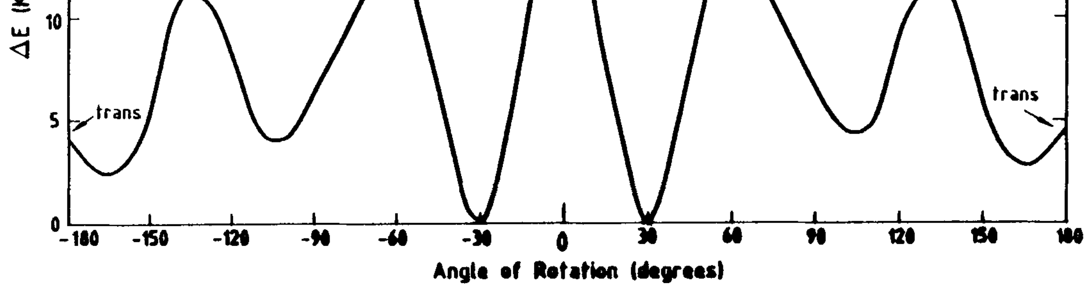


FIGURE 4 Energy difference in Kcal mol^{-1} vs. angle of rotation around the P—P bond for tetra t-butyldiphosphine. The trans "stable" rotamer occurs at a gauche angle of 165° whereas the most stable rotamer occurs at a gauche angle of 30°.

interconversion of II_a to II_c passes through yet a third barrier of approximately 6 kcal mol^{-1}. It is therefore possible to hypothesize the existance of two paths for the transformation between the two predominant gauche forms.

$$\begin{tikzcd}
\mathrm{II}_a \arrow[r, shift left] & \mathrm{III}_a \arrow[l, shift left] \arrow[r, shift left, "\text{Trans}"] & \mathrm{III}_c \arrow[l, shift left] \arrow[r, shift left] & \mathrm{II}_c \arrow[l, shift left] \arrow[d, shift left] \\
\mathrm{I}_a \arrow[u, shift left] \arrow[rrr, shift left] & & & \mathrm{I}_c \arrow[u, shift left] \arrow[lll, shift left, "\text{Cis}"]
\end{tikzcd}$$

This conclusion agrees very well with dynamic NMR work on tetra-t-butyldiphosphine. Bushweller and collaborators[10] and Harris and co-workers[11] came to the conclusion that the two gauche forms (I_a and I_c) are present in preference to the other conformers at low temperature. Harris's group also reported that the interconversion of these forms occurs through either the cis or the trans paths. Schweig and collaborators[21] have studied the tetra-t-butyldiphosphine by variable temperature photoelectron spectroscopy and have reported a preference of the trans over the gauche forms. The difference in energy between these two conformers was reported as 0.5 kcal mol^{-1} at 25°C. However, our results agree with their findings regarding a probable free rotation via the trans path.

CONCLUSION

The Extended Huckel method has been applied in order to study barriers to internal rotation around the P—P bond in an analogous series of tetraalkyldiphosphines. Symmetrically substituted diphosphines are predicted to favour the gauche and/or trans conformers. The tetraalkyldiphosphines considered differ only in the bulk of the substituent. Consequently, the difference in their dynamic and static stereochemistry is expected to be mainly due to steric effects. The lone pair electron effects have been reported to be of a rather insignificant nature due to the remarkable consistency of the stereochemistry of tetraalkyldiphosphines and the analogous tetraalkyldisilanes.[22] Our results show that the tetraethyldiphosphine exists mainly in the gauche form whereas tetraisopropyldiphosphine is predicted to favour a possible cis conformer. Tetramethyl and tetra-t-butyldiphosphine are predicted to favour gauche and trans structures. It was also made evident that the repulsion between the lone pair of electrons on the P atoms becomes less important than steric effects as the alkyl groups become bulkier. The relative destabilization of the cis conformer of tetramethyldiphosphine is thus attributed to repulsions between the lone pairs of electrons (9 kcal mol^{-1}) whereas this destabilization in the case of tetra-t-butyldiphosphine is attributed mainly to steric effects (17 kcal mol^{-1}). West and co-workers[22] have actually shown that in the case of (symmetrical) hexa-t-butyldisilane, the bulk of the t-butyl substituent is responsible for the apparent stability of the gauche forms (in disilanes, there are no lone pairs of electrons). The anomalous result concerning the tetraisopropyldiphosphine can be attributed to the relative stability of structure (g). However, rotations around the C—P bond by 30° would result in an even less sterically hindered structure but it is our contention that the relative stability of the gauche structure and the corresponding angle will be retained even after the suggested 30° rotation around the C—P bond is used. This conclusion is based on our observation that even in the case of sterically hindered structures, the relative stability of the gauche conformers are consistently observed.

ACKNOWLEDGMENT:

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