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# An *ab initio* Investigation of Rotation and Inversion Barriers in Formylphosphine

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Rotation about N—CO bonds in amides has been extensively investigated, but a corresponding barrier to rotation about the P—CO bond in an acylphosphine has yet to be observed. In the present 4-31G *ab initio* study of formylphosphine, rotation barriers of 9.6 and 13.5 kJ mol$^{-1}$ and a phosphorus pyramidal inversion barrier of 108.0 kJ mol$^{-1}$ are predicted. A comparison of STO-3G and STO-3G* barriers suggests that polarization functions are not needed to describe rotation in this system.

*(Keywords: Acylphosphines; Formylphosphine; Inversion barrier; Rotation barrier)*

*Eine ab initio Untersuchung von Rotations- und Inversions-Barrieren in Formylphosphin*

Die Rotation um N—CO-Bindungen in Amiden wurde bisher intensiv untersucht, eine entsprechende Rotationsbarriere für Drehungen um die P—CO-Bindung in Acylphosphinen wurde jedoch nicht beobachtet. Eine 4-31G *ab initio*-Untersuchung an Formylphosphin ergibt Rotationsbarrieren von 9,6 und 13,5 kJ mol$^{-1}$ und eine pyramidale Inversionsbarriere von 108,0 kJ mol$^{-1}$ als Voraussage. Ein Vergleich der STO-3G und STO-3G* Barrieren legt nahe, daß Polarisationsfunktionen für die Beschreibung der Rotation in diesen Systemen nicht nötig sind.

## Introduction

Internal rotation about the N—CO bond in amides has been extensively investigated both by experimental[1] and computational[2] methods. In contradistinction, though pyramidal inversion at phosphorus has been well studied in the analogous acylphosphines[3,4], no experimental measurement of a rotation barrier about a P—CO bond has been reported. The present work was undertaken in order to provide a reliable estimate of the magnitude for such a barrier.

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In the absence of substantial steric or electronic factors, rotation barriers about P—C and N—C bonds are essentially the same, e.g., 8.2 and 8.3 kJ mol$^{-1}$ for methylphosphine[5] and methylamine[6], respectively. When steric factors are important, as illustrated by a comparison of the rotation barriers for *tert*-butyldichlorophosphine[7] and *tert*-butyldichloroamine[8] (27.2 and 39.3 kJ mol$^{-1}$, respectively), P—$X$ rotation barriers seem to be less strongly affected than their N—$X$ counterparts, as might be expected on the basis of the greater P—$X$ vs. N—$X$ bond distance[9]. However, as illustrated by a comparison[10] of the rotation barriers for phosphinoborane and aminoborane (27.2 and 139.3 kJ mol$^{-1}$, respectively), electronic factors are far more important in their effect on relative barrier heights. Evidently, (3p-2p)$\pi$ overlap and formation of partial $\pi$ bonds in P—C systems is energetically far less favorable than (2p-2p)$\pi$ overlap in the corresponding N—C systems[11].

Accordingly, P—C rotation barriers in acylphosphines are expected to be much lower than N—C rotation barriers in comparable amides. Rough estimates by two previous computational studies tend to bear this out. *Grikina* et al.[12], employing CNDO/2 at the sp, spd and spd′ level and using best-fit electron diffraction parameters for input structures, calculated rotation barriers for acetyldimethylphosphine of 2.1 to 46.0 kJ mol$^{-1}$, depending on the choice of the basis set. *Dougherty* et al.[4a], employing CNDO/2 and STO-3G, and using unoptimized geometries and a rigid rotor model, calculated an upper limit of 25 kJ mol$^{-1}$ for the rotation barrier in triformylphosphine. In both calculations, the estimated P—CO rotation barriers were thus found to be significantly lower than N—CO rotation barriers (ca. 83 kJ mol$^{-1}$ for monoamides[1,2] and ca. 30 kJ mol$^{-1}$ for a triacyclamine[13]), in accord with expectations.

In the calculations described in the present paper, we employed a 4-31G extended basis set and fully optimized geometries to compute the P—CO rotation barrier (as well as the phosphorus inversion barrier) in formylphosphine, the simplest representative of the class of acylphosphines. Our primary goal in using these higher level *ab initio* methods was to obtain estimates which could serve as a reliable guide in the selection of appropriate conditions and methods for the experimental determination of the elusive P—CO rotation barrier.

## Methods

Calculations were performed using GAUSSIAN 70[14] at the 4-31G level and GAUSSIAN 76[15] at the STO-3G and STO-3G* level. Structures were optimized by the force method at the 4-31G level[16,17] until an RMS gradient[18] of 0.005 mdyn or less was realized. Initial 4-31G SCF convergence problems were solved by using a density matrix generated from a converged SCF calculation on formylphosphine with P—C and C—O bond lengths frozen at 100 pm as the initial guess. The STO-3G* calculation on the ground state generated the MO coefficients used as the initial guess for all other STO-3G* calculations.

Table 1. *Bonding parameters of formylphosphine structures (bond lengths in pm; anglers in degrees)*

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| *Bond* | | | | | |
| P—C | 191 | 194 | 193 | 181 | 189 |
| C—O | 120 | 120 | 120 | 121 | 120 |
| C—$H_3$ | 108 | 108 | 109 | 108 | 108 |
| P—$H_1$ | 142 | 143 | 144 | 139 | 139 |
| P—$H_2$ | 143 | 143 | 144 | 139 | 139 |
| *Bond Angle* | | | | | |
| $H_1$—P—$H_2$ | 97.1 | 95.4 | 94.1 | 119.9 | 120.3 |
| $H_1$—P—C | 96.6 | 94.9 | 94.5 | 119.1 | 119.8 |
| $H_2$—P—C | 95.7 | 94.9 | 94.5 | 120.9 | 119.8 |
| P—C—O | 123.4 | 123.8 | 121.8 | 125.0 | 123.8 |
| P—C—$H_3$ | 115.2 | 115.1 | 117.1 | 112.4 | 114.9 |
| $H_3$—C—O | 121.3 | 121.1 | 121.1 | 122.5 | 121.2 |
| *Torsion Angle* | | | | | |
| $H_1$—P—C—O | −41.1 | 47.9 | −132.8 | 180 | −91.6 |
| $H_2$—P—C—O | −138.9 | −47.9 | 132.8 | 0 | 91.6 |
| $H_3$—C—P—$H_2$ | 44.5 | 132.1 | −47.3 | 0 | −88.4 |

## Results and Discussion

The calculated bonding parameters for the ground state (**1**) of formylphosphine and for the transition states to rotation (**2, 3**) and inversion (**4, 5**) are collected in Table 1 (see Fig. 1). All structures were completely optimized, **2-5** under the assumption of $C_s$ symmetry. The absolute and relative energies for **1-5** at the 4-31G, STO-3G, and STO-3G* level are listed in Tables 2 and 3.

To facilitate discussion, the results obtained for P—CO rotation and phosphorus inversion will be dealt with in separate subsections.

### *Rotation Barriers*

As shown by 4-31G calculations, the formyl group in **1** is close to planar, and approximately perpendicular to the plane defined by the P—C bond axis and the bisector of the H—P—H bond angle. In the transition states to internal rotation (**2, 3**), these two planes fuse into

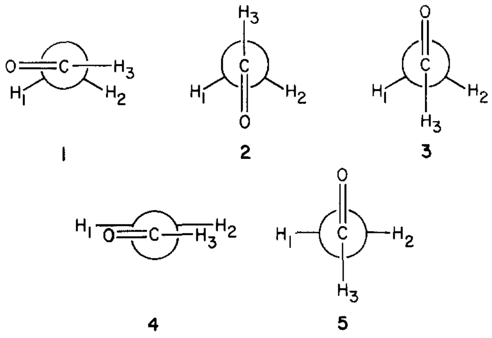

Fig. 1. Idealized schematic representation of formylphosphine structures. The view is along the C—P bond axis, from C to P

Table 2. *Absolute energies of formylphosphine structures (in Hartrees/molecule)*

| Structure | 4-31G | STO-3G | STO-3G* |
|---|---|---|---|
| **1** | —454.56944 | —449.85694 | —449.90772 |
| **2** | —454.56581 | —449.85205 | —449.90231 |
| **3** | —454.56431 | —449.85241 | —449.90432 |
| **4** | —454.52833 | —449.78125 | —449.81431 |
| **5** | —454.50484 | —449.75615 | —449.78584 |

Table 3. *Relative energies of formylphosphine structures (relative to the ground state* **1***; in kJ/mole)*

| Structure | 4-31G | STO-3G | STO-3G* |
|---|---|---|---|
| **2** | 9.6 | 12.8 | 14.2 |
| **3** | 13.5 | 11.9 | 8.9 |
| **4** | 108.0 | 198.7 | 245.2 |
| **5** | 169.6 | 264.6 | 320.0 |

the molecular symmetry plane (Fig. 1). For the conversion of **1** to **2** and to **3**, 4-31G calculations yield energy requirements of 9.6 and 13.5 kJ $mol^{-1}$, respectively (Table 3). Before we discuss the implications of these findings, we shall first comment on the trustworthiness of the calculated barriers.

Although few 4-31G *ab initio* calculations on phosphorus compounds have been reported in the literature[19, 20], the structure obtained for phosphine by complete geometry optimization at this level[20a] is reasonably good: calculated (observed[9]) P—H bond length 143.3 pm (142 pm); H—P—H bond angle 95.0° (93.8°). In addition, a comparison of our calculated bond lengths for **1** (Table 1) with related values found[21] by electron diffraction for acetyldimethylphosphine shows very good agreement: calculated (observed[21], average of models I and II) P—C bond length 191 pm (avg. 185.3 pm); C—O bond length 120 pm (avg. 121.9 pm). Other parameters compare well with standard values: calculated (standard[9]) P—H bond lengths 142–143 pm (142–143 pm); C—H bond length 108 pm (108–109 pm). While these results do not allow for a general discussion of 4-31G calculations on phosphorus compounds, they do suggest that our structures are reasonable.

One obvious drawback in using 4-31G in the study of acylphosphines is a lack of polarization functions on heavy atoms. Since STO-3G* places five d orbitals on phosphorus, we calculated STO-3G and STO-3G* rotation barriers for formylphosphine, using optimized 4-31G geometries. As shown by a comparison of the results (Table 3), the barriers so calculated differ by no more than 3 kJ $mol^{-1}$, suggesting that polarization functions may not be necessary in the description of rotation in this system.

Rigid rotor calculations[2] on the analogous formamide at the 4-31G level predict a rotation barrier of 103.3 kJ $mol^{-1}$ while the experimental value is only ca. 80 kJ $mol^{-1}$ [22]. If it is permissible to extrapolate from formamide to formylphosphine, this suggests that any systematic error in our calculations is likely to lead to an overestimation of the barrier height.

In addition to the fact that these calculations were not performed at the *Hartree-Fock* limit, correlation effects were also not considered. However, since such effects are expected to contribute at most 4 kJ $mol^{-1}$ to the rotation barrier in partial $\pi$ systems of the second period[23], we are confident that our results represent reasonable estimates of the rotation barriers in formylphosphine. In summary, our calculations predict that the mechanism of lowest energy (threshold mechanism) for internal rotation in formylphosphine corresponds to enantiomerization of **1** via **2**, with a barrier of ca. 10 kJ $mol^{-1}$. Because the rotation barrier in a triacylphosphine is not expected to be higher than that in a monoacylphosphine (by analogy to amide systems[13]), this result also yields a revised (i.e., lowered) upper limit to the calculated[4a] rotation barrier in triformylphosphine.

On the basis of our prediction, the experimental observation of hindered rotation in acylphosphines will therefore require the use of methods capable of measuring barriers below the range accessible by the dynamic NMR approach[1] at the current level of technology, e.g., microwave or infrared spectroscopy. These calculations do not, however, exclude the possibility that higher rotation barriers, capable of measurement by dynamic NMR, might be found for some derivatives of formylphosphine. Thus, although the threshold barrier calculated for formylphosphine in this work is consistent with the failure by *Kostyanovsky* et al.[24] to observe hindered rotation in the room temperature NMR spectrum of acetyldimethylphosphine (barriers of at least ca. 60 kJ mol$^{-1}$ are required for such an observation), and also with the results of a recent gas phase electron diffraction study[21] on the same compound, which are compatible with structures of the types **1**, **2**, or **3**, and which qualitatively suggest the possibility of a low barrier to interconversion between **1** and **2**, some disparities still remain. In particular, the average bond angle at phosphorus calculated for the ground state structure of formylphosphine (96.5°, see Table 1) is much less expanded than the corresponding angle of ca. 104° found[21] for acetyldimethylphosphine (see below); furthermore, a recent *Raman* and gas phase IR study of various acyldialkylphosphines[25] indicates ground state conformations of type **2** or **3**, rather than of type **1**. It is therefore conceivable that substitution on phosphorus or carbon in formylphosphine may change the shape of the potential energy hypersurface, and thus lead to changes in the structures of ground and transition states, as well as to changes in barrier heights.

## *Inversion Barriers*

The threshold mechanism for pyramidal inversion at phosphorus in formylphosphine corresponds to enantiomerization of **1** via **4**, with a calculated barrier of 108.0 kJ mol$^{-1}$ (Table 3). The magnitude of this barrier is in fair agreement with a previous CNDO/2 estimate[4a] of 119.6 kJ mol$^{-1}$. Also in qualitative agreement with previous reports[4], an alternative transition state to inversion (**5**) that does not allow $\pi$ orbital overlap between phosphorus and carbon (unlike **4**), is 61.6 kJ mol$^{-1}$ higher in energy than **4** (Table 3). Since it appears that the STO-3G basis set grossly overestimates inversion barriers[19], as also found in the present work (Table 3), a comparison between STO-3G and STO-3G* calculated inversion barriers, along the lines described above for rotation barriers, would have little significance.

A hybrid rotation-inversion mechanism[26] for the enantiomerization of **1** is rendered unlikely by the great disparity between the rotation and inversion barriers. The present work thus fully supports our view[3a, 27] that in acylphosphines the rate-limiting conformational process is inversion, in contrast to amides, where it is rotation.

A final word concerns the relation between ground state pyramidality in phosphines and the height of phosphorus inversion barriers. Though close to the "normal" bond angles of 93.8° and 98.6° found for phosphine[28] and trimethylphosphine[29], respectively, and to the 95.9° angle found for tribenzoylphosphine oriented in a nematic phase[30], the average bond angle of 96.5° calculated for formylphosphine differs significantly from the average angle of ca. 104° found[21] for acetyldimethylphosphine. The flattening of the phosphorus pyramid in the ground state may be regarded[4a, 21] as evidence for increased (3 p-2 p) $\pi$ overlap between the phosphorus lone pair and the carbonyl orbitals, an effect whose most dramatic manifestation is the substantial lowering of the inversion barrier in acylphosphines (ca. 60-120 kJ mol$^{-1}$)[3, 4], as compared to phosphine or trialkylphosphines (ca. 150 kJ mol$^{-1}$)[28]; a similar correlation between the ground state pyramidality in amines and nitrogen inversion barriers has been firmly established[31]. On the other hand, our earlier conclusion[27], that factors which have little or no effect on the ground state pyramidality of phosphorus are nevertheless capable of manifesting themselves in significant decreases in the inversion barrier, seems to be borne out by the normal values of the phosphorus bond angles in formylphosphine, tribenzoylphosphine, and trisilylphosphine (96.5°)[32], all of which are expected[27] to exhibit lowered phosphorus inversion barriers. Further experimental work in this area is clearly desirable.

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## References

[1] For example, *L. M. Jackman* and *F. A. Cotton*, Dynamic Nuclear Magnetic Resonance Spectroscopy, p. 204 ff. New York: Academic Press. 1975.

[2] For example, *L. Radom*, *W. A. Lathan*, *W. J. Hehre*, and *J. A. Pople*, Austral. J. Chem. **25**, 1601 (1972).

[3] Experimental: (a) *W. Egan* and *K. Mislow*, J. Amer. Chem. Soc. **93**, 1805 (1971); (b) *R. G. Kostyanovskii*, *Yu. I. El'natanov*, *L. M. Zagurskaya*, *K. S. Zakharov*, and *A. A. Fomichev*, Izvest. Akad. Nauk S.S.S.R., Ser. Khim. **1972**, 1891; (c) *R. G. Kostyanovskii*, *A. A. Fomichev*, *L. M. Zagurskaya*, and *K. S. Zakharov*, Izvest. Akad. Nauk S.S.S.R., Ser. Khim. **1973**, 1915; (d) *R. G. Kostyanovskii*, *Yu. I. El'natanov*, *K. S. Zakharov*, and *L. M. Zagurskaya*, Doklady Akad. Nauk S.S.S.R. **219**, 137 (1974).

[4] Computational: (a) *D. A. Dougherty*, *K. Mislow*, and *M.-H. Whangbo*, Tetrahedron Lett. **1979**, 2321; (b) *A. Rauk*, *J. D. Andose*, *W. G. Frick*, *R. Tang*, and *K. Mislow*, J. Amer. Chem. Soc. **93**, 6507 (1971).

[5] Experimental: *T. Kojima*, *E. L. Breig*, and *C. C. Lin*, J. Chem. Phys. **35**, 2139 (1961).

[6] Experimental: *D. R. Lide, jr.*, J. Chem. Phys. **27**, 343 (1957).

[7] Experimental: *C. H. Bushweller*, *J. A. Brunelle*, *W. G. Anderson*, and *H. S. Bilofsky*, Tetrahedron Lett. **1972**, 3261.

[8] Experimental: *C. H. Bushweller*, *W. G. Anderson*, *J. W. O'Neil*, and *H. S. Bilofsky*, Tetrahedron Lett. **1973**, 717.

[9] Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, pp. M43–M57. London: The Chemical Society Burlington House. 1958.

[10] Computational: *O. Gropen*, J. Mol. Struct. **36**, 111 (1977).

[11] *M. J. S. Dewar* and *P. Rona*, J. Amer. Chem. Soc. **91**, 2259 (1969).

[12] *O. E. Grikina*, *N. F. Stepanov*, *L. S. Khaikin*, *E. A. Bovina*, and *L. V. Vilkov*, J. Mol. Struct. **37**, 251 (1977).

[13] *E. A. Noe* and *M. Raban*, J. Amer. Chem. Soc. **97**, 5811 (1975).

[14] *W. J. Hehre et al.*, QCPE **11**, 236 (1973).

[15] *J. A. Pople et al.*, QCPE **11**, 368 (1978). Converted to the IBM version by *C. Cook*, Princeton University.

[16] *P. Pulay*, Mol. Phys. **17**, 197 (1969).

[17] *H. B. Schlegel*, Ph.D. Thesis, Queen's University, 1975.

[18] For example, *H. B. Schlegel*, *K. Mislow*, *F. Bernardi*, and *A. Bottoni*, Theoret. Chim. Acta **44**, 245 (1977).

[19] *A. H. Cowley*, *D. J. Mitchell*, *M.-H. Whangbo*, and *S. Wolfe*, J. Amer. Chem. Soc. **101**, 5224 (1979).

[20] For example, (a) *H. B. Schlegel*, *S. Wolfe*, and *F. Bernardi*, J. Chem. Phys. **63**, 3632 (1975); (b) *J. M. Howell*, J. Amer. Chem. Soc. **99**, 7447 (1977).

[21] *L. S. Khaikin*, *L. G. Andrutskaya*, *O. E. Grikina*, *L. V. Vilkov*, *Yu. I. El'natanov*, and *R. G. Kostyanovskii*, J. Mol. Struct. **37**, 237 (1977).

[22] *T. Drakenberg* and *S. Forsén*, J. Phys. Chem. **74**, 1 (1970).

[23] *P. W. Payne* and *L. C. Allen*, in: Applications of Electronic Structure Theory (*H. F. Schaefer III*), p. 29. New York: Plenum Press. 1979.

[24] *R. G. Kostyanovsky*, *U. V. Yakshin*, and *S. L. Zimont*, Tetrahedron **24**, 2995 (1968).

[25] *E. R. Razumova*, *Y. I. El'natanov*, *Sh. M. Shikhaliev*, and *R. G. Kostyanovskii*, Akad. Nauk S.S.S.R., Ser. Khim. **1978**, 85.

[26] For example, (a) *C. H. Bushweller*, *W. G. Anderson*, *P. E. Stevenson*, *D. L. Burkey*, and *J. W. O'Neil*, J. Amer. Chem. Soc. **96**, 3892 (1974); (b) *F. Bernardi*, *I. G. Csizmadia*, *A. Mangini*, *H. B. Schlegel*, *M.-H. Whangbo*, and *S. Wolfe*, J. Amer. Chem. Soc. **97**, 2209 (1975); (c) *C. H. Bushweller*, *W. G. Anderson*, *P. E. Stevenson*, and *J. W. O'Neil*, J. Amer. Chem. Soc. **97**, 4338 (1975); (d) *M. Raban* and *E. Carlson*, J. Amer. Chem. Soc. **93**, 685 (1971); (e) *S. Wolfe*, *L. M. Tel*, and *I. G. Csizmadia*, Canad. J. Chem. **51**, 2423 (1973); (f) *S. Wolfe*, *H. B. Schlegel*, *I. G. Csizmadia*, and *F. Bernardi*, J. Amer. Chem. Soc. **97**, 2020 (1975).

[27] *K. Mislow*, Trans. N. Y. Acad. Sci. **35**, 227 (1973).

[28] Experimental and computational: *J. M. Lehn* and *B. Munsch*, Mol. Phys. **23**, 91 (1972), and references therein.

[29] Experimental: *L. S. Bartell* and *L. O. Brockway*, J. Chem. Phys. **32**, 512 (1960).

[30] *A. Cogne*, *L. Wiesenfeld*, *J. B. Robert*, and *R. Tyka*, Org. Magn. Res., in press.

[31] *J. Stackhouse*, *R. D. Baechler*, and *K. Mislow*, Tetrahedron Lett. **1971**, 3437.

[32] Experimental: *B. Beagley*, *A. G. Robiette*, and *G. M. Sheldrick*, J. Chem. Soc. **A 1968**, 3002.