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Conformation Analysis of Diphosphine

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Extended basis set *ab initio* computations are performed on HF, PNO-CI and CEPA level to determine the structure of P_2H_4 and the potential curve $E(\varphi)$ for rotation around the P-P axis. The structure parameters are optimized for dihedral angles φ of 0° (cis), 50°, 80° (gauche or semi-eclipsed), 130°, and 180° (trans). It turns out that P_2H_4 has a gauche equilibrium structure, a local minimum for trans which is ≈ 2.5 kJ/mol above gauche, a rather large cis barrier of ≈ 20 kJ/mol and a gauche → trans barrier of ≈ 3.5 kJ/mol. The potential $E(\varphi)$ is extremely flat in the region $50° < \varphi < 310°$, where $E(\varphi)$ varies by less than 5 kJ/mol. Electron correlation tends to reduce the barriers but has no drastic effect on $E(\varphi)$.

Key words: P_2H_4, conformation analysis of ~

1. Introduction

Experimental studies of gaseous diphosphine, P_2H_4, by means of vibrational [1] electron diffraction [2] and microwave [3] investigations indicated that the gauche conformer is most stable. These experiments left some open questions, however. Beagley *et al.* [2] note that their electron diffraction results did not rule out a mixture of several isomers or free rotation around the P-P axis. The microwave work of Durig *et al.* [3] could not exclude the presence of small amounts of trans P_2H_4. In a recent vibrational study of P_2H_4 and P_2D_4 - which appeared after completion of the computations to be presented in this work - Odom *et al.* [4] conclude that only the gauche conformer exists in both solid and gas phase. The Raman spectrum of liquid diphosphine appears to be compatible with the gauche and the trans structure [5].

It has been impossible until now to obtain (from experiments) information on the quantitative behaviour of the potential as a function of the dihedral angle φ (rotation around P-P axis). Such information can so far only be obtained from quantum mechanical computations.

Ab initio HF level computations for P_2H_4 have been reported by Absar *et al.* [6] and by Wagner [7] - who also demonstrated that the semi-empirical CNDO method does not yield reliable barrier heights in this case. Wagner [7] predicts the trans conformer to be insignificantly more stable than the gauche by about 0.4 kJ/mol, whereas Absar *et al.* obtain gauche as the most stable conformer. No attempt was made for a thorough conformation analysis in these theoretical studies, however. The dependence of the energy on the dihedral angle was computed under the simplified assumption that the remaining structure parameters are identical for all φ. The structure parameters actually used were based on reasonable assumptions, no attempt for a theoretical determination is reported and reliable experimental data were not available at that time.

We further note that both previous theoretical studies [6, 7] use a small Gaussian basis in which only a single GTO is available to represent the valence $3s$ and $3p$ AOs on P.

The conformation analysis reported in this work is based on extended basis set computations which go beyond the HF approximation and include effects of electron correlation. Extensive structure optimizations were performed to determine "equilibrium geometries" for various different dihedral angles.

2. Method of Computation

The correlation energy is calculated by means of PNO-CI [8, 9] and CEPA [9, 10] computations. A detailed description of these methods and of the technical details of the computer programs used has been given elsewhere [11, 12]. For this reason we just mention that PNO-CI denotes a CI computation which includes the HF wave function and the doubly substituted configurations on the basis of pair natural orbitals (PNOs) [12]. Within the CEPA (Coupled Electron Pair Approximation) one further accounts in an approximate way for the effects of higher substituted configurations.

The inner shells of phosphorous ($1s^2$, $2s^2$, $2p^6$) were left uncorrelated in the present investigations. The occupied valence shell MOs were localized according to Boys' method [13]. This helps to save a considerable amount of computer time, at least for the present program version, and facilitates the interpretation of correlation energies.

The following contracted GTO basis set was used

P: ($10s$, $7p$, $1d$) contracted ($6s$, $4p$, $1d$)
H: ($4s$, $1p$) contracted ($2s$, $1p$).

The ($10s$, $7p$) set on P and the $4s$ for H were taken from Huzinaga's tables [14]. The respectively steepest Gaussians were contracted with coefficients as in the $1s$, $2p$ HF-AOs of P and the $1s$ AO of H. The same orbital exponent, $\eta = 0.55$, was taken for the d set on P and the p set on H. Functions of p- and d-type are constructed from lobes as described elsewhere [15]. Our basis set is thus of the type "double zeta plus polarization functions", since we have two adjustable linear parameters for each occupied AO and, in addition, a set of polarization functions.

It has been claimed in the previous studies [6, 7] on P_2H_4 that d functions on P are of little importance. Lehn and Munsch, however, have reported a careful extended basis set investigation [16] of the inversion of PH_3 which showed a strong influence of polarization functions on equilibrium geometries, the inversion barrier and other molecular properties. Although the internal rotation of diphosphine and inversion of phosphine are not directly comparable, the results of Lehn and Munsch indicate that care is recommended.

The selection of the s and p basis functions on P has been made on the following grounds. The behaviour of $E(\varphi)$ - energy as a function of rotation angle - depends crucially on the P-P distance (larger P-P distances favour the trans conformer). As r(PP) is known very precisely from the microwave measurements of Durig *et al.* [3], we could check whether or not a given basis is flexible enough to reproduce the correct r(PP). The $10s$, $6p$ basis contracted ($6s$, $3p$), fails in this respect since it yields $r(\mathrm{PP}) = 2.3$ Å, which is 0.1 Å too large. The basis set specified above reproduced the experimental $r(\mathrm{PP}) = 2.219$ up to 0.011 Å.

3. Determination of Structure Parameters

In order to compute the energy of diphosphine as a function of the dihedral angle φ we first had to determine the corresponding structure parameters. This was done on the HF level. We did not include functions of $p\pi$ type - with respect to the P-H axis - on H in these computations. The contribution of these functions to the HF energy amounts to 10^{-3} a.u. only and is virtually constant.

To get an idea of the accuracy required in the determination of structure parameters, we note that the following distortions out of the equilibrium lead to an increase of 10^{-4} a.u. ≈ 0.25 kJ/mol in the energy

$$\Delta r(\mathrm{PP}) \approx 0.02\ \text{Å} \tag{1}$$

$$\Delta r(\mathrm{PH}) \approx 0.004\ \text{Å} \tag{2}$$

$$\Delta \angle \mathrm{PHP} \approx 1.4^\circ \tag{3}$$

$$\Delta \angle \mathrm{PPH} \approx 1.4^\circ \tag{4}$$

(2) refers to a simultaneous change of all four P-H distances and (3) and (4) to a simultaneous change of the corresponding two identical angles, in C_2 molecular symmetry.

Pilot calculations showed that $r(\mathrm{PH})$ varies by 0.0015 Å at most for different conformers. We therefore used

$$r(\mathrm{PH}) = 1.399\ \text{Å} \tag{5}$$

for all cases, which is optimal for $\varphi = 80^\circ$.

We further found only minor variations of the HPH angles which scattered around 95° by 0.6 at most. We consequently used

$$\angle \mathrm{HPH} = 95^\circ \tag{6}$$

in the further computations.

The remaining structure parameters were determined by a chain optimization. The accuracy is certainly better than indicated in (1)-(4), within the given basis set and within the HF approximation, of course. The use of even larger basis sets and inclusion of correlation effects for the determination of structure parameters is prohibitive by virtue of the enormous requirements of computation time.

4. Results and Discussion

We have considered dihedral angles φ of 0° (cis), 80° (pilot calculations indicated $\varphi \approx 80^\circ$ for the gauche structure), 180° (trans) and further 40° and 130° which are in between gauche and cis or trans respectively. The optimized structure parameters as well as the HF, PNO-CI, and CEPA energies are collected in Table 1 and shown in Fig. 1.

Table 1. Geometry, energy and dipole moment of P_2H_4 as function of dihedral angle φ[a]

				Energy [kJ/mol][b]			
φ	r(PP) [A]	$\angle$PPH$_1$	$\angle$PPH$_2$	HF	PNO-CI	CEPA	μ[D]
0 (cis)	2.275	95.3	95.3	21.2	19.2	17.7	1.51
40	2.244	96.0	99.0	8.5	7.9	7.5	1.42
80 (gauche)	2.230	95.6	100.0	0.0	0.0	0.0	1.20
130	2.244	96.7	97.5	4.3	3.6	3.0	0.67
180 (trans)	2.249	94.3	94.5	3.9	2.5	1.5	0.0
m.w.[c] 74.0 ± 2.2	2.2191 ± 0.0004	94.3 ± 0.2	99.1 ± 0.1				0.93
e.d.[d] 81 ± 8	2.218 ± 0.004	95.2 ± 0.6	95.2 ± 0.6				–

[a] Remaining structure parameters were kept constant: r(PH) = 1.399, $\angle$HPH = 95°, see text.

[b] Relative to gauche, the total energies for gauche are, in a.u., HF: −683.63684, PNO-CI: −683.88514, CEPA: −683.91731.

[c] Microwave results [3], remaining structure constants: r(PH) = 1.414 ± 0.002; r(PH′) = 1.417 ± 0.002 (H′ denotes the nearly eclipsed hydrogen), $\angle$HPH = 92.0 ± 0.8°.

[d] Electron diffraction results [2], remaining structure parameters: r(PH) = 1.451 ± 0.005, $\angle$HPH = 91.3 ± 1.4°.

The energy barrier curves $E(\varphi)$ show the same general behaviour in all degrees of approximation, HF, PNO-CI, and CEPA:

1) extremely small variations of less than 5 kJ/mol in the range $50° < \varphi < 310°$,
2) an absolute minimum for the gauche structure,
3) a shallow local minimum for trans which is roughly 2.5 kJ/mol higher in energy than gauche,
4) a rather large cis barrier of ≈ 20 kJ/mol,
5) a small barrier of ≈ 3.5 kJ/mol between gauche and trans.

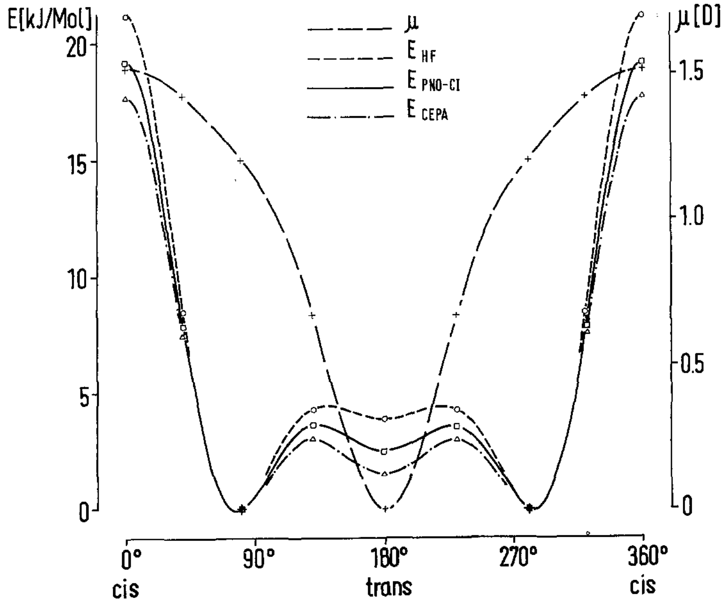

Fig. 1. Dipole moment μ and energy barrier curve – on HF, PNO-CI, and CEPA level – of P_2H_4 as a function of rotation angle φ

Inclusion of electron correlation tends to reduce the barrier heights as can be seen from Fig. 1. We make the following comment on the deviation between the PNO-CI and the CEPA curves. As the PNO-CI neglects all higher than doubly substituted configurations, it certainly underestimates slightly the correlation effects [9, 10]. These higher substituted configurations are included in the CEPA in an approximate way. Due to the approximations made [9, 10], the present version of the CEPA appears to overestimate the correlation energy. The correct energy curve $E(\varphi)$ - within the given basis set - should thus be in between the PNO-CI and CEPA, probably closer to the CEPA.

We have fitted the computed $E(\varphi)$ to an analytic function of the form

$$E(\varphi) = \sum_{m=0}^{4} a_m \cos(m\varphi). \tag{7}$$

The results for a_m are given in Table 2 for the HF, PNO-CI and CEPA energies and the dipole moment. A fit which included terms $\cos(m\varphi)$ up to and including $m = 3$ only leads to rather large maximal deviations of 0.4 kJ/mol between computed energies and the analytic expression corresponding to the r.h.s. of Eq. (7). The computed curves show in fact a "periodic" behaviour between 130° and 230°, and such a "local" periodicity of $\approx 100°$ can only be described if the term $\cos(4\varphi)$ is included, at least. From the analytic expression (7), with a_m taken from Table 2, we obtain the following dihedral angles φ_0 for the most stable conformer (gauche) in the corresponding approximations

$$\text{HF:} \quad \varphi_0 = 76° \tag{8}$$

$$\text{PNO-CI:} \quad \varphi_0 = 77° \tag{9}$$

$$\text{CEPA:} \quad \varphi_0 = 78° \tag{10}$$

These results are in surprisingly close agreement - by virtue of the general "flatness" of $E(\varphi)$ - with the dihedral angle obtained from the microwave experiments [3]: $\varphi_0 = 74 \pm 2.2°$. Almost perfect agreement is also found for r(PP), r(PH) and the PPH angles, where deviations are less than 0.015 Å and 1.3° respectively, see Table 1, if we compare the theoretical results for $\varphi = 80°$ with the experimental ones [3]. The only noticeable disagreement concerns ∠HPH, where the theoretical result, 95°, is 3° larger than the experimental one: 92.0 ± 0.8°. This should have no marked influence on $E(\varphi)$, however.

The variation of r(PP) with φ is in accordance with the change of $E(\varphi)$, since the shortest (longest) P-P distance is found for the most stable (unstable) conformation. The difference in the PPH angles for the gauche structure - the larger angle corresponds to the "eclipsed" hydrogen atoms - seems to indicate a repulsion between the PH bonds. This

Table 2. Fourier coefficients of energy and dipole moment for internal rotation in P_2H_4 [a]

	Energy [kJ/mol]			
	HF	PNO-CI	CEPA	μ[D]
a_0	6.014	5.262	4.694	0.967
a_1	5.032	5.018	5.037	0.666
a_2	5.931	5.129	4.570	−0.190
a_3	3.618	3.332	3.063	0.089
a_4	0.624	0.459	0.335	−0.022

[a] As obtained from a fit of the corresponding quantities given in Table 1 to the analytic expression (7).

effect could also be caused by a change in hybridization which results from the repulsion between the lone pairs. The independent optimization of the two PPH angles is of decisive importance, since the energy for the gauche conformer is raised above that of trans if we use identical PPH angles.

The dipole moment computed from the HF wave function for the $\varphi = 80^\circ$ conformer, $\mu = 1.20$ D, is in rather poor agreement only with the experimental result [3] (for P_2D_4), $\mu = 0.928$ D. This deviation had to be expected, however, since dipole moments are in general more sensitive with respect to small changes in the basis set and the structure parameters than total energies.

We finally mention that all theoretical results refer to fixed nuclear positions whereas the experimental results correspond to averages over zero point vibrations (or even thermal averages if kT is in the order of lowest vibrational excitations) and are not directly comparable. As $E(\varphi)$ is a slowly varying function with quite unharmonic behaviour in the neighbourhood of the gauche structure, it is conceivable that zero point vibrations give rise to non-negligible effects.

5. Conclusions

The theoretical investigations reported in this study first of all show the gauche conformer of P_2H_4 to be most stable. The energy $E(\varphi)$ as a function of the dihedral angle has a shallow minimum for the trans structure, but a localized wave packet, say between 150° and 210°, would have an energy $\gtrsim 1$ kJ/mol, which is roughly the same as the trans → gauche barrier. This means that the gauche conformer only is present in the gas phase. Our results therefore confirm the results of recent microwave and vibrational studies which arrived at the same conclusion [3, 4].

We have decided not to analyse wave functions or to decompose total energies in order to explain the behaviour of $E(\varphi)$, since none of the methods available for this purpose appears, at present, to be accurate enough to give a reliable interpretation of the small variations of $E(\varphi)$.

We point out, however, that the qualitative features of the barrier curve $E(\varphi)$ for P_2H_4 - as distinguished from N_2H_4 - may be explained from the hybridization of valence AOs. We consider for this purpose the limiting cases of

1) an sp^2 hybridization with pure p^2 lone pair and
2) pure p-type valence AOs with an s^2 lone pair.

$E(\varphi)$ is dominated in the first case by the repulsion between the lone pairs caused by the Pauli principle. We then expect $E(\varphi) \sim \cos(2\varphi)$, with minima at 90° and 270° and maxima for cis, $\varphi = 0^\circ$, and trans, $\varphi = 180^\circ$. If the lone pair AOs are of s-type, as in case 2), they should have no influence on $E(\varphi)$, which is now determined by the interaction of AH bonds. Consequently we expect the following characteristics of $E(\varphi)$: an absolute minimum for $\varphi = 180^\circ$ (trans or staggered), a local maximum for $\varphi \approx 90^\circ$ (semi-eclipsed), a local minimum for gauche, $\varphi \approx 45^\circ$, and the total maximum for cis. Furthermore the barriers should be smaller than for case 1).

As P_2H_4 should be closer to case 2) (more p character of valence AOs) than N_2H_4, we expect the following changes of $E(\varphi)$ in going from N_2H_4 to P_2H_4, which are all in agreement with the present results of P_2H_4 and those of earlier studies of N_2H_4 [7, 17-19]:

1) smaller barriers for P_2H_4 than for N_2H_4;

   P_2H_4: $\Delta E \approx 20$ kJ/mol,

   N_2H_4: $\Delta E \approx 50$ kJ/mol;

2) relative stabilization of the trans structure, the trans barrier is roughly 40% of the cis barrier in N_2H_4 but only about 20% in P_2H_4, and there seems to be no local minimum for trans N_2H_4;

3) a shift of the gauche minimum to a smaller dihedral angle φ_0 (the shift is from 90° to 45° in the limiting cases),

   N_2H_4: $\varphi_0 \approx 94°$, P_2H_4: $\varphi_0 \approx 78°$.

We finally mention that the theoretical investigation of diphosphine proved to be much more difficult and tedious than anticipated. As the energy barrier curve $E(\varphi)$ depends crucially on the P-P distance and on the PPH angles, we had to use extended basis sets and had to optimize all structure parameters to compute $E(\varphi)$ accurately.

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