

**Figure 13.** Model for dihexanoyl-PC micelles based on SANS contrast variation results. The orientation of the dihexanoyl-PC is based on truncating the chains of crystal structures of dilauryl-PC and dimyristoyl-PC (i.e., all *trans* chains tilted with respect to the surface normal). The glycerol backbone and carbonyls are not included in the hydrocarbon core.

means that about half of the terminal methyls are in the surface layer. This is in contrast to the more ordered behavior (as monitored by neutron diffraction) of terminal methyl groups in dipalmitoyl-PC bilayers in the liq. cryst. phase.<sup>42</sup> A degree of ordering of the hydrocarbon chain in the core region does exist, but certainly the terminal methyls are not packed closely in the center of the hydrocarbon core.

### Conclusions

The SANS results of the structure of dihexanoyl-PC micelles can be summarized in the following five main points:

1. The micellar structure of this short-chain lecithin can be well represented by a prolate ellipsoid with two uniform regions. From the radii of gyration from external and internal contrast variation measurements, we have determined uniquely the radii of gyration for the two regions: the region consisting of the fatty acyl chains has a radius of gyration of  $11.8 \pm 0.2$  Å, and the region containing the hydrophilic head groups has a radius of gyration of  $18.4 \pm 0.3$  Å.

2. The hydrocarbon tails for a close-packed core of a spheroidal shape have a minor axis equal to the fully stretched tail length 7.83 Å and a major axis equal to 23.95 Å. The head groups are distributed in a shell region surrounding the hydrocarbon core with a shell thickness of 10 Å in the direction of the minor axis and 6 Å in the direction of a major axis. This structural model satisfactorily predicts the entire  $Q$  dependence of the SANS spectra at various contrast conditions. The space between the

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hydrophilic head groups is considerably larger in a micelle structure ( $102 \text{ \AA}^2$  per head group) than in a monolayer structure ( $65 \text{ \AA}^2$  per head group<sup>4</sup>). This may in part explain why these micelle aggregates are much better substrates for phospholipases than lecithin bilayers. With the larger area per head group, the phospholipase presumably has better access to the substrate. The thickness of the hydrophilic shell region implies that the head group must have an orientation parallel to the surface of the hydrocarbon core. This model for the dihexanoyl-PC molecule is schematically shown in Figure 13.

3. Dihexanoyl-PC micelles were found to be monodispersed in the whole concentration range studied. The aggregation number remains at  $19 \pm 1$  throughout the range from 0.027 to 0.361 M. We have confirmed that dihexanoyl-PC micelles do not grow with increasing concentrations,<sup>4</sup> in contrast to most micelles.<sup>28</sup>

4. The interaction between dihexanoyl-PC micelles was found to be attractive at all concentrations. It can be modeled successfully by an effective potential of the form of a hard core plus an attractive Yukawa tail. The parameters characterizing the interaction were determined from fitting the SANS spectra at different concentrations with the micellar interaction model. A constant effective core diameter of 51 Å was found that could be explained well by considering the micellar structure together with the effect of a hydration layer. The strength of the attraction turns out to be between 1 and  $2 k_B T$ , which is comparable to the magnitude of the Hamaker constant. The decay length of the attraction is about 3.64 Å, which is of the order of the size of the solvent molecule. This result suggests that the structure of the solvent around the interface may be important in determining the effective interaction between micelles.

5. The distribution of the fatty acyl chain terminal methyl groups in the hydrophobic core was studied by comparing the radius of gyration of the di(hexanoyl-*6,6,6-d*<sub>3</sub>)-PC to that of proteodihexanoyl-PC micelle. There is no preferential ordering near the center of the micelle. Instead, the terminal methyls are distributed in the whole core with a slightly higher probability toward the center. Such a highly disordered structure is, in fact, consistent with spectroscopic studies of these micelles.

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## Communications to the Editor

### On the Stability of the PdH<sub>2</sub> Molecule

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The  $\text{Pd}(4d^{10}5s^0, ^1S) + \text{H}_2(^1\Sigma_g^+) \rightleftharpoons \text{PdH}_2$  reaction has been studied for the  $C_{2v}$  symmetry by several authors.<sup>1-3</sup> They agree

that a weakly bound  $^1A_1(C_{2v})$  palladium dihydride if formed without any appreciable activation barrier for this side-on approach of H<sub>2</sub> on the ground state Pd atom. No theoretical studies exist, to our best knowledge, for the alternative head-on approach of H<sub>2</sub> on the same Pd state that could in principle lead to a Pd-H-H dihydride where the H atom moieties would *not* be equivalent for the IR absorption bands of this complex, as would be the case of the side-on complex.

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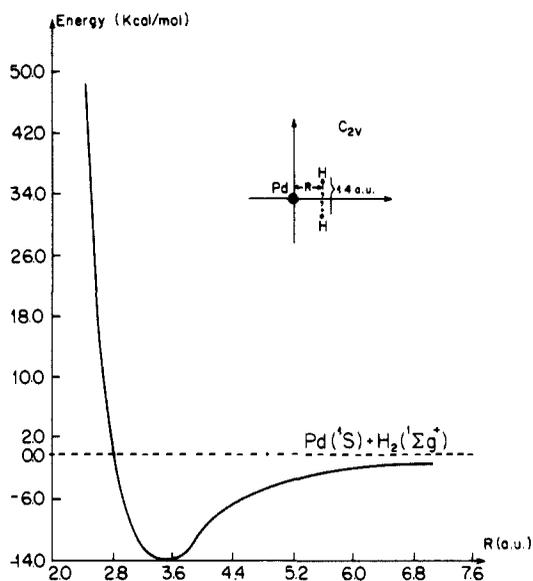


Figure 1. Relative energy as a function of the Pd-H<sub>2</sub>-midpoint distance for the side-on reaction.

Here we address a series of theoretical calculations to both the side-on and head-on approaches for the ground-state  $\text{Pd} + \text{H}_2 \rightleftharpoons \text{PdH}_2$  reaction. Our calculations are of the molecular orbital type including the valence electron correlation effects that have been found to be fundamental in the description of transition-metal-H<sub>2</sub> interactions.<sup>4</sup> For the Pd atom we used the model potential method of Barthelat, Durand, and Serafini.<sup>5</sup> The correlation effects were studied through full-configuration interaction (CI) calculations using the CIPSI program described in ref 6. This program performs both variational and perturbational CI calculations. In the present case the variational configuration space is composed of 15 determinants and is used as zeroth order function for a second-order perturbative scheme which in turn includes of the order of  $10^5$  configurations. The Pd pseudopotential and basis set (of double- $\zeta$  quality) have been already reported elsewhere<sup>7,8</sup> while the double- $\zeta$  plus polarization basis set used for H has also been reported elsewhere.<sup>9</sup>

The results obtained with this method for the side-on approach of the H<sub>2</sub> molecule to the Pd atom are reported in Figure 1. We see that no activation barrier is observable, the energy diminishing steadily as the H<sub>2</sub> approaches Pd even when, as in Figure 1, the H-H distance is fixed at its equilibrium value for isolated hydrogen. This energetic stabilization continues until a deep well of more than 14 kcal/mol is reached for a Pd-H<sub>2</sub> midpoint separation of 3.38 au. This all coincides quite well with previous studies of the side-on Pd-H<sub>2</sub> reaction,<sup>1-3</sup> and in fact our equilibrium separation between the Pd and H<sub>2</sub> moieties is quite similar to that reported by Low and Goddard<sup>2</sup> and only slightly shorter than that of ref 1. Our well depth is deeper than theirs, predicting a somewhat more stable situation than previously<sup>1-3</sup> assumed. We, however, did some tests for the basis set superposition effects which were found to be important<sup>1</sup> for this system and which furthermore has been shown to be large for other calculations of our own group using the very same basis set and model potential for systems like Pd-Pd<sup>10</sup> and Pd-ethylene.<sup>7</sup> We consequently calculated the CI counterpoise<sup>11</sup> corrections to the results of our Figure 1. The overall superposition error is found to be approximately 4 kcal/mol

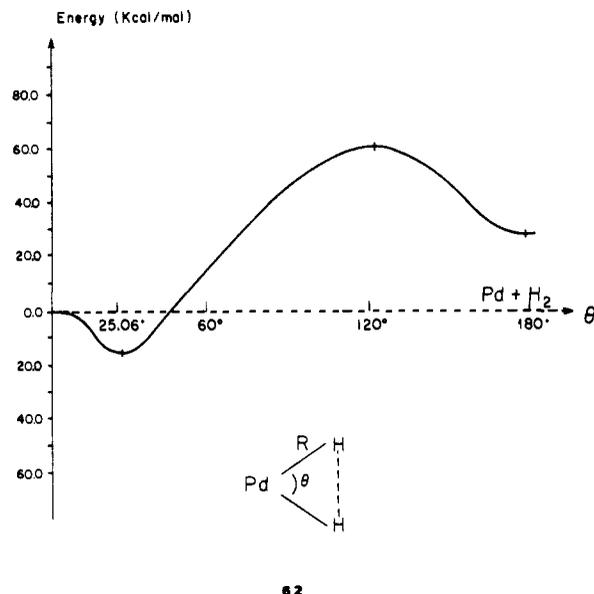


Figure 2. Relative energy as a function of the H-Pd-H angle  $\theta$  for the side-on reaction.

and the binding energy then becomes of the order of 10 kcal/mol. If we further allow for H-H bond relaxation within the PdH<sub>2</sub> side-on complex as shown in Figure 2 the energy can still stabilize a little bit more, although not very significantly. This stems from the fact that the minimum for the HPdH angle appears at a very small angle of 25.1° (Goddard and Low<sup>2</sup> report a similar value of 26°) which implies that the H-H distance is only stretched by a tenth of an atomic unit. For larger angles the energy shoots up and only goes down again approaching the linear H-Pd-H structure, as Figure 2 shows. This secondary minimum at 180° is of very limited interest, however, as it lies 26.4 kcal/mol above the dissociation limit and separated from the absolute minimum by a large energy barrier of more than 40 kcal/mol. The overall information that Figure 2 gives us then is that while Pd captures H<sub>2</sub> easily in a side-on reaction it does *not* provoke the scission of the H-H bond. This is in complete contrast with the Cu + H<sub>2</sub> side-on reaction for instance.<sup>9</sup> This contrasting H<sub>2</sub> activation by Pd as compared to Cu, Pt, Ag, and other metals will be discussed elsewhere.<sup>12</sup>

In any case we see from Figures 1 and 2 that a relatively stable and in principle observable side-on Pd dihydride complex is formed, at a Pd-H<sub>2</sub> distance of 3.38 au, Pd-H bonds of 3.46 au, H-H bond of 1.50 au, and HPdH angle of 25.1° with a binding energy of over 10 kcal/mol. All of this predicts the existence of a "ligand-free" molecular dihydride complex involving a transition metal like Pd. Experimental results showing transition-metal atom dihydrides *with* other ligands are becoming common,<sup>13</sup> but to our knowledge no direct observation of ligand-free Pd-dihydride complexes existed until the recent work of Ozin et al.<sup>14</sup> inspired by the present calculations. In their matrix isolation experiments they are able to conclusively infer from the infrared band structure the existence of a stable Pd-H<sub>2</sub> complex with side-on structure (i.e., with C<sub>2v</sub> symmetry) for which both hydrogen moieties are exactly equivalent when Pd and H<sub>2</sub> are deposited in solid Xe matrices at 10-12 K. The <sup>1</sup>A<sub>1</sub> (C<sub>2v</sub>) symmetry is established from isotopic mixture experiments using H<sub>2</sub>, HD, and D<sub>2</sub>.<sup>14</sup> In short all of these matrix isolation experiments fully confirm our results for the side-on reaction.

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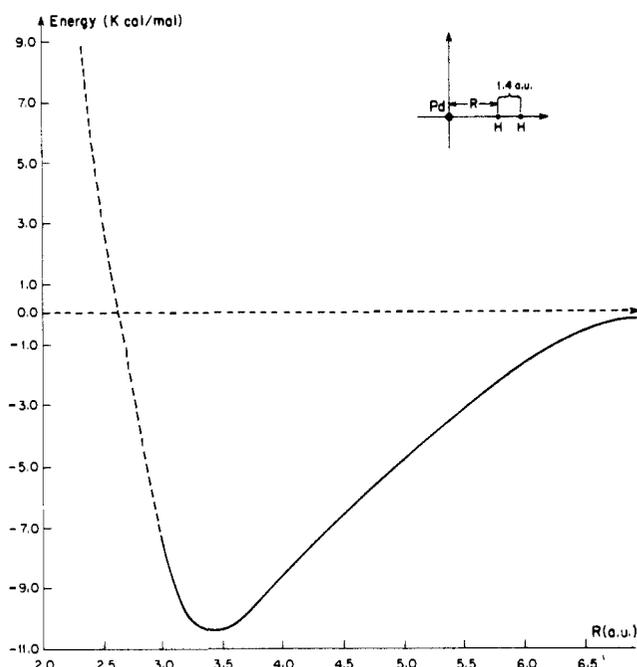


Figure 3. Relative energy as a function of the distance between Pd and the closest H atom in  $H_2$  for the head-on reaction.

Interestingly, the very same experiments were carried out in ref 14 using Kr matrices for the reaction products of Pd atoms with  $H_2$ , HD, and  $D_2$  under exactly equivalent matrix isolation conditions as for the case of Xe matrices. Surprisingly enough they found that the lines for the HD reactant presented additional splitting of the IR bands implying "two inequivalent hydrogen sites for a bound dihydrogen moiety attached to a Pd atom". This is of course incompatible with a  $C_{2v}$  (i.e., side-on)  $PdH_2$  molecule. This experimental situation can be understood, however, by proposing a head-on reaction of Pd and  $H_2$  where one of the H atoms is preferentially interacting with Pd over the other one. One such case is a linear  $Pd\cdots H-H$  approach just as that represented in our CI potential energy curve depicted in Figure 3. We see that the head-on approach of  $H_2$  on Pd is also free from any activation barrier and leads to a bound  $Pd-H-H$  dihydride complex where the H-H bond is not relaxed and the distance between the Pd and the nearest H atom is 3.39 au. This structure has a well depth of slightly more than 10 kcal/mol, which is quite similar to that of the side-on structure. This confirms one of the hypotheses advanced in ref 14 to explain the simultaneous existence of side-on (for Xe matrices) and head-on (for Kr)  $PdH_2$  complexes, i.e., that both structures must have very similar binding energies in order for the small matrix changes to alter the mode of dihydride coordination from side on to head on and vice versa. This is further reinforced by recent experiments<sup>15</sup> not yet reported where both head-on and side-on structures may be observed in a single rare gas matrix (at least in the case of Kr).

Finally we would like to mention that the present results may also have relevance for  $H_2$  adsorption and interactions with Pd clusters. A very interesting study on this problem has recently been published by Pacchioni and Koutecký,<sup>16</sup> where they, however, show that in clusters an "intermediate" Pd state (between  $d^{10}$  and  $d^9s^1$ ) is found. Going back to the isolated Pd atom reaction, on the other hand, we must stress that both the present calculations as well as the experimental data of Ozin et al.<sup>14</sup> clearly point out to a pure  $d^{10}$  ground-state reaction.

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## Topological Dichotomy in the Ring Inversion of [N.8.8](2,1,4)Cyclophanes: Implications for Stereochemical Definition of Hosts<sup>1</sup>

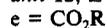
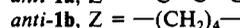
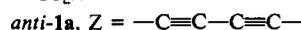
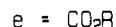
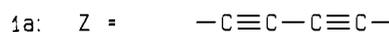
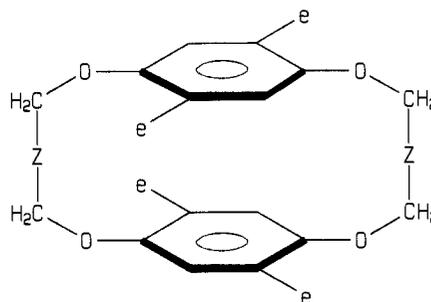
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There is considerable interest in cavity-based host-guest chemistry with respect to "artificial enzymes".<sup>2</sup> To probe the dynamics of guest insertion into molecular cavities, we have studied the syn-anti interconversion of **1**.<sup>3</sup> Passage of the ester appendage through the cavity depends on cavity rigidity (**1a** vs. **1b**) and



especially on the flexibility of the ester's alkyl chain.<sup>3b</sup> We now describe a related interconversion of "bicyclic" cyclophanes (Scheme I) which differs from that above, in requiring concerted disrotation of the arene rings.

For discussion, we postulate two limiting mechanisms: a "donut-hole" process wherein the diester chain threads through the cavity (Scheme I, A) and a "jump rope" process wherein the diester chain whips around the end of the molecule (B).<sup>4</sup> We find that the inversion mechanism depends on the length ( $n$ ) of the spanning diester.

The following hypotheses were tested: (a) For small  $n$ , the donut-hole mechanism should hold. Rates should be lower than for analogous processes in **1**. (b) For large  $n$  the jump rope mechanism should hold. High rates should be observed for sufficiently large  $n$ , as then only a hydrogen-substituted edge of a benzene ring passes through the cavity. (c) The jumprope process should be relatively favored by the more compact flexible series **3-n**. The donut-hole process, however, should be relatively favored by the rigid series **2-n**, as was observed for **1**.<sup>3</sup>

(1) Dedicated to Professor Donald J. Cram on the occasion his 65th birthday.

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(4) This distinction is relative, in that the jump rope process involves donutlike passage of the dioxaoctadiyne unit: "One boy's donut is another boy's jump rope" (Whitlock, B. J., personal observation).