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 preferently interacting with Pd over the other one. One such case is a linear Pd---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[15] 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,[16] where they, however, show that in clusters an "intermediate" Pd state (between d^{10} and d^{9}s^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.[14] clearly point out to a pure d^{10} ground-state reaction.

(15) Ozin, G. A., private communication.
(16) Pacchioni, G.; Koutecký Surf. Sci. **1985**, *154*, 126.

Topological Dichotomy in the Ring Inversion of [*N*.8.8](2,1,4)Cyclophanes: Implications for Stereochemical Definition of Hosts[1]
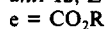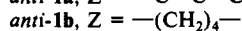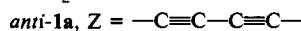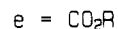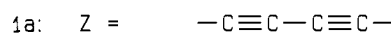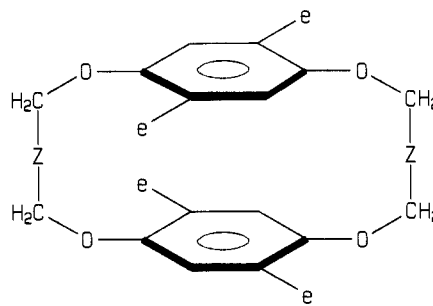
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There is considerable interest in cavity-based host–guest chemistry with respect to "artificial enzymes".[2] To probe the dynamics of guest insertion into molecular cavities, we have studied the syn–anti interconversion of **1**.[3] Passage of the ester appendage through the cavity depends on cavity rigidity (**1a** vs. **1b**) and

1a: Z = $\quad$ —C≡C—C≡C—

1b: Z = $\quad$ —(CH$_2$)$_4$—

e = CO$_2$R

anti-**1a**, Z = —C≡C—C≡C—
anti-**1b**, Z = —(CH$_2$)$_4$—
e = CO$_2$R

especially on the flexibility of the ester's alkyl chain.[3b] 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).[4] 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**.[3]

(1) Dedicated to Professor Donald J. Cram on the occasion his 65th birthday.
(2) (a) *Host Guest Complex Chemistry: Macrocycles*; Vögtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, 1985. (b) Breslow, R. In *Biomimetic Chemistry*; Yoshida, Z.-I., Ise, N., Eds.; Elsevier: Amsterdam, 1983; pp 1–20. (c) Cram, D. J.; Katz, H. E.; Dicker, I. B. *J. Am. Chem. Soc.* **1984**, *106*, 4987–5000.
(3) (a) Whitlock, B. J.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 838–844. (b) Whitlock, B. J.; Whitlock, H. W., Jr. *Ibid.* **1985**, *107*, 1325–1329.
(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).

Scheme I[a]
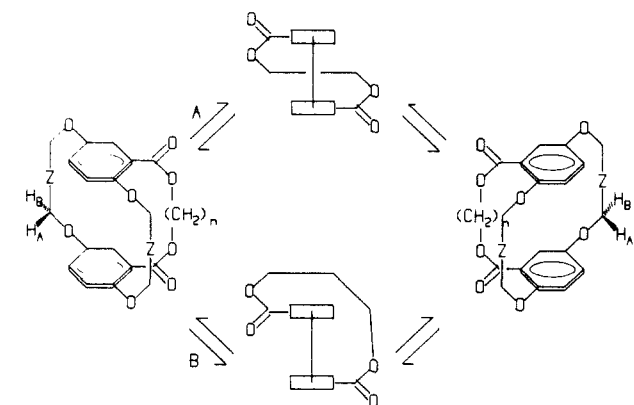
[a] A, donut-hole, mechanism; B, jump rope mechanism. **2**·*n*, Z = —C≡C—C≡C—, *n* = 3–11; **2**·11', (CH₂)ₙ = —(CH₂)₅CMe₂-(CH₂)₅—; **3**·*n*, Z = "bd(CH₂)₄—, *n* = 3–11.

Table I. Stereodynamics of **2**·*n* and **3**·*n*

	RT^a	T_c^b	ΔG^*_{298}, kcal/mol	ΔH^*, kcal/mol	ΔS^*
2·3	slow	>>180	21.4	14.2	−24
2·4	slow				
2·6	slow	>180	~20–21		
2·7	slow	~160	19.2	16.4	−12.7
2·8	slow	103			
2·9	slow	+73	16.5	13.6	−9.6
2·10	int.	+12	13.8	15.0	+4.0
2·11	fast	−43	10.4	13.8	+11.5
2·11'	fast	−35			
3·3	slow	>>180	>26		
3·7	slow	>>160	>23.3		
3·8	slow	~110			
3·9	int.	+16			
3·10	fast	−24	12.8	9.4	−11.4
3·11	fast	<<−50			

[a] Behavior on NMR time scale (room temperature, 270 MHz).
[b] Coalescence temperature (°C), 270 MHz.

Cyclophanes were synthesized[5,6] from Br(CH₂)ₙBr.[7] Inversion rates were measured by line-shape analysis of the interconverting OCH₂ AB quartets[8] or by the Forsén–Hoffman saturation-transfer technique.[9] Results for series **2**·*n* and **3**·*n* are shown in Table I.

When *n* is less than ~8, ring-inversion barriers are *much* greater for **2**·*n* and **3**·*n* than for the corresponding **1**. A ΔG^*_{298} of 17 kcal/mol for **1a**·3 (*N*-propyl ester)[3a] may be compared with $\Delta G^*_{298} \geq$ 21 kcal/mol for **2**·3 and >26 kcal/mol (minimum estimate) for **3**·3. These results are consistent only with a donut-hole process.

For large *n* (*n* ≥ 9), the barriers are much *smaller* for **2**·*n* and **3**·*n* than for **1**·*n*. We assign the jump rope mechanism here: (a) For large *n* the donut-hole barrier should be *no less* for **2**·*n* and **3**·*n* than for **1**·*n*. The jump rope process, however, passes the unsubstituted side of the arene through the cavity; this has a very low barrier. (b) The compact cyclophanes have *lower* barriers than the rigid cyclophanes (e.g., **3**·10 vs. **2**·10). The jump rope mechanism predicts this, as the diester passes around the exterior

of the cyclophane; the donut-hole mechanism predicts the opposite.[3a] (c) Geminal dimethylation of the middle of the chain of **2**·11 (to give **2**·11') does not increase the barrier: the quaternary carbon must not be passing through the cavity.[3a,10]

A Rationally Designed, Chiral Lewis Acid for the Asymmetric Induction of Some Diels–Alder Reactions

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Development of methods for the asymmetric induction of Diels–Alder reactions is of considerable current interest.[1] The use of chiral auxiliaries to this end has provided some notable solutions to specific problems, but the need to invest separate reaction steps in the incorporation and subsequent jettisoning of the auxiliary is a generally inherent limitation. Chiral Lewis acids, were they available, would offer an attractive alternative, particularly if three results attended their use: predictable absolute chirality of product, high levels of enantiomeric excess (ee), and compatibility with varied substrate structures. To date, there have been only a few reports[2] of attempts to employ chiral Lewis acids in Diels–Alder reactions, and none satisfies any of the above criteria. We now describe a system which does.

peri-Hydroxyquinones such as juglone (**1**) are attractive can-
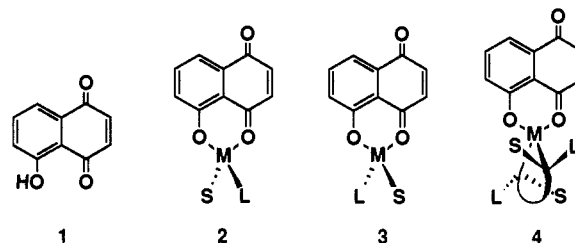
S=small group, L=large group, M=metal

didates for the use of chiral Lewis acids because the hydroxy group can serve as a second ligand to the Lewis acid, thereby greatly diminishing conformational mobility in the complex. Thus in the generalized complex **2**, if L is sufficiently large to block attack of a diene on the top face of the quinone while S is sufficiently small to still permit approach of the diene on the bottom face, asymmetric induction should result. The utility of **2** appears severely compromised, however, because it must be prepared without simultaneous generation of its enantiomer (**3**). But this apparent difficulty can be circumvented by incorporating both S and L into a single, bidentate ligand possessing C_2 symmetry,[3]

(5) (a) Jarvi, E. T.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 657–662. (b) Brown, A. B.; Haller, K. J.; Whitlock, H. W., Jr. *Tetrahedron Lett.* **1982**, *23*, 3311–3314.

(6) (a) Jarvi, E. T.; Whitlock, H. W. *J. Am. Chem. Soc.* **1982**, *104*, 7196–7204. (b) Miller, S. P.; Whitlock, H. W., Jr. *Ibid.* **1984**, *106*, 1492–1493.

(7) (1) 2-Hydroxy-5-(propargyloxy)benzoic acid, Et₃N, DMF; (2) Cu(O-Ac)₂, pyridine, 40 °C; (3) HC≡CCH₂Br, K₂CO₃, DMF; (4) Cu(OAc)₂, pyridine, 40 °C (to give **2**·*n*); (5) H₂, Rh/Al₂O₃, EtOAc (giving **3**·*n*).

(8) Binsch, G. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 45–81.

(9) Led, J. J.; Gesmar, H. *J. Magn. Reson.* **1982**, *49*, 444–463.

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(2) Guseinov, M. M.; Akhmedov, I. M.; Mamedov, E. G. *Azerb. Khim. Zh.* **1976**, 46–48; *Chem. Abstr.* **1976**, *85*, 176925z. Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437–438. Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716–3717; **1983**, *105*, 6968–6969. Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451–3454.