structure.[20] Removal of the methyl protecting groups (BBr_3, CH_2Cl_2) gave the hexahydroxy ligand **1a** which exhibited a parent ion at 779 $[M + H]^+$ in the positive ion FAB mass spectrum. However, the ^1H NMR of this material in Me_2SO-d_6 is quite complex,[21] and variable-temperature experiments indicate a fluxional process is occurring.[22] A simplified spectrum of the ligand was observed upon coordination of gallium(III),[23] indicating that the metal complex is the D_3 symmetry complex, while cis–trans isomerization leads to a mixture of conformers for the free ligand.[24]

A conceptually simple synthetic approach which circumvents the high-dilution reaction involves the use of a transition-metal template.[25,26] Elegant examples of the use of metal ions as templates can be found in the synthesis of macrobicyclic cobalt amine sepulchrate complexes by Sargeson and co-workers[27,28] and the preparation of catenands by Dietrich-Buchecker, Sauvage, and Kern.[29,30] In the present case, preorganizing three suitably functionalized catechol ligands about a metal ion enables the macrobicyclic complex to be formed by combining with 2 equiv of TREN[31] (Scheme II).

The template reaction proceeded to give a 90% yield, estimated by HPLC, of the intermediate **9a** identified on the basis of its IR ($1734\ cm^{-1}$) and the properties of its monobutyl amide derivative **9b**.[32] When heated in the presence of 4-(dimethylamino)pyridine, **9a** was slowly converted to Fe(bicapped TRENCAM) (**10**), remarkably in 70% yield! Demetalation ($Na_2S_2O_4$/HCl) of the ferric complex obtained from the template reaction provided bicapped TRENCAM, as ascertained by positive ion FAB mass spectrometry (m/e 779 $[M + H]^+$), NMR, and HPLC.

Ferric(bicapped TRENCAM) was characterized by cyclic voltammetry (Figure 1) in 0.4 M $NaClO_4$ at pH 12.00 by using a hanging drop mercury electrode. The peak-to-peak separation was 60 mV and the ratio of the cathodic to anodic peak currents was 1.0. Normal pulse polarography indicated an $E_{1/2} = -1.19$ V vs. SCE and a plot of E vs. log $[i_L - i)/i]$ was linear with a slope of 60 mV, indicating reversible electron transfer was occurring. The negative reduction potential, characteristic of other ferric tris catecholate complexes we have studied,[33,34] demonstrates that the strong preference for coordination of the ferric ion over the ferrous ion ($K_{Fe(III)}/K_{Fe(II)} = 10^{29}$) is retained in the cage complex.

The syntheses of bicapped TRENCAM illustrate the benefits derived from utilizing the coordination template effect for the synthesis of macrobicyclic catechoylamide ligands. We intend to investigate the scope of the approach, including the synthesis of unsymmetrical macrobicycles via a "half-cage" template reaction. In addition, quantitative determination of the formation constant for ferric bicapped TRENCAM is in progress in our laboratory.

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Registry No. **1a**, 107712-27-6; **1b**, 107742-32-5; **2**, 7169-12-2; **3**, 4097-89-6; **4**, 7168-94-7; **5b**, 107712-28-7; **6**, 75956-62-6; **7**, 107712-29-8; **8**, 107712-30-1; **9a**, 107712-31-2; **9b**, 107712-32-3; **10**, 107712-33-4; $Ga(TRENCAM)^{3-}$, 107712-34-5; *N*-hydroxysuccinamide, 6066-82-6.

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(20) Elemental anal. Calcd for $C_{42}H_{54}N_8O_{12}{\cdot}2H_2O$: C, 57.26; H, 6.41; N, 12.72. Found: C, 57.52; H, 6.34; N, 12.43. + FAB–MS m/e 863 $(M + H)^+$.

(21) NMR (200 MHz, Me_2SO-d_6) δ 12.666 (s, 3 H), 11.84 (s, 2 H), 10.0 (br s, 1 H), 9.00 (br s, 3 H), 8.29 (br s, 3 H), 6.80 (q, 6 H, $J = 8$ Hz) 3.78 (br, s, 6 H), 3.59 3.52 (br s, 12 H plus H_2O), 2.821 (s, 6 H).

(22) T_c (Ar H) = 70.1 °C; the T_c(amide H) is < 100 °C, at 200 MHz.

(23) Other catechol ligands readily complex the diamagnetic gallium(III) ion; see ref 3–5.

(24) ^1H NMR (200 MHz, D_2O, pH 10.5) δ 6.962 (s, 6 H); 3.690 (br s, 12 H), 2.833 (br s, 12 H).

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(31) Abbreviations used in the text: TREN, tris(2-aminoethyl)amine; DMAP, 4-(dimethylamino)pyridine; DCC, dicyclohexylcarbodiimide; SSCE, standard saturated calomel electrode; HMDE, hanging mercury drop electrode.

(32) IR 1609 cm^{-1}; – FAB MS 903 $[M + 2H^+]^-$.

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Torsional Motion in Aromatic Molecules. Conformational Analysis of Methyl-, Ethyl-, and *n*-Propylbenzenes[‡]

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To an ever increasing extent, information regarding torsional vibrations of organic molecules is being provided by theoretical treatments rather than by experimental observation.[1] When experimental data are available, all too frequently they pertain to mole fraction weighted averages of the individual contributing conformations rather than the individual conformations themselves.[2] We now demonstrate that supersonic molecular jet spectroscopy can provide a novel means (a) to determine experimental values for torsional potential barriers in S_0 and S_1, (b) to "freeze out" molecular conformations which have very low (ca. 1–5 kcal mol^{-1}) free energy barriers between themselves, (c) to "count" the number of stable ground state conformations and, by doing so, establish their molecular geometries, and (d) to observe spectroscopic properties of these individual conformations.

Much current interest exists in the conformational analysis of alkyl-substituted benzene substrates, and herein we focus specific attention on the first three members of this class of compounds: methyl, ethyl, and *n*-propyl. Both time of flight mass spectra (TOFMS) and dispersed emission (DE) spectra are determined for the systems studied.[3] Figure 1 presents the TOFMS of *m*-xylene (**1**) for the 0^0_0 region of the $S_1 \leftarrow S_0$ transition. The various features of this spectrum are attributed to transitions between internal rotor states of the two methyl groups. A double one-dimensional rigid rotor model can be employed to fit these data.[4-6] Parameters of this quantum mechanical model can be

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[‡] Dedicated to Professor Ernest L. Eliel, to commemorate his 65th birthday and to honor his committments to science, education, society, and professionalism.

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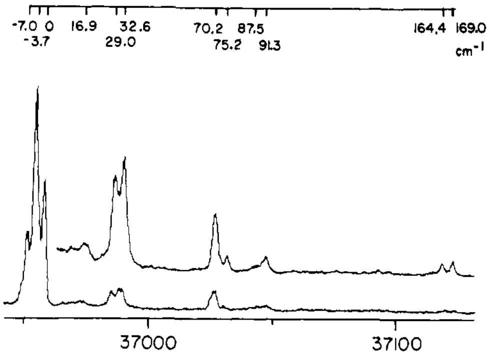


Figure 1. Electronic absorption spectrum of the 0_0^0 region of *m*-xylene, obtained with time-of-flight mass detection (TOFMS). The origin occurs at 36956.3 cm^{-1}. The two features at 3.7 and 7.0 cm^{-1} to lower energy of the origin are due to methyl torsions, and their positions are indicative of differences in the potential barrier to methyl rotation in S_0 and S_1.

Table I. Summary of the Hamiltonian Parameters Used To Fit the Experimental Data for the Alkyl Benzenes[a]

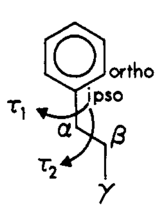
	S_0		S_1			
	V_3	V_6	V_3	V_6	χ[b]	V'_3[c]
toluene	0	10	0	25		
p-xylene	0	10	0	25		
m-xylene	0	25	81	−30		
o-xylene	425	18	166	0	0.72	−25
3-*n*-propyltoluene	0	23	75	0		

[a] Values of potential parameters are given in cm^{-1}; 1 kcal mol^{-1} = 350 cm^{-1}. [b] Kinetic cross term. [c] Potential cross term.

found for both the ground (S_0) and excited (S_1) states and are reported in Table I for *m*-xylene and the other compounds discussed herein.

The TOFMS and DE spectra of *o*-xylene (**2**) are considerably different from those of *m*-xylene. The methyl groups of *o*-xylene act as independent hindered rigid rotors in the S_0 state,[7] whereas both kinetic and potential interactions between the two neighboring groups can be identified in the S_1 state. The relevant rigid rotor model parameters for S_0 and S_1 states are presented and compared with those for other systems in Table I.

For *n*-alkylbenzenes, τ_1 (C_{ortho}–C_{ipso}–C_α–C_β) is the first torsional angle which defines the orientation of the alkyl group relative to the aromatic ring (cf. **3**). Ethylbenzene (**4**) is the prototypical example, with a barrier to rotation[2] about τ_1 of <5 kcal mol^{-1}. While some recent theoretical and experimental studies have concluded that the orthogonal conformation is preferred for **4**, some controversy remains and a number of reports conflict with this assignment.[8] The TOFMS and DE spectra of 1,3-diethylbenzene (**5**) reveal *two* origins, one each for the syn and anti orthogonal conformations, **5s** and **5a**, respectively. Had planar (τ_1 = 0) or angular conformations (0 < τ_1 < 90°) been obtained, then more than two origins for **5** would have been observed. Importantly, the TOFMS experiment is sufficiently sensitive to molecular symmetry to distinguish between **5s** and **5a**.



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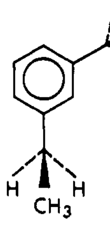
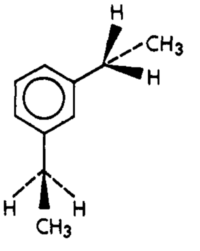


5s



5a

n-Propylbenzene (**6**) serves as the prototypical example to define the second torsional angle τ_2 (cf. **3**). In their pioneering report, Hopkins, Powers, and Smalley had observed two origins in the TOFMS for **6** but could not distinguish between the possible (anti, gauche, or eclipsed) conformations.[9] Over the last few years, evidence has accumulated from detailed studies of **6** and related compounds that CH···π attractive interactions can stabilize conformations when appropriate molecular geometries are possible.[10] Most studies have assumed that anti and gauche conformations are predominant,[11] and this assumption has been found to be consistent with empirical force field (EFF) calculations;[10] however, EFF calculations are not specifically parameterized for CH···π interactions. Indeed, Hopkins, Powers, and Smalley[9] suggested that the eclipsed form could be the preferred conformation for *n*-propylbenzene, pending unambiguous experimental data.

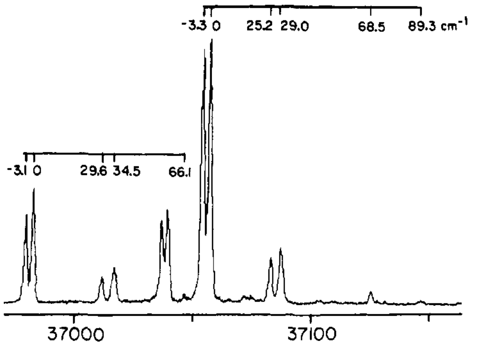
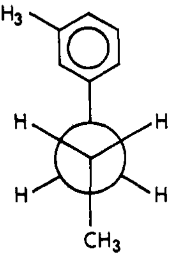


Figure 2. Electronic absorption spectrum (TOFMS) of the 0_0^0 region of 3-*n*-propyltoluene. The spectrum contains three origins at 36982.8, 37040.4, and 37060.1 cm^{-1}, corresponding to three different propyl group conformations. Accompanying each origin peak is a second peak to lower energy which is assigned as due to a methyl torsion. The doublet structures are indicative of differences in the potential barrier height to methyl rotation in S_1 and S_0.

Figure 2 shows the TOFMS of 3-*n*-propyltoluene (**7**). Three origin transitions, appearing as doublets, are observed. These correspond to the anti conformation **8** and the two gauche conformations, syn-gauche **9s** and anti-gauche **9a**. Had the eclipsed conformation **10** and the anti conformation **8** been predominant to the exclusion of the gauche conformations, only two origin transitions would have appeared. The doubling of the origins is due to two nonequilibrating methyl rotor states of **8**, namely, the 0a and 1e states. The doublets at ca. 25 cm^{-1} from each origin



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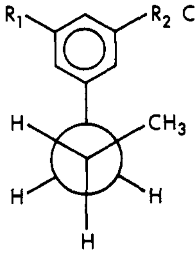
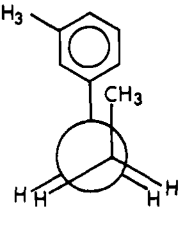


9s: R_1 = H; R_2 = CH_3
9a: R_1 = CH_3; R_2 = H



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are due to propyl torsions, features also noted in the spectra of *n*-propylbenzene and 4-*n*-propyltoluene. The observation of only three origins also substantiates the conclusion derived from the data on the ethylbenzenes that $\tau_1 = 90°$.

These results show (a) supersonic molecular jet spectroscopy is capable of observing specific molecular conformations which have very low barriers to conformational interchange, (b) aromatic ring methyl groups in the *p*- and *m*-xylenes can be considered as independent, nearly free rotors in S_0 and S_1, (c) the aromatic ring methyl groups in *o*-xylene are considerably more hindered in S_0 and S_1, and for S_1, cross kinetic and potential terms must be introduced, (d) the barriers for rotation are greater in S_1 than S_0, (e) the dynamic nature of the motion of the ring methyl groups is contrasted by a more static, locked-in character of the aromatic ethyl and *n*-propyl substituents, (f) aromatic *n*-alkyl substituents have their first C–C torsion perpendicular to the plane of the aromatic ring, and (g) aromatic *n*-propyl substituents exist in anti and gauche conformations, as observed in these TOFMS/DE experiments.

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Potential Energy Profile of a Full Catalytic Cycle of Olefin Hydrogenation by the Wilkinson Catalyst

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It is only in the last few years that for elementary reactions of organotransition-metal compounds the transition-state geometry can be optimized and the potential energy profile can be obtained from ab initio molecular orbital calculations.[2] Elementary reactions thus studied include oxidative addition/reductive elimination,[3] olefin insertion/β-elimination,[4] carbonyl insertion,[5] thermolysis of ketene complexes,[6] and isomerization of metallacycle to an alkylidene–olefin complex.[7] Despite such success, a study of an entire cycle of a catalytic process, consisting of several elementary reactions, has been a challenge to theoreticians.

We communicate here the results of the first such study, on homogeneous olefin hydrogenation by the Wilkinson catalyst.[8] We concentrate on the dominant catalytic cycle of the mechanism proposed by Halpern.[8b-d] The model of the cycle we adopted, shown in Scheme I, consists of oxidative addition of H_2, coordination of ethylene, ethylene insertion, isomerization, and reductive elimination of ethane. In the present study we use PH_3 as L,[9] and neglect the effect of solvent proposed in the Halpern mechanism for **1**, **2** and **5**.

The geometries of the intermediates, **1**–**5**, and the transition states connecting them have been optimized with the Hartree–Fock energy gradient method,[10] and some important geometries are

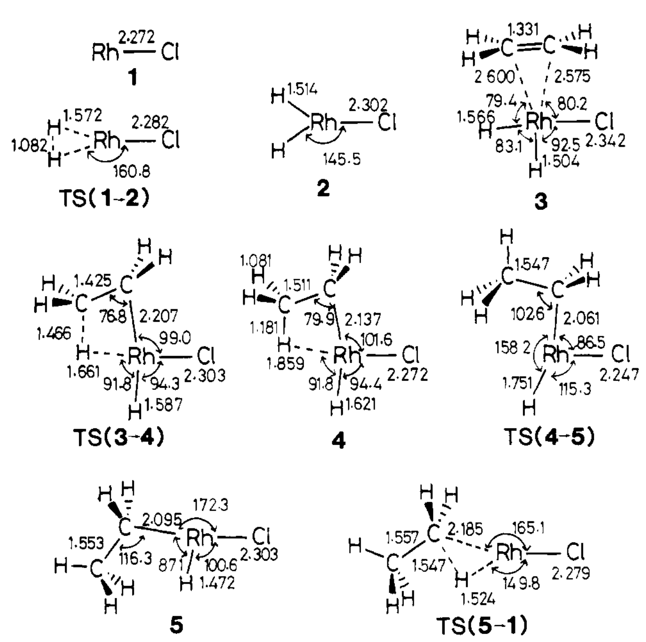
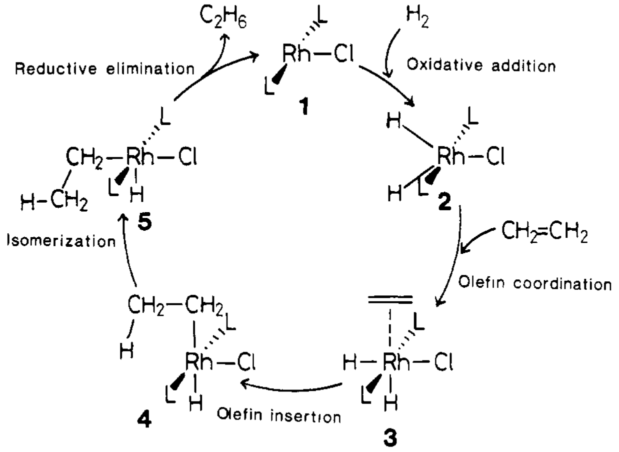


Figure 1. Optimized geometries of some important species in angstroms and degrees. TS(1→2), for instance, denotes the transition state connecting **1** and **2**. Though practically all the geometrical parameters were optimized, only essential values are shown. Two PH_3's, one above and one below the plane of the figure, are omitted for clarity.

Scheme I



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[9] We are aware of the fact that the actual catalysis takes place with L = PPh_3, and we plan to examine in the future the role of the phenyl group.