

Figure 4. Comparison of the relative stability constants for $M^{2+} \cdot 18C6$ measured by using EHMS in glycerol (●) with those measured by using calorimetric titrations in water (Δ) and in methanol (\square).

than the others, correlating with an extremely good match between the ionic radius of these ions and the cavity of 18C6 (1.34–1.43 Å).

A good test of the reliability of the relative K_s 's of Table IX would be a comparison with literature values. Suitable data have been reported for calorimetric titration studies in aqueous and methanol solutions^{11,13} and are listed in Table X, along with corresponding data from this study. A comparison of the trend of $K_s(M^+ \cdot 18C6)$ vs. M^+ ionic radius in the three different solvents (Figure 3) shows reasonable qualitative and even semiquantitative agreement. This suggests that for complexes of singly charged

cations, there are only minor solvent effects on the relative magnitude of K_s . This is consistent with the observation of little interaction between the solvent and $M^+ \cdot 18C6$ complexes ($\bar{n} \sim 0$) or uncomplexed M^+ ($\bar{n} \lesssim 3$) (see above).

By contrast, agreement is not as close for a similar comparison for M^{2+} (Figure 4). For example, $K_s(Ba^{2+} \cdot 18C6)$ varies in the ratio of 1.0:9.6:69.2 in glycerol, methanol, and water, respectively. These substantial solvent effects are consistent with the observation of more extensive interaction between the solvent and ions containing doubly charged metals ($M^{2+} \cdot 18C6$ ($\bar{n} \sim 2$), $(MA)^+ \cdot 18C6$ ($\bar{n} \sim 1$), M^{2+} ($\bar{n} \sim 6$), and $(MA)^+$ ($\bar{n} \sim 4$)). The small K_s values for $M^{2+} \cdot 18C6$ in glycerol suggest that free M^{2+} cations are strongly solvated by this solvent, disfavoring complexation by the crown.

Conclusion

In summary, this work has clearly demonstrated the high sensitivity of EHMS and its ability to resolve individual species in the study of complexation chemistry. For example, we have been able to obtain K_s 's for weakly bound complexes ($Li^+ \cdot 18C6$ and $(CH_3)_4N^+ \cdot 18C6$) which have not been detected by less sensitive methods such as calorimetric titration. The EHMS spectra gave detailed information about the individual species existing in solution, providing better insight into the complex solution chemistry, including solvation and ion pairing.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-84-06825 jointly funded by the U.S. Army Research Office).

Registry No. Glycerol, 56-81-5.

Rotation of Methyl Groups in Hexamethylbenzene

V. Melissas, K. Faegri, Jr., and J. Almlöf*

Contribution from the Department of Chemistry, University of Oslo, Oslo Norway. Received December 17, 1984

Abstract: The structure of hexamethylbenzene has been studied by Hartree-Fock calculations. The equilibrium geometry possesses D_{3d} symmetry, with a barrier of 1.0 kcal/mol toward a geared rotation of the methyl groups. The results support neutron diffraction data but disagree with electron diffraction experiments and molecular mechanics calculations.

Hexamethylbenzene (HMB) is a prototype molecule for studying coupled, internal rotation, and its structural and dynamical properties have attracted considerable interest. It exhibits at least two crystal-phase transitions, the origin of which has sometimes been attributed to the different degree of correlation between the rotations of the methyl groups.¹⁻³

The molecular structure of HMB has previously been determined by X-ray,⁴ neutron,⁵ and electron diffraction.⁶ Molecular mechanics calculations have also been reported.^{7,8}

The low-temperature crystal phase, i.e., the one for which the methyl groups were most accurately determined, exhibits approximate D_{3d} conformation (Figure 1b). The benzene ring is accurately planar, but the methyl carbons are bent 0.04–0.10 Å out of the ring plane, alternantly above and below.

The ED structure,⁶ on the other hand, is of S_6 symmetry, with a methyl group orientation quite different from that of ref 5. The out-of-plane distortion of the methyl carbons is 0.26 Å, much larger than in the solid.

MM calculations also arrive at a large out-of-plane distortion for the methyl groups.⁸ In addition, the benzene ring shows a strong and unexpected distortion, the dihedral angle being 9.6°.

Table I. Structural Parameters Obtained for HMB, Compared with Previous Experimental and Theoretical Results^a

	present work	molecular mechanics, ref 8	electron diffraction, ref 6	neutron diffraction, ref 5	X-ray diffraction, ref 4
HCH	106.9	111	107.4	112.4	
ΔZ_1	0.011	0.034	0	0	0.004 ^o
ΔZ_2	0.047	0.18	0.26	0.07 ^c	0.02 ^c
ϕ^b	90°	90°	114.4 ^o	90°	102°
R_{C-C}	1.413 ^c	1.406	1.427	1.413 ^c	1.410 ^c
R_{C-C}	1.506 ^b	1.517	1.531	1.506 ^c	1.518 ^c
ΔE^d	1.0	2.6		0.46	

^a ΔZ_1 and ΔZ_2 denote displacements of the ring and methyl carbons out of the least-squares plane. Distances are in Å, angles in degrees, and energies in kcal/mol. ^b Torsion angle; $\phi = 90^\circ$ corresponds to a D_{3d} conformation (Figure 1a). ^c Average value. ^d ΔE is the barrier to coupled, conrotatory torsion of the methyl groups. ^e Assumed value.

The present calculations were undertaken in order to resolve some of these discrepancies. In particular, the low symmetry of

* Address correspondence to this author at his present address: Department of Chemistry, University of Minnesota, 207 Pleasant St., Minneapolis, MN 55455.

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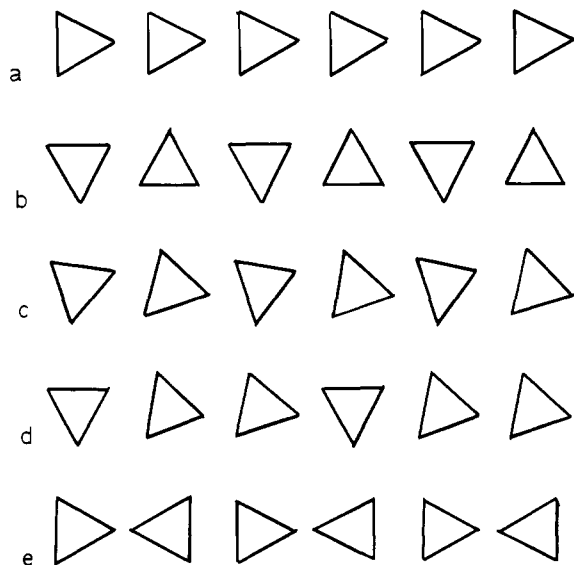


Figure 1. Schematic diagrams showing some of the different methyl group orientations studied in this work. Situations shown are (a) $m = 0$, $\phi_1 = 60^\circ$, (b) $m = 0$, $\phi_1 = 90^\circ$, (c) $m = 0$, $\phi_1 = 75^\circ$, (d) $m = 1$, $\phi_1 = 90^\circ$, and (e) $m = 3$, $\phi_1 = 60^\circ$, where the parameters ϕ_1 and m are those defined in eq 2.

the ED structure and the ring distortion in the MM calculation are subject to our interest.

Calculations and Results

The calculations were performed at the Hartree-Fock level of approximation, using the program package DISCO.⁹ In most of the calculations, a Gaussian contracted basis set of double- ζ quality was used.^{10,11} The bond lengths were kept fixed at standard values in all our calculations ($R_{CC} = 1.413$ and 1.506 Å, $R_{CH} = 1.10$ Å), and only bond angles were varied. These standard values are close to those actually observed in diffraction experiments on HMB.⁴⁻⁶ As conformational changes are governed by nonbonded interactions, which normally change little upon modest changes of bond lengths, the above restriction is not expected to significantly affect the calculated conformers and their energies.

The methyl groups were first rotated in a completely geared mode, keeping the internal methyl group geometry tetrahedral and the carbon skeleton fixed. These calculations found the C_{6h} conformation (Figure 1a) to be the more stable one, with a rotation barrier of 0.4 kcal/mol for the D_{3d} geometry (Figure 1b).

As a further refinement, the HCH angles were varied, keeping the local 3-fold symmetry of the methyl groups. The optimization changed the angles from 109.5° to 106.9° and lowered the energy by about 3.6 kcal/mol for both the C_{6h} and the D_{3d} form, thus having minor effect on the torsion potential.

Allowing the methyl carbon to move out of the ring plane lowered the energy by another 0.9 kcal/mol for the D_{3d} form. In C_{6h} geometry only the in-plane C-Me bend is symmetry allowed, but this variation does not significantly improve the energy. The rotational barrier was thus changed to 0.5 kcal/mol, with the D_{3d} form now being the more stable one. The optimal out-of-plane distortion was 2.0° (0.05 Å) in agreement with the ND result⁵ but much smaller than the values obtained in the ED and MM investigations.

A rather significant ring puckering was reported from the MM calculations. As this disagrees with the experimental observations,

a detailed analysis of the planarity of the benzene ring has been made. Optimizing the methyl groups and the ring simultaneously yielded a slightly puckered ring, with carbon atoms 0.011 Å out of the mean ring plane. The out-of-plane distortion for the methyl groups was not changed, however, although their tilt angles were reduced to 0.9° . This optimization led to an energy gain of only 0.3 kcal/mol altogether and changed the barrier to 0.7 kcal/mol. Keeping the nearest environment around each ring carbon perfectly planar (i.e., zero tilt angle) did not significantly affect the ring puckering or the total energy. The internal methyl group geometry was also found to be relatively independent of these variations, the optimal HCH angle being 106.9° in all cases.

Finally, the two extremum points of the potential were studied with a larger basis set. A (C (10s)(6p)(1d)/H(5s)(1p)) primitive set¹² contracted to (C (6s)(3p)(1d)/H (3s)(1p)) yielded a total of 360 basis functions. This lowered the total energy by some 0.7 hartree and changed the barrier height from 0.7 to 1.0 kcal/mol. A basis set effect of that magnitude is rather typical and does not change the other conclusions drawn from the calculations with the smaller basis set.

All conformers studied in this work correspond to a coupled, disrotatory motion of the methyl groups. A perfectly geared structure is characterized by the S_6 symmetry element. In terms of torsion angles, this is equivalent to the condition

$$\phi_{n+1} = (-1)^n \phi_1 \quad (1)$$

where ϕ_n is the rotation of the n th methyl group, i.e., the angle between the ring and one C-C-H plane. It is plausible that condition 1 is compatible with a minimum-energy path for the rotation. However, a cyclic disrotatory arrangement is also obtained with the more general requirement

$$\phi_{n+1} = (-1)^n (\phi_1 + nm\pi/9) \quad (2)$$

For $m \neq 0$ this leads to a more strained situation and gives an estimate of the energies required for a noncorrelated motion of the methyl groups. The geared rotation is the most likely process at low temperature, whereas at higher temperature less correlated motion may occur. (Some evidence for this is given by the high-temperature crystal structure.⁵) Rotating the methyl groups with $m = 1$ (Figure 1d) results in an 18-fold potential, with its minimum 4.7 kcal/mol above the ground state. The conformation with $m = 3$ and $\phi_1 = 0$ (Figure 1e) gives an energy of 10.1 kcal/mol, which may be considered an upper bound for any conformational energy.

Comparison with Experimental Data

From the potential barrier of 1.0 kcal/mol calculated with the larger basis set, a torsional frequency around 100 cm^{-1} may be estimated. This compares reasonably well with values around 120 cm^{-1} observed in solid HMB,¹⁴ considering the approximations involved in such an estimate.

From our data the frequency for the symmetric methyl out-of-plane bend may also be calculated. If coupling to all other modes, except the ring puckering, is neglected, a frequency of 296 cm^{-1} is obtained.

The ED results are not strictly comparable to ours, as no attempt was made to correct for shrinkage effects. The results given in ref 6 refer to a thermally averaged structure, or, more precisely, to a static mode fitted to observed, thermally averaged interatomic distances. Indeed, ref 6 claims excellent agreement between their ED results and the ND structure⁵ (which is close to ours), provided thermal effects are accounted for.

This claim, however, is based upon an erroneous assumption about the out-of-plane frequencies, and we therefore found it worthwhile to reinvestigate the subject. It is reasonable to assume that the information about out-of-plane deformations in the ED structure stems largely from distances between methyl carbons in the ortho position. With that assumption, the effective out-

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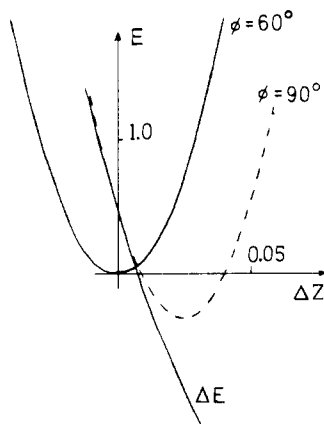


Figure 2. Puckering potentials calculated for different methyl group orientations. $\phi = 60^\circ$ and 90° correspond to the orientations shown in Figure 1, parts a and b, respectively. The torsion barrier ΔE is also shown as a function of the puckering coordinate. Energies are in kcal/mol; the puckering coordinate ΔZ is in Å.

of-plane distortion observed by ED may be estimated as $h = \langle (h_0 + x)^2 \rangle^{1/2}$, where h_0 is the distortion of the equilibrium structure and x is the vibrational coordinate. With our calculated potential, vibrational effects lead to only a minute increase of the distortion at 340 K, from 0.047 to 0.060 Å. A treatment of all vibrational modes in the molecule is beyond the scope of this investigation, and accordingly the above procedure gives only a rough estimate of the vibrational effect. However, the mode considered here is the one most obviously affecting the determination of the out-of-plane distortion by gas-phase ED techniques. We conclude that a more detailed treatment of dynamic effects would not add much to the effective, observed distortion and would under no circumstances bring our thermal average value close to that of the ED investigation.

The nonplanarity of HMB may seem unexpected in light of the fact that even C_6I_6 adopts a planar equilibrium structure,¹³ despite its considerably more bulky substituents. One may obtain a more detailed insight into the steric repulsion effects by considering not only the equilibrium geometry but also the vibrational force constants. The puckering mode (B_{2g} in D_{6h} notation) which brings the substituents out of the ring plane—alternantly above and below—is the one most directly affecting the nonbonded interaction. The corresponding force constant is therefore sensitive

to steric repulsion between the ligands.

With the methyl twist angle fixed at 60° , the minimum energy is obtained for a planar carbon skeleton, i.e., a conformation of C_{6h} symmetry. The puckering force constant is $244 \text{ cal mol}^{-1} \text{ deg}^{-2}$, close to the values 230 and $224 \text{ cal mol}^{-1} \text{ deg}^{-2}$ previously obtained for C_6F_6 and C_6Cl_6 ¹³ (the value found for C_6I_6 was $82 \text{ cal mol}^{-1} \text{ deg}^{-2}$). Since the global minimum has a twist angle of 90° (D_{3d} symmetry) and a nonplanar carbon framework, it is evident that the torsion and the puckering modes are strongly coupled. Already at an out-of-plane distortion of 0.05 Å, the torsion barrier has changed from 0.4 to -1.0 kcal/mol . This is illustrated in Figure 2, where the torsion barrier is shown as a function of the puckering coordinate, along with the potential functions for $\phi = 90^\circ$ and 60° . The barrier becomes numerically smaller again at very large out-of-plane distortions, so that the function has a positive curvature. One thus expects a larger force constant for $\phi = 90^\circ$ than for $\phi = 60^\circ$, the former potential being simply a superposition of the other two curves. Indeed, the calculated value for the force constant in the $\phi = 90^\circ$ case is $272 \text{ cal mol}^{-1} \text{ deg}^{-2}$. This is significantly larger than for any of the perhalogenated benzenes, in spite of the fact that these are all planar, whereas HMB is not. In conclusion, it appears that the nonplanar geometry of HMB must be rationalized in terms of the low symmetry of the ligands, rather than as a result of steric repulsion due to their size.

Conclusions

The equilibrium geometry of HMB is of D_{3d} symmetry, with a nearly planar benzene ring and with the methyl carbons 0.05 Å out of the ring plane.

Our analysis of vibration effects for the ED investigation shows that the disagreement between ED and ND structural parameters is not an artifact due to shrinkage effects in the ED case. Our results strongly support the ND parameters, for which agreement is fair. The gas-phase ED results are indeed in surprising disagreement with ours, showing approximate C_{6h} symmetry and an out-of-plane distortion more than 5 times our value.

It is interesting to note that this seems to be a general problem for gas-phase ED. The particular case of per-halogenated benzenes has been discussed previously.¹³ Molecular mechanics calculations also seem unable to predict a reasonable structure for HMB. The methyl bend is much too large, and the ring puckering of nearly 10° is in sharp contrast to our result as well as other experimental findings.

Registry No. Hexamethylbenzene, 87-85-4.