# The Structure of Hexamethyl(Dewar benzene)

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**Abstract:** The structure of hexamethyl(Dewar benzene) (bicyclo[2.2.2]hexa-2,5-diene) has been determined by gas phase electron diffraction. In the model preferred by the authors the bonded distances in the cyclobutene rings are: (–C–C–) = 1.63 ± 0.01 Å, (=C–C–) = 1.52 ± 0.01 Å and (–C=C–) = 1.35 ± 0.01 Å. The flap angle between the rings is 124 ± 1.5° and the terminal methyl groups extend 16° out of the cyclobutene planes away from the bridge. If the minimum energy structure is assigned $C_{2v}$ symmetry, the molecule appears to be undergoing large amplitude twisting motions. This fits well with symmetry-correlation diagrams for the reversion path to benzene and with recent extended Hückel calculations which also indicate that the twisting motion should be very facile.

The argument regarding the assignment of a structure to benzene over a century ago constitutes an interesting bit of chemical history. More important, it serves as a classic illustration of the development of procedures to establish the consistent set of mapping operations for atom connectivities in molecular compounds.[1] The simple rules in use in 1860 apparently did not apply to benzene so that alternate proposals had to be formulated; several of them were quite imaginative, such as those of Kekulé and Claus (Figure 1). The chemical evidence against the Dewar and Ladenburg forms soon convinced chemists of their inappropriateness for benzene, and there the matter rested until the middle third of the present century when these structures and benzevalene[2] were recognized as possible *valence isomers* of benzene.[3,4] Whether these serve as reaction intermediates, and whether these were capable of isolated existence, proved to be legitimate questions for investigation. Finally, in the 1960's the first valence isomer of benzene, tri-*t*-butyl(Dewar benzene), was synthesized and isolated.[5] Since that time all three of the isomers have been prepared.[6,7] These syntheses depend essentially on the isolation of products generated during the ultraviolet irradiation (~1800 Å) of substituted benzenes.

In this paper we present the results of a structure determination of one of the valence isomers of hexamethylbenzene, the Dewar form. It is the first of the group which is currently under investigation in this laboratory. HMDB was studied first because it can be conveniently handled at room temperature. As will become clear from the following report, from the point of view of structural precision it would have been better to study the parent hydrocarbon, which is now available. Those results could have been used effectively to guide the analysis of the diffraction data for the hexamethyl derivative. In HMDB there are 435 atom pairs with over 150 different distances. The computing cost of analysis proved to be excessive and the procedure unwieldy.

## Experimental Section

HMBD was obtained from Aldrich Chemical Co. Its estimated purity was greater than 97%. Decomposition of the compound is minimized if it is light shielded and kept in an ordinary freezer. We checked its purity by gas chromatography and found no indication of impurities. Benzene was added to one run to ensure proper separation by the column; it was quite substantial.

Two sets of diffraction photographs were obtained with our new electron diffraction apparatus;[8] these were taken months apart and the two sets of data checked exactly. Both runs were at 62 KV with nozzle-to-plate distances of 12 and 25 cm. MgO patterns from a very fine powder sample, rigidly mounted and aligned directly above the inlet nozzle, provided the (Lλ) calibration (*i.e.* of wavelength and nozzle–plate distance). The long and short sample–plate distances were obtained by a rotation of a bent inlet tube through 180°. The fact that for the short and long distances the peak and valley positions aligned well eliminates the possibility of a scale factor error to within the limits specified below. Figure 2 shows the reduced intensities from the second set of data plotted against the scattering angle variable $q$ [$\equiv (40/\lambda)(\sin \theta/2)$]. These data range from $q = 6$ to $q = 120$. The photographs were taken with the sample held slightly above room temperature (32°). Typical exposure times were of the order of 60 sec. The intensity scale in Figure 2 for the "short-distance" data is enlarged to twice the scale of that for the "long-distance" data.

Light and dark photographs were taken in order to provide calibration for the nonlinear response of the photographic plates. We used a previously developed procedure.[9] Optical densities were obtained with a Jarrell-Ash microdensitometer fitted with a rapidly rotating stage. The plates (Kodak electron image) were rotated about their scattering center at approximately 600 rpm as the plates were slowly scanned. The microdensitometer is coupled through a shaft encoder to a programmed drive to provide positioning of the plate stage to a precision of 5 μ. The total drive was checked with a vernier scale. The digitized optical densities were recorded on punched paper tape. This unit is described in more detail elsewhere.[10] The computational procedures, use of complex atom form factors, and other details were described in previous publications.[11]

## Analysis and Results

The background line shown in Figure 2 was obtained by a sequence of radial distribution function refinements. It is typical of the backgrounds generally found for diffraction photographs of hydrocarbons in this laboratory; the final background is only slightly changed from the one drawn in at first.

A $C_{2v}$ structure was initially assumed and a series of 200 model intensity and synthetic radial distribution

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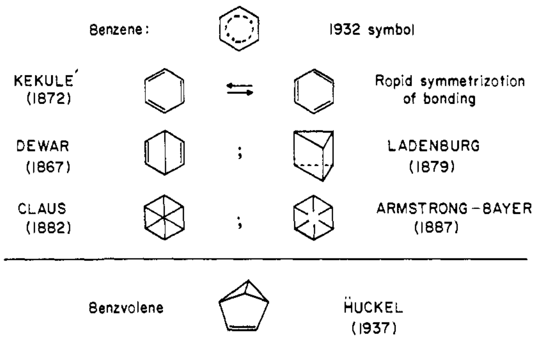

Figure 1. The valence isomers of benzene.

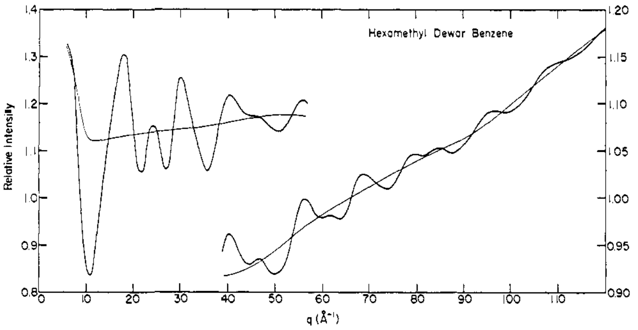

Figure 2. Reduced intensities plotted *vs.* $q \equiv (40/\lambda)(\sin \theta/2)$; accelerating voltage, 62 kV; nozzle-to-plate distance, 12 cm and 25 cm. The smooth lines (drawn in) are the refined backgrounds. Note the scale change for the right curve.

functions were calculated, in search of a good zero-order structure to serve as a starting point for the subsequent analysis. None proved to be close to the experimental curves; we later recognized this to be due to the fact that "normal" bond lengths were assumed. What *appeared* to be the best fitting of these models was then used as a starting point for a series of least-squares calculations. After many runs and extended attempts to fit the radial distribution curve a minimization of the total standard deviation was achieved. The value, 0.06, is at least twice that which is normally acceptable in our laboratory. This model has the two methyl groups attached to the bridge bond almost colinear with that bond.

There are two serious faults in this model. The first is that there are no rotational positions of the methyl groups which permit sufficient separation for *all* the hydrogens on different methyls, *i.e.*, greater than 1.8 Å. The second appears in the radial distribution curve. Two large area discrepancies of opposite sign could not be eliminated even when all the features were aligned. This indicated that at least two distances must be shifted. A variation in the resolution factor (in the least-squares program) partially alleviated the latter problem, and brought the standard deviation down to 0.043. However, this required a change of about 60% in the resolution factor, which is unacceptable in view of the high quality of the data. After extensive attempts to resolve these problems we were forced to the conclusion that this model represents a false minimum as found by the least-squares procedure.

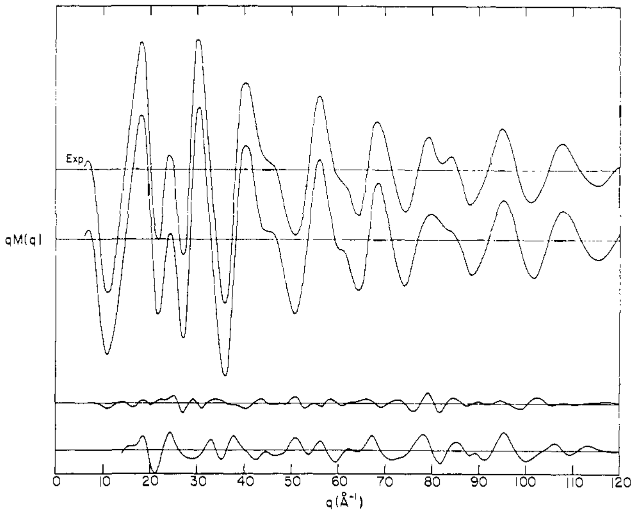

Figure 3. The experimental and the theoretical $qM(q)$ curves ("best" model). Below them is the difference function. The lowest curve represents the difference between the experimental and false minimum model, prior to allowing variation of the resolution factor.

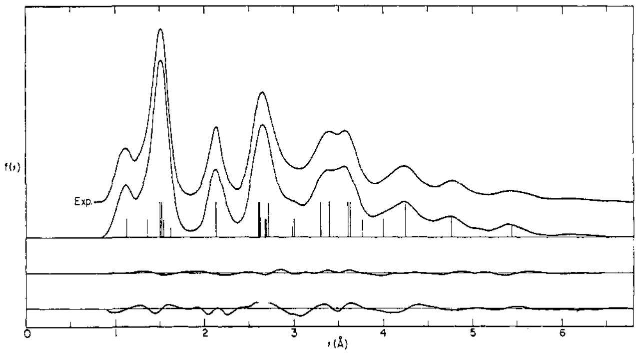

Figure 4. The experimental and final theoretical radial distribution functions. Their difference is plotted below them; the lowest curve is the corresponding difference function for the false minimum model. The spikes indicate the distance spectrum for the carbon skeleton.

The successful search for a better model was then initiated by assuming that all the angles were close to their most reasonable magnitudes from a steric point of view, but that the bond lengths were those derived for the first model. The next least-squares analysis indicated that indeed this was the proper direction to pursue. The general refinement procedure consisted of iterating the following sequence: in the least-squares analysis allow only the bonded parameters to vary, then only the nonbonded ones, then all of the geometric parameters together. A radial distribution function was then generated to check whether the new model suggested a change in the background (which was always very small). The resolution factor was not varied. The mean-square amplitudes were then varied in the least-squares program. Finally, the sequence was repeated. Until the *initial* set of values inserted in the program (in each cycle) were quite close to the *best* set, the calculation in which all the geometric parameters were varied did not converge. Figures 3 and 4 show the experimental and the theoretical intensity and radial distribution functions calculated for the final structure. For comparison the error curve for the false minimum model was also included. Two projections of HMDB are shown in Figure 5.

**Table I.** Parameters for Hexamethyl(Dewar benzene)

| | Set 1 | Set 2 | Set 3 | False minimum |
|---|---|---|---|---|
| $C_1$–$C_2$ (bridge), Å | 1.629 ± 0.010 | 1.595[a] | 1.575[a] | 1.565[a] |
| $C_1$–$C_3$= (ring), Å | 1.523 ± 0.010 | 1.540 | 1.546 | 1.512[b] |
| -C-$CH_3$ (bridge), Å | 1.541 ± 0.015 | 1.497 | 1.490 | 1.523[b] |
| =C—$CH_3$ (terminal), Å | 1.504 ± 0.009 | 1.506 | 1.506 | 1.515[b] |
| $\langle C\text{–}H\rangle_{av}$, Å | 1.134 ± 0.008 | 1.333 | 1.132 | 1.107[a,b] |
| $C_3$=$C_4$, Å | (1.352) | (1.351) | (1.349) | (1.337) |
| Flap angle, deg | 124.5 ± 1.1 | 124.1 | 120.8 | 125.1 |
| $\angle C_2\text{–}C_1\text{–}C_7$, deg | 115.9 ± 1.0 | 116.9 | 117.4 | 174.1 |
| $\angle C_1C_3\text{–}C_9$, deg | 120.1 ± 0.8 | 121.3 | 121.9 | 125.0 |
| Out-of-plane $CH_3$, deg | (16.1) | (15.0) | (15.1) | (18) |
| Bridge $CH_3$ (rot.), deg[c] | 52.4 ± 4.5 | | | |
| Terminal $CH_3$ (rot.), deg[c] | 180.0 | | | |
| $\langle <C\text{–}C\text{–}H\rangle_{av}$, deg | 110.9 ± 1.4 | | | |
| Standard deviation[d] | 0.031 | 0.034 | 0.035 | 0.043[e] |

[a] Constrained to this value during the least-squares reduction. [b] These are $r_g(1)$ values; *i.e.*, center of gravity of resolved $[P(r)/r]$ peaks. [c] Zero angle is assigned to that orientation of $CH_3$ groups when C–H and the nearest C–C bonds are in an eclipsed position. [d] Defined by $[\sum_{q(\min)}^{q(\max)}[qM(q)_{\text{calcd}} - qM(q)_{\text{obsd}}]^2/\text{data pts} - \text{no. of parameters}]^{1/2}$ at integral $q$'s (6–120). Values and error estimates for the geometric parameters were obtained by constraining root mean square amplitudes to Table III values during the least-squares analysis. [e] Including variation of the resolution factor.

Throughout the analysis, as the model slowly evolved, the number and grouping of the mean-square amplitudes were changed in order to maintain consistency with possible types of motion for each model. The total number of amplitude terms was kept at a minimum to avoid overparameterizing the structure and thereby generating complications on the residuals surface as seen by the least-squares program. When the model and experimental data neared their final agreement the number of mean-square amplitudes was increased to 17, to allow for as large a set as we thought necessary, judged from the radial distribution function and the overall molecular shape. In the latter stages of analysis all of these, with the exception of the adjacent H···H and the bridge-bond mean-square amplitudes, could be varied concurrently. These are the smallest contributors to the total scattered intensity. Figure 6 shows the most pertinent values for the root mean square amplitudes derived in the final least-squares variation.

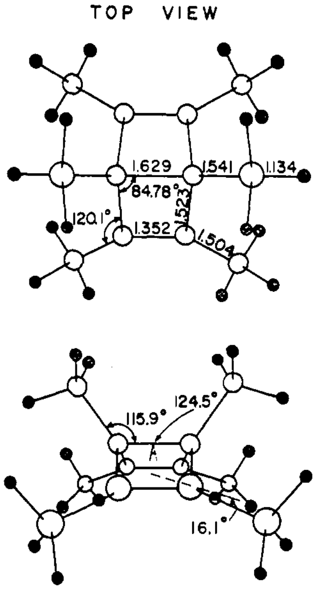

Figure 5. Top and side projections of HMDB, with the final geometric parameters indicated.

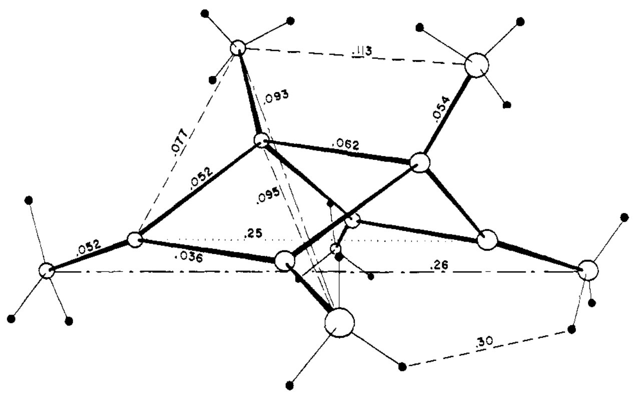

Figure 6. Isometric view of HMDB with selected values of root mean square vibrational amplitudes.

The converged values obtained from a final concurrent variation of all the geometric parameters in the least-squares program are listed in Table I. These are given in the column labeled set 1; sets 2 and 3 are results derived by similar variations but with the bridge bond constrained to the specified smaller values. Note that the angles are nearly equal and the principal difference lies in the bridge methyl C–C single bonds. The last column gives typical values obtained for the false minimum model. Here the significant parameter is the $\angle C_2C_1C_7 = 173°$. For comparison, the total standard deviations obtained for the fit to the $qM(q)$ functions are also listed in Table I. The error limits for the parameters are three times the uncertainties of the least-squares program using a diagonal weighting matrix. A nondiagonal weighting matrix was tested with the first off-diagonal rows nominally assigned 0.35, and the other elements set to 0, but convergence was not achieved and the attempt was dropped. The bonded distances are corrected for the harmonic vibrational phase shifts in the sinusoidal intensity expression, and an approximate correction for anharmonicity of vibration was also added.[12,13] The distances are thus considered to be $r_g(0)$'s; they correspond to the centers of gravity of the resolved radial distribution peaks for the corresponding atom pairs.

The torsional angles for the methyl groups found in the least-squares variation place the hydrogens in a staggered conformation relative to the nearest C–C bond. A model with $C_2$ symmetry for the total molecule but with a $C_{2v}$ carbon skeleton was tested for hydrogen staggering but no improvement in the fit was found. We have not estimated how much the constraining of the bridge carbon–carbon mean-square amplitude affects the value of that bond length. However, we do believe that the strong dependence of the total geometry on this parameter establishes its magnitude much more firmly than it would be were it solely an isolated pair of scattering atoms.

## Discussion

A preliminary gas phase structure for HFDB ($C_6F_6$), based on limited electron diffraction data ($5 < q < 51$), is currently available for comparison with the above results. Andersen, Seip, and Beagley[14] found that $C_{2v}$ symmetry gave the best fit between the experimental and theoretical curves, when they inserted bond distances in the carbon skeleton which are considerably smaller than the corresponding values listed in Table I (by 0.02–0.04 Å). Difficulty with a scale factor is indicated, but these differences may be real. The replacement of six $CH_3$ groups by F atoms probably reduces the magnitude of the nonbonded repulsion terms in addition to affecting the electronic charge distribution in the rings. X-Ray crystal-structure analyses of HMDB complexes with palladium[15] and rhodium[16] show that complexing distorts the molecular geometry, as expected. On the side away from the metal atom, the C–C bond lengths are within 0.02 Å of those in the free molecule except for $C_1$–$C_2$ (1.56 *vs.* 1.63 Å) and $C_3$=$C_4$ (1.28 *vs.* 1.35 Å). There is also a significant difference in the flap angle (112° *vs.* 124°), but the latter difference may be due to the crystal packing forces which constrain the rather loose molecular frame of HMDB (see below).

The results of our electron-diffraction analysis of the gas phase structure for HMDB raised a number of interesting questions. The first is whether other structural information is available to provide a clue for selection between sets 1, 2, and 3. There has now accumulated a substantial amount of data on dimensions of strained carbon atom rings.[17,18] One feature common to most of these is the presence of "long" carbon–carbon bonds. The 1.63 Å value for $C_1$–$C_2$ in HMDB (set 1) appears to be the longest single bond on record. However, this value is consistent with the trend indicated in Table II in which we have summarized the results of several recent structure determinations of cyclobutene rings. As listed from top to bottom, with increasing substitution, the frame dimensions get larger, and the C–C bond opposite the double bond shows this trend most clearly. In HMDB the observed bonded mean-square amplitudes listed in Figure 6 are also substantially larger than were found in any of the other cyclobutene rings.

**Table II.** Molecules with "Long" C–C Bonds

| | C=C<br>/ \\,<br>Å | C—C<br>/ \\\\,<br>Å | C—C<br>/ \\,<br>Å | Ref |
|---|---|---|---|---|
| Cyclobutene | 1.342 | 1.517 | 1.566 | *a* |
| *cis*-3,4-Dichloro-cyclobutene | 1.349 | 1.505 | 1.583 | *b* |
| Tricyclo-[3,3,0,$0^{2,6}$]-oct-3-ene | 1.345 | 1.503 | 1.580 | *c* |
| Perfluorocyclo-butene | 1.342–1.352 | 1.508–1.503 | 1.595–1.598 | *d* |
| HMDB | 1.352 | 1.523 | 1.629 | |
| Bicyclo[2.1.0]-pentane | | | 1.44 (Δ base)<br>1.52 (Δ side)<br>1.54 (□ side)<br>1.62 (□ base) | *e* |

[a] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969). [b] O. Bastiansen and J. L. Derissen, *Acta Chem. Scand.*, **20**, 1089 (1966). [c] D. Zebelman and S. H. Bauer, to be published. [d] C. H. Chang and S. H. Bauer, to be published. [e] Y. H. Tai and R. K. Bohn, private communication.

Two interesting features appear in the methyl groups attached to the double bonded atoms. On referring to Figure 5 one notes that the axes of these methyl groups do not bisect the internal angles (*i.e.*, $\angle C_1C_3C_4$, etc.), nor do they lie in the planes of the cyclobutene rings. This may be a consequence of the large steric repulsions between the closely packed methyl groups on the periphery of this molecule. The $C_8$–$C_7$, $C_9$–$C_7$, $C_{10}$–$C_9$, and $C_{11}$–$C_9$ pairs are between 3 and 4 Å apart, and the corresponding closest H–H distances are between 2.4 and 3.3 Å.

In Table III the final values of the 17 mean-square amplitudes are tabulated; most of these are as expected. However, the across-the-ring amplitudes are extremely large as shown in Figure 6. There are two arguments for accepting the amplitudes as derived from the least-

**Table III.** Root Mean Square Amplitudes of Vibration (HMDB), in Å Units

| | | |
|---|---|---|
| $C_2$–$C_1$ | 0.062 | Constrained |
| $C_7$–$C_1$ | 0.054 | ±0.006[a] |
| $C_9$–$C_3$ | 0.052 | ±0.002 |
| $C_4$–$C_3$ | 0.036 | ±0.002 |
| $C_4$–$C_1$ | 0.053 | ±0.002 |
| $C_7$–$C_3$ | 0.077 | ±0.001 |
| $C_5$–$C_4$ | 0.254 | ±0.022 |
| $C_8$–$C_7$ | 0.113 | ±0.004 |
| $C_9$–$C_8$ | 0.093 | ±0.006 |
| $C_{12}$–$C_9$ | 0.263 | ±0.070 |
| $C_9$–$C_2$ | 0.096 | ±0.004 |
| $C_9$–$C_6$ | 0.085 | ±0.006 |
| $C_7$–$H_1$ | 0.085 | ±0.002 |
| $C_1$–$H_1$ | 0.123 | ±0.006 |
| $C_9$–$H_1$ | 0.092 | ±0.001 |
| $H_1$–$H_2$ | 0.078 | Constrained |
| $H_{13}$–$H_7$ | 0.320 | ±0.032 |

[a] These are the calculated standard deviations. Values in this table were calculated by the least-squares program while the geometric parameters were constrained to the magnitudes given in Table I.

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(17) J. F. Chiang and S. H. Bauer, *Trans. Faraday Soc.*, **64**, 2247 (1968).

(18) D. Zebelman and S. H. Bauer, to be published.

squares analysis. First, the diametrically opposed methyl groups are well resolved (5.4-Å peak) in the radial distribution curve and the fit in that region is quite good (Figure 4). In addition 180 long H–H nonbonded distances are included in the average H–H mean-square amplitude in question and they constitute a discernible amount of scattering despite their individual small scattering power and their large damping factor. The second reason is the relative consistency of these values, *i.e.*, 0.25, 0.26, and 0.32. The uncertainties indicated are simply the diagonal elements which were calculated in the least-squares error matrix.

Thus it appears that HMDB consists of a somewhat loosely bonded framework of two cyclobutene rings which are undergoing considerable across-the-ring motions. If the minimum energy conformation had only $C_2$ symmetry, obtained by twisting the double bonds in either of two opposite directions, the potential function would have a double minimum rather than a single flat minimum as required for $C_{2v}$. The present electron-diffraction technique cannot distinguish between these symmetries. While the $C_2$ configuration would have slightly split longer distances, the corresponding effect in the $C_{2v}$ model with a flat potential is large amplitudes of vibration for the long $C \cdots C$ distances. Further study of this problem was not undertaken at this time. Clearly, temperature-dependent data are needed, and HMDB is not a good model compound for investigating this question. Indeed, the unsubstituted Dewar benzene will prove more suitable for study of these subtler points.

If a $C_{2v}$ model is accepted and with it the corresponding large mean-square amplitudes for across the ring motions, then a very interesting correlation with another investigation can be made. The currently accepted general mechanism for concerted reactions, such as valence isomerization, is that proposed by Hoffmann and Woodward,[19,20] based on symmetry correlation diagrams and extended Hückel molecular orbital calculations. These have proved quite successful, particularly with respect to the cyclobutenes. They also considered the Dewar benzene isomers. Hexamethylbenzene is 65 kcal more stable than is the Dewar form.[7] The conversion of the latter to the former occurs with an activation energy of 35 kcal.[4] On analyzing the transition path for conversion, Hoffmann and Woodward found that a simple cleavage of the bridge bond is symmetry forbidden, the correlation diagram requires that the intermediate nonbonding orbitals which are substantially higher energy are occupied. Although the 35 kcal might be sufficient for this process it is possible that a lower energy route may be available. In this reaction path the molecule would distort into a $C_2$ structure, approximating two uncoupled allylic radicals, which would then collapse to benzene. The conversion of Dewar benzene to the two allylic system of $C_2$ symmetry is a symmetry allowed process, and one anticipates that this is reflected in the ground-state geometry of Dewar benzene by a low force constant and thus a relatively large amplitude for the twisting motion.

The presence of a large amplitude twisting oscillation may, in part, account for the considerable difficulty we encountered in improving the fit of the calculated to the observed intensity and radial distribution functions. Large amplitude twisting motions lead to significant shrinkages across the rings which proved difficult to take into account in this electron-diffraction analysis due to the large number of parameters already required to specify the molecule. These presumed shrinkages would also tend to put the terminal methyl groups out of the cyclobutene planes, as observed, although it is not claimed that this is the only reason for the apparent nonplanarity.

It is plausible to assume that HMDB and HMB are related with respect to the structure of the excited electronic state through which the latter passes prior to its conversion. Indeed, it may well be that the various isomers of benzene, in their excited electronic states, execute vibrations which carry them into overlapping geometries so that the products isolated following irradiation depend in detail on the conditions of the experiment. Haller[21] reported that in the photoisomerization of hexafluorobenzene the Dewar isomer is generated in vibrationally excited states, which revert to the benzene unless they are deactivated by collisions. The photolysis of benzene vapor with 1849-Å light was shown to produce fulvene[22] but in the liquid phase benzvalene is generated.[23]

**Acknowledgments.** The authors thank the National Science Foundation for support of this work, under Grant No. GP-7794. One of us (M. J. C.) wishes to thank Professors R. H. Hoffmann and C. F. Wilcox for many helpful discussions. Finally we appreciate the kindness of Drs. B. Andersen and W. S. McDonald for sending us copies of their manuscripts prior to their publication.

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