

Phase III crystal structure and 115 K phase transition of hexamethylbenzene¹

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Abstract

High-resolution spectroscopic data—Raman, infrared, and electronic—have been employed for the study of low-temperature, phase III, hexamethylbenzene and its associated λ -type phase transition. Phase III is trigonal, with point group S_6 and one molecule per primitive unit cell, giving an S_6 site group, an S_6 molecular group, and a trivial interchange group. The λ -type phase transition is not second order, and it is not related to a free rotation of the methyl groups. Restricted, geared methyl-group rotations do exist both above and below the phase transition temperature, and are sensitive to it. The molecular point symmetry is S_6 in phase III and effectively so in phase II.

Introduction

The crystal structure of hexamethylbenzene (HMB) is known for the room-temperature phase II (Brockway and Robertson, 1939) and for the high-temperature phase I (Watanabe et al., 1949), where the structures are triclinic with one molecule per unit cell and orthorhombic with four molecules per unit cell, respectively. However, the crystal structure of the low-temperature phase III (<115 K) has not been determined, although it has been assumed to be similar to the phase II structure (Prasad et al., 1973; Schnepf, 1958, 1959). The phase III crystal structure is important to the

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analysis of the excited states of the HMB molecule and as a popular matrix for other molecules. It would also aid in understanding the nature of the 115 K λ phase transition, which has been an intriguing problem for nearly 50 years (Schnepp, 1959; Pauling, 1930; Hamilton et al., 1969; Bertinelli and Stremmenos, 1973; Andrew, 1950).

While an exact solution of a crystal structure requires a diffraction experiment to get the intermolecular distances and angles, it is well known that, by using group theory to analyze optical transitions and their selection rules, a great deal can be determined about a crystal structure at the molecular level, using optical spectroscopy. Such is the case for HMB where sufficient data are now available to determine uniquely the site symmetry of the molecule in its phase III structure, and, by correlation to the phase I and phase II crystal structures, a reasonable phase III structure may be inferred. The data come from a combination of the electronic, Raman, and infrared spectra of HMB in its two lower-temperature phases, II and III.

Implicit in the phase III crystal structure is a better understanding of the low-temperature 115 K λ phase transition. This transition has been of interest because of its past association with a change in the methyl torsional motion from a free to a hindered rotor (Pauling, 1930). The nature of the phase III crystal structure casts new light on previous studies of this phase transition by demonstrating that although the methyl torsion is an excellent probe with which to study the phase transition, the transition is actually due to a significant change in the crystal lattice, which results in a higher site symmetry in phase III, to which the methyl torsion is highly sensitive. However, no free methyl rotation is involved.

Experimental

Figures 1-3 and 5 describing Raman and electronic spectra, are taken from Woodruff (1976). The experimental details are found there, as well as, in part, in Prasad et al. (1973). No far-infrared spectra could be detected below 200 cm^{-1}

Results and discussion

The basis for this investigation of the phase III crystal structure of HMB is the effect of the crystal site symmetry on the vibrational and electronic optical transition selection rules. The infrared and Raman spectra of phases II and III of the HMB crystal establish the minimum possible symmetry elements for the crystal site symmetry. The electronic spectra of phase III HMB were then used to determine conclusively the symmetry group of the crystal site.

It has been shown that for phase II HMB, the only possible site symmetries are C_i or C_s (Brockway and Robertson, 1939; Lonsdale, 1929). Subsequent investigations of the infrared spectra (Mann and Thompson, 1952; Leech et

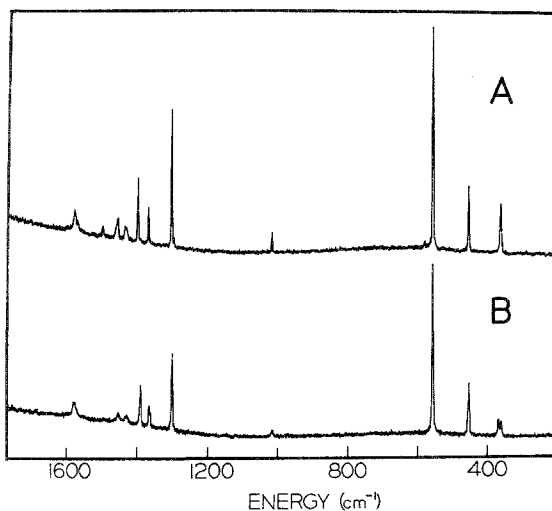


Fig. 1. Raman spectra of hexamethylbenzene in the region 200–1800 cm^{-1} for phase II at 115 K and phase III at 100 K. *A* is the phase III spectrum and *B* is the phase II spectrum. Note the splitting of the bands at 364 and 1370 cm^{-1} in phase II due to the loss of the threefold symmetry axis in the crystal site symmetry.

al., 1966; Ware et al., 1968; Durocher, 1969) and Raman spectra (Prasad et al., 1973; Murray and Andrews, 1934; Ron and Hyams, 1972; Girlando and Pecile, 1973) demonstrated clearly the mutual exclusion of the Raman versus infrared active states, providing hard evidence for the presence of a center of inversion in the site symmetry of the phase II crystal. Hence the site symmetry is C_i in the phase II HMB crystal. Likewise, in phase III HMB, the mutual exclusion of Raman versus infrared active states is retained, demonstrating again as hard evidence the presence of a center of inversion in phase III HMB (Prasad et al., 1973; Spoliti et al., 1976; Ron and Hyams, 1972). This center of inversion is the first symmetry element demonstrated for the phase III site symmetry of HMB.

An important aspect in determining the phase III site symmetry is the fact that the phase II crystal structure has only one molecule per unit cell. This aspect manifests itself in two ways in the optical spectra of the crystal. First, for all intramolecular excited states of the molecule, there is only one Davydov component per excited state due to the intermolecular interactions of the molecule. Thus, only one optical component per excited state can be observed, and any apparent splitting of an excited state will be due to reasons other than multiple allowed components of a single exciton band. Second, the number of optically allowed phonon states is restricted to no more than three. This aids in interpreting the phonon spectrum in the Raman and

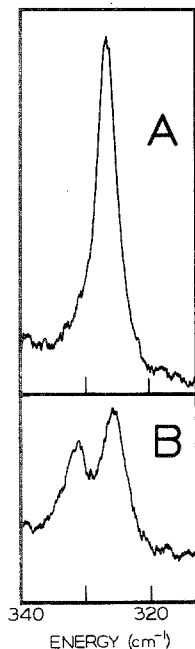


Fig. 2. Raman spectra of perdeuterohexamethylbenzene in the region 315–340 cm^{-1} . *A* is the spectrum of phase III at 100 K. *B* is the spectrum of the same transition at 135 K in phase II. Note the splitting due to the loss of the threefold symmetry axis in the phase II site symmetry.

infrared spectra and turns out to indicate *indirectly* the number of molecules per unit cell in the phase III crystal of HMB.

In a high-resolution Raman study of the 115 K phase transition of HMB, two doublet bands are observed in the phase II spectrum which become singlet lines in the phase III spectrum (Prasad et al., 1973). The first doublet at 360 cm^{-1} and 369 cm^{-1} goes to 364 cm^{-1} , while the second at 1365 cm^{-1} and 1368 cm^{-1} goes to 1370 cm^{-1} (see Fig. 1). The first doublet has also been observed in the perdeuterohexamethylbenzene (HMB- d_{18}) phase II Raman spectrum, at 327 cm^{-1} and 333 cm^{-1} , with the corresponding phase III singlet at 329 cm^{-1} (see Fig. 2). The fact that the first doublet is observed in both HMB and HMB- d_{18} phase II crystal spectra with corresponding singlets in phase III and that the isotope shift ratio for each of these transitions is almost identical and imply that each transition involves molecular motions of the same kind. Thus the near degeneracy of the phase II doublets is not an

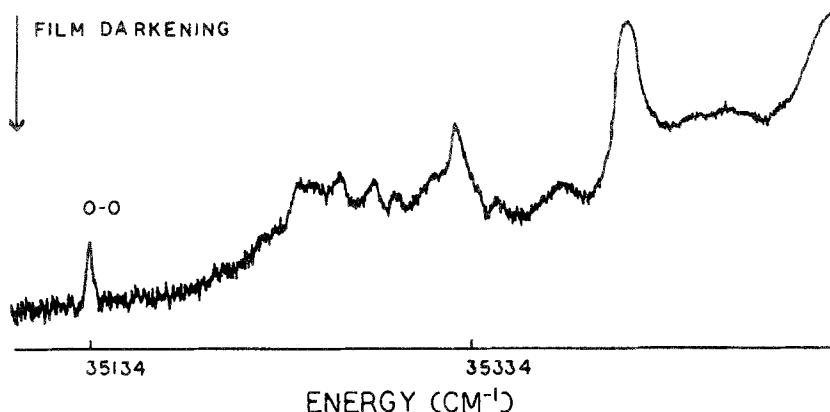


Fig. 3. Absorption origin of hexamethylbenzene at 2 K. The single $k = 0$ component of the first excited singlet exciton band of hexamethylbenzene is observed at 35134 cm^{-1} in the 2 K absorption spectrum of a thin ($\sim 10 \mu$) crystal of hexamethylbenzene; the half-width at half-height is 4 cm^{-1} .

accidental one, and the bands become totally degenerate in phase III through the addition of a higher symmetry element in the site group.

The now obvious presence of degenerate bands in the phase III Raman spectra due to the effect of the crystal site gives hard evidence for a new symmetry element in the site group of the phase III crystal structure. The presence of degenerate bands implies a threefold or higher symmetry axis of rotation. The known structure of the HMB molecule would allow only a three- or sixfold axis, and any group containing a sixfold axis contains also a threefold axis. Hence, it can be concluded that the molecular site group of the HMB phase III crystal contains at least C_i and C_3 as subgroups. It then follows that the molecular site group is either C_{6h} , D_{6h} , D_{3d} , or S_6 .

With the molecular or crystal site-group symmetry narrowed down to four possible symmetry groups, it is possible to eliminate three of those groups with one last piece of spectroscopic evidence, and to specify uniquely the molecular *site group* for the phase III crystal structure of HMB. In the absorption spectrum of the first excited singlet electronic state of HMB, a single transition to the allowed $k = 0$ level in the singlet electronic exciton band is observed at 35134 cm^{-1} (Fig. 3). This transition has been found to be polarized out of the plane of the molecule, that is, along the z axis of the molecule (Schnepp, 1958, 1959; Wolf, 1958). Thus, the polarization and the fact that the O-O transition is allowed in the crystal is determined from this observation. Also, the appearance of a single $k = 0$ band in the absorption spectrum agrees with but does not verify that HMB has one molecule per unit cell in phase III.

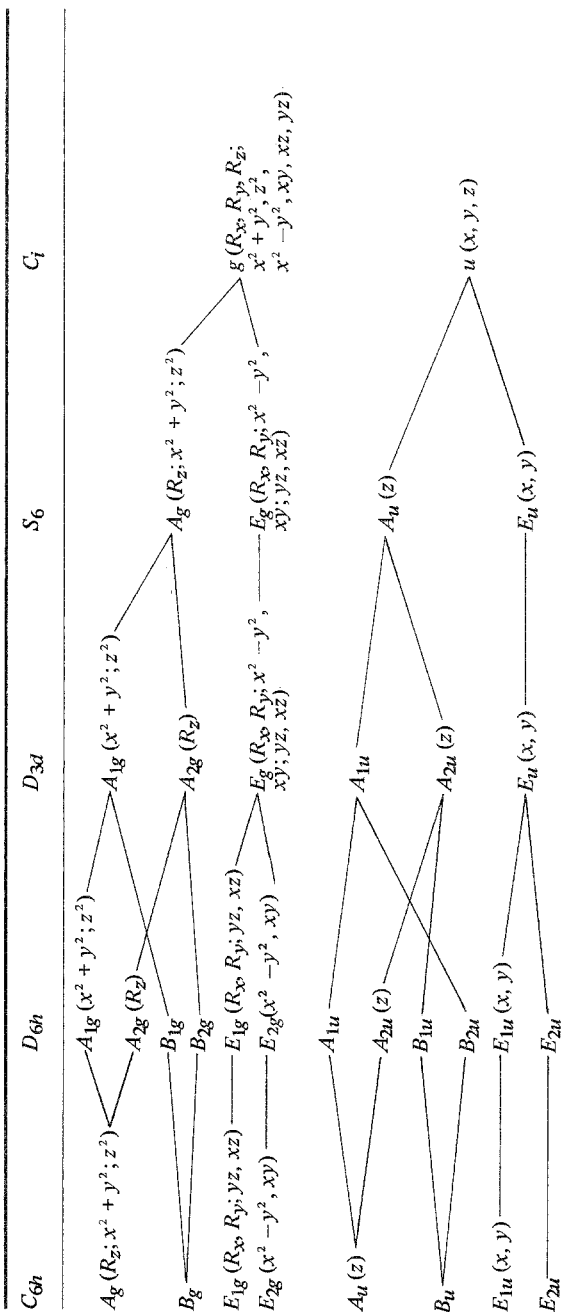
The only assumption that must be made in determining the molecular-crystal site symmetry of HMB is that the symmetry of the first excited singlet state of HMB can be correlated to the first excited singlet state of benzene for which the symmetry is well characterized (Callomon et al., 1966; Sklar, 1937; notation is that of Wilson et al., 1955). An investigation of the u.v. absorption spectrum of HMB and its relationship to the similar spectrum of benzene offers strong experimental evidence to support the correlation (Nelson and Simpson, 1955). Also theoretical calculations on the first excited singlet states of benzene and HMB using the B_{2u} symmetry of benzene give very good agreement with experimental measurement (Gray et al., 1955). These experimental and theoretical studies based on the realization that both benzene and HMB have virtually identical carbon ring skeletons from which the π -electron excited states originate, combine to support the correlation.

The benzene molecule has D_{6h} symmetry in the gas phase and its first excited singlet state has been assigned ${}^1B_{2u}$, which gives an optically forbidden transition in D_{6h} . Using the correlation diagram in Table 1, the four possible site groups for the HMB phase III crystal site group can be examined according to their suitability in light of the available data for HMB with respect to benzene.

Beginning with the D_{6h} group, the B_{2u} representation is of course not dipole allowed. This, in addition to the geometrical impossibility in a model of nonfreely rotating methyl groups, excludes D_{6h} as a possible site group since the pure electronic transition (O-O) to the first excited singlet state of the HMB crystal is observed and is therefore a dipole-allowed transition. Similarly, for the C_{6h} group, the B_{2u} representation of D_{6h} correlates with the B_u representation of C_{6h} , which also does not give a dipole-allowed transition, thus excluding C_{6h} as a possibility. In the case of the D_{3d} group, the C_2'' symmetry element from D_{6h} must be preserved to form the correlation table, since by convention the C_2'' axis passes through the center of the C-C ring bond (Callomon et al., 1966; Sklar, 1937; notation is that of Wilson et al., 1955) and the C_2' axis cannot be preserved with a model of semirigid methyl groups.² Thus, the B_{2u} representation of D_{6h} correlates with the A_{1u} representation in D_{3d} and, as with C_{6h} and D_{6h} , this does not give a dipole-allowed transition. The final possible site group is S_6 where the B_{2u} representation of D_{6h} correlates with the A_u representation. In S_6 , the A_u representation gives a dipole-allowed transition, polarized in the z direction, i.e., perpendicular to the molecular plane. This is in agreement with the experimental data (Schnepp, 1958, 1959; Wolf, 1958) and demonstrates that the only possible site group for the phase III HMB crystal is S_6 . A schematic view (Fig. 4) of our suggested phase III crystal structure shows the aromatic rings only. It has an effective D_{3d} symmetry,

² Note that in the paper by Prasad et al. (1973), Table 1 was generated preserving C_2 of D_{6h} in D_{3h} i.e. the opposite convention.

Table 1. Correlation of D_{6h} to possible site groups for phase III hexamethylbenzene



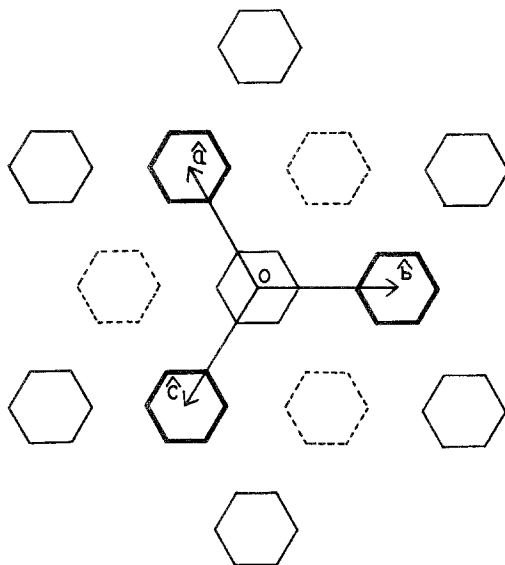


Fig. 4. Trigonal Lattice with basis vectors. Three successive layers of molecules are seen in this view of the predicted phase III crystal structure of hexamethylbenzene. The benzene rings are oriented to give the (maximum) D_{3d} site symmetry and the methyl groups have been omitted. The true S_6 site symmetry is realized by consideration of the methyl group positions and/or a rotation of the benzene rings about their sixfold axes. The basis vectors extending from the origin molecule in the middle layer to the three out-of-plane nearest-neighbor molecules in the top layer were chosen to simplify the exciton band dispersion relation (Woodruff and Kopelman, 1977).

which is consistent with our Raman phonon work (Prasad et al., 1973). This implies that only the geared positions of the methyl groups reduce the symmetry further to S_6 .

The S_6 site symmetry is a very reasonable model for HMB since it allows the methyl groups to move as a set of coupled gears. Thus the molecular point group is S_6 in phase III (effectively also in phase II, see below). It should be noted that the gear coupled configuration is also consistent with the C_7 site symmetry of the phase II HMB crystal. The knowledge of the molecular site symmetry also gives a new interpretation to previous studies on the 115 K phase transition.

This phase transition has been discussed in terms of its being a λ or second-order phase transition involving only small changes in the crystal lattice (Schnepp, 1958, 1959). A complimentary interpretation has been that

the phase transition involves the onset of free methyl-group rotation (Pauling, 1930). However, if the minimum changes in the phase II crystal lattice needed to attain a C_3 axis are considered, it is easily seen that a slippage of 2.4 Å between the ab crystal planes is necessary. This, in itself, is a large change in the crystal structure. The other changes from the phase II crystal structure needed to fit the S_6 model are a tilt of about one degree to bring the molecule into the ab plane and changes in the in-plane intermolecular distances of about 0.1 Å to equalize those distances. These changes are in line with those observed in the phase II to phase I transition, where a plane slippage changes the crystal structure from triclinic to orthorhombic with little change in the in-plane intermolecular distances or the interplanar spacing (Brockway and Robertson, 1939; Watanabe et al., 1949).

The fact that the phase III crystal structure has a C_3 axis in the crystal site group is sufficient to prove that large changes in the crystal structure are taking place during the 115 K phase transition. While this is not inconsistent with the nature of a λ -type phase transition (Westrum and McCullough, 1963; Frankosky and Aston, 1965), it is easily shown that this phase transition is not second order. By the criteria of Landau and Lifshitz (1958), a second-order phase transition necessitates a change in the order of the space group of the crystal by a factor of 2 or less. Hence in the HMB phase II to phase III transition, the transition cannot be second order because the site group is changing from C_i to S_6 , which is a threefold change in the order of the space group. We note that the interchange group (Kopelman, 1967) stays constant (C_1) throughout the transition.

It is also possible now to determine the role of the methyl torsion modes in the phase transition. The fact that the methyl torsion can be observed in the Raman spectrum as a diffuse broad band at temperatures significantly above the phase transition temperature of 115 K proves that the transition does not involve the onset of free methyl-group motion in Phase II (see Fig. 5). However, it is obvious that the phase transition does have a profound effect on the Raman band of the torsion mode; it becomes sharper rapidly in going to phase III. Therefore, it is not a drastic change in the methyl motion which brings about the phase transition but, rather, the methyl motions are sensitive to the lattice and its changes, like the change in site symmetry, thus changing in character with the changes in the molecular site. These changes then manifest themselves in the differences between the spectra of HMB phases II and III.

In summary, the Raman and infrared data on HMB in phases II and III show the presence of an inversion center and at least a threefold axis in the phase III crystal. This has been supported by Edmonds (1973), who has found C_i and C_3 symmetry elements in a low-temperature (phase III) preliminary neutron diffraction study. Also, studies of hexachlorobenzene in a host of HMB by PMDR methods indicate that the host site preserves the threefold symmetry of hexachlorobenzene, thus being completely consistent

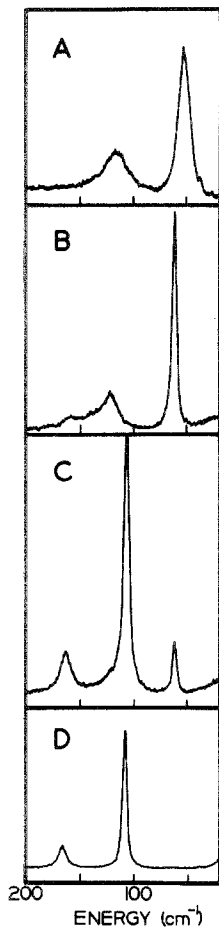


Fig. 5. Raman spectra of hexamethylbenzene crystal in the region 25–200 cm^{-1} . *A* and *B* are spectra of the crystal in phase II at room temperature and 116 K, respectively. *C* is the spectrum of the partially supercooled crystal at 113 K where both phases II and III are observed. *D* is the spectrum of the crystal in phase III at 93 K. The special resolution is $\sim 1 \text{ cm}^{-1}$. Note that the band above 150 cm^{-1} represents the methyl torsion (Prasad et al., 1973).

with the S_6 site symmetry (El-Sayed et al., 1972). The electronic spectrum demonstrates clearly that the phase III crystal site symmetry is not higher than $C_3 \times C_i$ which is S_6 . Thus it can be concluded that the site group is definitely S_6 , which here is also the factor or unit cell group (Bertie and Kopelman, 1971) as well as the molecular group in the phase III crystal

structure. Also, the methyl groups' motions remain restricted, probably with a geared configuration, throughout the λ -type phase transition. Thus the molecular structure in phase II is probably very close to that of the S_6 in phase III, even though it must be slightly distorted by the C_i environmental symmetry. We thus agree with the S_6 picture of the molecule suggested by Schnepf and McClure (1957), and with the loss of its threefold axis in phase II suggested by Schnepf (1958, 1959), but only in part with the approximate D_{3d} symmetry in phase II suggested by Hamilton et al. (1969). As far as the torsional motion is concerned, we agree with the nature of the phase transition suggested by Rush and Taylor (Rush, 1967; Rush and Taylor, 1966) [but not with that suggested in earlier u.v. work (Schnepf, 1958, 1959; Schnepf and McClure, 1957; Broude, 1951, 1952)].

Conclusions

The λ -type phase transition of HMB is first order. The low-temperature phase III is trigonal, with an S_6 point group, a trivial interchange group, and one S_6 site group per primitive unit cell. This is consistent with an S_6 molecular symmetry and with methyl groups that are geared but restricted in their motion both below and above the 115 K phase transition.

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