$$\sum_{i,j=m+1}^{m'} A_{ki}\langle(\hat{u}_i-\bar{u}_i)\,(\hat{u}_j-\bar{u}_j)\rangle A_{jl}=0$$

in (4).

In the centrosymmetric case it is impossible to describe $\varrho_0(\mathbf{r})$ by a two-centred description of the probability density of two approximately coincident half-weight atoms. However such a probability density can be most conveniently described as a single-centred description using higher-order cumulants.

Rae (1975) has indicated how three third-order cumulant parameters and six fourth-order cumulant parameters may be used as an alternative to the three extra positional parameters and six extra temperature parameters to describe the electron density distribution as a deviation from the electron density for a single anisotropic atom. The mean of the electron density of two half-weight atoms is the mean of the means of the individual half-weight atoms, and the use of the three third-order cumulant parameters more accurately describes the mean, as it allows the mean and position of maximum probability to be non-coincident, the three parameters describing this displacement. The six fourth-order cumulants allow the electron density at the maximum to be different from that imposed by the single anisotropic atom that best describes the electron density. The seven third-order cumulant parameters omitted are incapable of displacing the mean from the position of maximum probability and the nine fourth-order cumulant parameters omitted are incapable of changing the value of the electron density at the maximum. This approach however does not eliminate covariance problems, the third-order cumulant parameters and the positional parameters being highly covariant, as are the fourth-order cumulant parameters and the anisotropic thermal parameters. It is possible to fit two almost coincident anisotropic atoms to the probability density function described by the cumulant model, but this procedure is very dependent on the accuracy of the higher-order cumulants. Constraints on parameters and their consequent non-inclusion in the least-squares equations can be used to reduce the apparent variances of the remaining parameters, but this advantage can be illusory if the excluded parameters covary with the included parameters and suffer from systematic error.

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The Crystal Symmetry and Powder Pattern of Hexamethylbenzene Below 116 K

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Laue patterns of very thin single-crystal platelets of hexamethylbenzene at a temperature (80 K) below the cold-phase transition (116 K) have been recorded. In this colder phase (Ph. III), whose flat plate pattern is interpretable as a precession photograph because of the probable ordered fragmentation of the sample, the crystal symmetry appears to be hexagonal (or trigonal), as confirmed also by previous optical and spectroscopic observations. The X-ray diffraction spectrum of the powder taken at the same temperature gives 3·59 Å as the distance between the planes containing the molecular rings, and was indexed on the basis of a hexagonal cell with $a=31{\cdot}5$, $c=3{\cdot}59$ Å, containing 12 molecules (probable space group $P6mm$, with all molecules lying in special positions); the length of the basal axis is exactly four times that of the elementary mesh obtained from the hexagonal grid on which the single-crystal pattern lies.

Triclinic crystals of hexamethylbenzene (HMB) (Brockway & Robertson, 1939) undergo a λ-type phase transition at 116 K (Frankosky & Aston, 1965) and until now conclusive structural data on the colder phase (Ph. III) have not been obtained either by X-ray or by neutron diffraction techniques because of the severe fragmentation of the crystals following the phase transition (Hamilton, Edmonds, Tippe & Rush, 1969).

In a previous investigation (Bertinelli & Stremmenos, 1973) it was observed that thin (001) platelets of the triclinic structure seem to undergo the phase transition with adequate preservation of their single-crystal habit. Conoscopic patterns exhibited by triclinic (001) crystal platelets transformed to Ph. III, the presence of a double degenerate band in the low-frequency Raman spectra, and the disappearance of the ν_{00} band in the electronic spectra in polarized light (41000–35000 cm^{-1}) of the (001) face gave strong indications that below 116 K HMB crystallizes in a uniaxial group.

In order to obtain further information on the crystal symmetry in the colder phase, we undertook an X-ray investigation, the results of which are reported here.

The brittleness of the crystal plates thick enough for the analysis (about 25 μm) prevented the use of complete structural techniques such as the Weissenberg goniometer, the precession camera or the four-circle diffractometer, and therefore the flat-film Laue photographic method at low temperature was employed. The crystals, with the (001) face of Ph. II oriented normally to the X-ray beam, were kept in close thermal contact with a cold finger in an evacuated cell, but at the same time were left free to relieve the macroscopic mechanical stress caused by the phase transition.

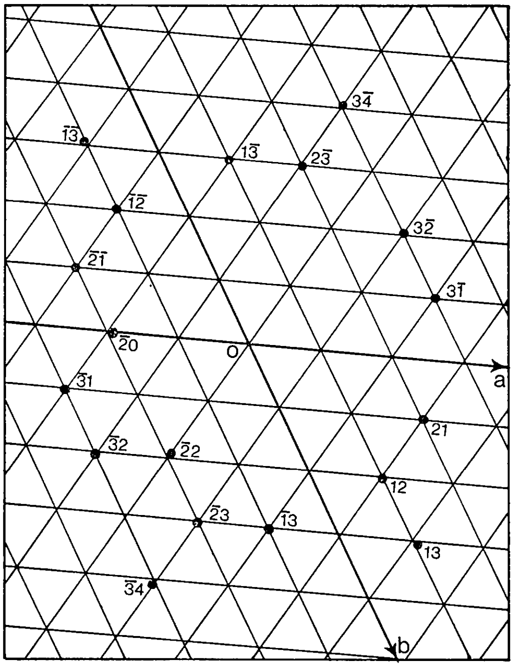


Fig. 2. Interpretation of Fig. 1(*b*) as an (*hk*0) precession pattern, owing to the probable ordered micro-fragmentation of the single crystal during the transition. The simplest possible hexagonal grid is drawn and the spots due to characteristic Cu $K\alpha$ radiation accordingly indexed.

The apposite cell was then surrounded by a water-free nitrogen stream to prevent ice formation. Fig. 1 shows the diffraction patterns of the best crystal platelet (*a*) at room temperature and (*b*) in thermal equilibrium with liquid N_2 (Ph. III).

To minimize exposure times so as to ensure good thermal stability during the recording of the Laue patterns, a Polaroid type 57 film was employed. One can see that the triclinic pattern [Fig. 1(*a*)], devoid of any symmetry element, changes to a new pattern [Fig. 1(*b*)] with an evident hexagonal (or trigonal) symmetry axis. We note, however, that while Fig. 1(*a*) is a typical Laue photograph from a well-crystallized specimen, Fig. 1(*b*) from the transformed one is not. Although the crystal was stationary, it has very probably broken up (on a microscopic scale) into an ordered 'powder' of crystallites, thus giving the equivalent of an oscillation photograph. Moreover pairs of spots are visible which are clearly due to characteristic α and β radiations. It is also possible to trace on Fig. 1(*b*) a hexagonal grid on which all the reflexions may lie (Fig. 2 shows the simplest). Of course the layer lines will not be exactly straight, because of the flat-plate stationary geometry, but they are nearly straight when close to the origin, particularly in the presence of long crystallographic axes. This picture is equivalent to a precession photograph with the beam perpendicular to the plate (*ab*) of the crystal, at least to a good approximation. Unfortunately true precession photographs of our crystals were impossible to obtain because the usual procedure of cooling the free-mounted crystal by a flow of cold gas results in complete fracture of the sample, and the device built to enclose and support the crystal during the transition is too large to be employed in a precession camera.

In Fig. 2 the spots were indexed on the basis of the simplest grid, but it is probable that the length obtained for the *a* axis is only a submultiple of the actual length, so we prefer now to call it a/n, where n is an integer presently unknown.

Employing the relation valid for precession photographs with the beam parallel to the *c* axis:

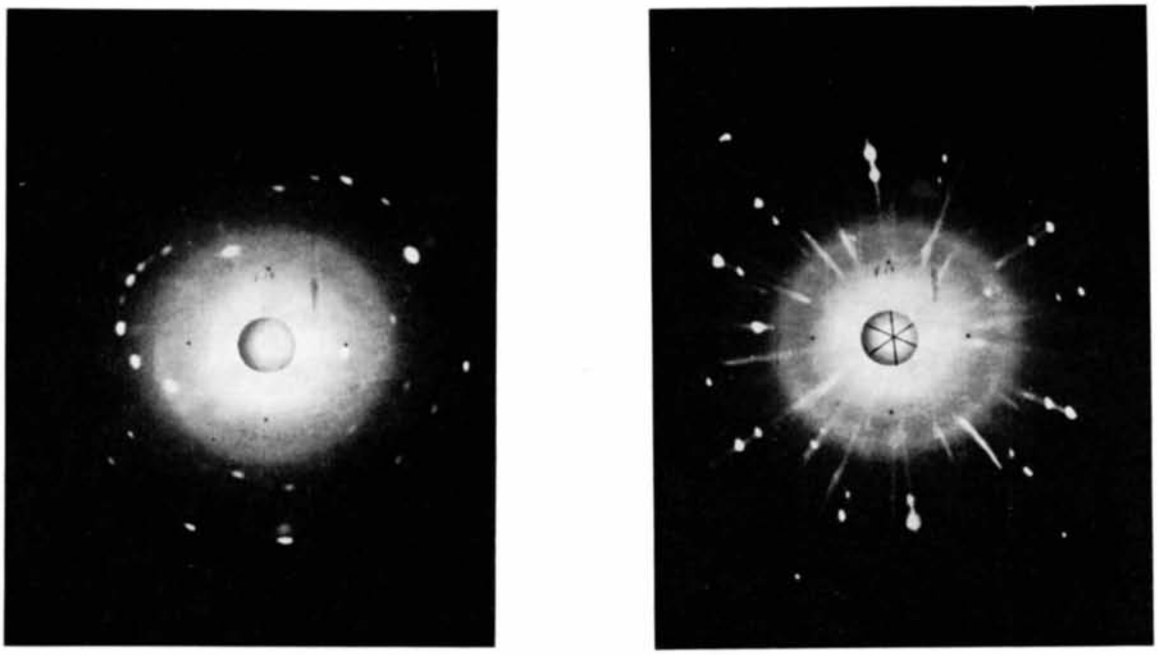
$$d_{hk0} = D\lambda/r\ ,$$

where d_{hk0} is the interplanar spacing, D the sample-to-film distance measured along the X-ray beam, λ the X-ray wavelength and r the distance on the film between the origin and the considered spot, we obtain: $d_{200}=3{\cdot}41$, $d_{210}=2{\cdot}47$, $d_{310}=1{\cdot}76$ Å. Remembering that:

$$a/n = d_{100}\sqrt{\tfrac{4}{3}} = 2d_{200}\sqrt{\tfrac{4}{3}}\ ,$$

from the spots nearest the origin (and therefore the most reliable for the smallest distortions) we found: $a/n=7{\cdot}88$ Å.

To collect more data, a powder spectrum below 116 K was recorded with Cu (Ni-filtered) radiation, on a Rigaku-Denki diffractometer (mod. SG-7) equipped with scintillation counter and a cryostat (mod. A-3)



(*a*) (*b*)

Fig. 1. Transmission Laue patterns of (001) HMB single-crystal platelet: (*a*) at room temperature; (*b*) at 80 K. Unfiltered Cu X-radiation; 50 kV, 30 mA; sample-to-film distance about 49·5 mm; 6 min exposure; magnification 0·79 ×. Amorphous halo is due to greased-paper window of cooling cell.

in which the microcrystalline sample was mounted in the form of a pressed disc about 2 mm thick.

The most prominent feature in the spectrum is, even allowing for probable effects of preferred orientation, the very high intensity of the line at 3·59 Å; also, higher diffraction orders up to the fourth with considerable relative intensities are observed. Table 1 (columns *A* and *B*) gives 64 observed interplanar spacings and intensity data at 80 K.

In the triclinic (Ph. II) and in the orthorhombic (Ph. I) forms, lines of high intensity are found at 3·66 and 3·77 Å respectively (Donnay, 1963). Since these high-intensity reflexions are due to the interplanar distance between molecular layers, we believe that this may also be the case in the Ph. III form.

Moreover, the absence of any spot, among those certainly due to characteristic Cu $K\alpha$ X-radiation, with $d > 3\cdot59$ Å in the single-crystal pattern (in photographs taken with unfiltered Mo radiation the same spots were shifted towards lower θ values, so that the interplanar spacings were maintained with respect to the Mo $K\alpha$ wavelength), strongly supports the hypothesis that the *c* axis (pointing along the incident beam) is not longer than 3·59 Å and all other spacings with higher *d* values arise only from *hk*0 reflexions.

On this basis a satisfactory indexing of the whole powder pattern has been obtained (see Table 1, columns *C* and *D*) for a hexagonal cell with $a=31\cdot5$, $c=3\cdot59$ Å ($c/a=0\cdot114$, $V=3085$ Å^3, $Z=12$ and $\varrho_x=1\cdot05$ g cm^{-3}).

It is now of interest to compare the value of $a/n=7\cdot88$ Å, obtained from the interpretation of Fig. 1(*b*) as a precession pattern, with the length of the *a* axis (31·5 Å) for the cell obtained by indexing the powder spectrum. We deduce that $n=4$, so that this cell is compatible with the single-crystal data if any layer line in Fig. 2 is considered as a fourth order; all *h* and *k* values have to be multiplied by a factor of 4.

For the corresponding interplanar spacings calculated from the proposed hexagonal cell, we have: $d_{800}=3\cdot41$, $d_{840}=2\cdot58$, $d_{12\cdot4\cdot0}=1\cdot89$ Å; clearly the agreement, very good for the spacing nearest the origin, becomes worse for other more remote reflexions, owing to the approximations involved in interpreting Fig. 1(*b*) as a true precession photograph.

The sole presence of fourth-order layer lines and multiples thereof is difficult to explain, since such an

Table 1. *Powder diagram of HMB at* 80 K

A d_{obs} (Å)	*B* I_{rel}	*C* d_{calc} (Å)	*D* *hkl*
9·00	4	9·09	300*
7·59	90	7·57	310*
6·25	240	6·26	320*
5·84	220	5·95	410*
5·37	390	5·45	500
5·05	260	5·15	420*
4·66	610	4·55	600*
4·40	460	4·37	520
3·97	100†	3·94	440
3·59	10000‡	3·59	001
3·46	270	3·47	201
3·06	130	3·07	411
2·92	12	2·90	511
2·79	12	2·80	431
2·60	7	2·60	621
2·54	80	2·55	711
2·43	30	2·44	721
2·32	40	2·32	901
2·24	25	2·24	651
2·14	60	2·14	11·3·0
2·08	65	2·08	12·2·0
1·970	7	1·969	880
1·921§	4	1·921	12·0·1
1·877	6	1·878	14·1·0
1·846	5	1·843	10·7·0
1·791	260‡	1·795	002
1·728	4	1·726	881
1·682	7	1·685	512
1·666	6	1·666	432
1·528	2	1·533	13·5·1
1·510	4	1·511	14·4·1
1·467	2	1·462	932
1·423	2	1·424	13·9·0
1·349	3	1·349	15·6·1
1·324	3	1·324	13·9·1
1·269	1	1·271	14·9·1
1·245	2	1·244	16·9·0
1·220	2	1·221	14·4·2
1·209	2	1·210	12·7·2
1·193	10‡	1·197	003
1·150	2	1·150	613
1·136§	2	1·136	713
1·124	1	1·125	14·14·0
1·090§	1	1·089	663
1·084§	1	1·085	843
1·056	1	1·056	773
1·045	0·5	1·047	16·8·2
1·020	1	1·020	14·0·3
1·010§	1	1·009	14·1·3
0·9823	1	0·9820	12·6·3
0·9704	1	0·9702	10·9·3
0·9484§	1	0·9477	13·7·3
0·9261	1	0·9245	15·6·3
0·9120§	1	0·9136	14·8·3
0·8942	4‡	0·8975	004
0·8696§	1	0·8693	544
0·8530§	1	0·8525	10·0·4
0·8433	0·5	0·8427	10·2·4
0·8285	1	0·8275	11·3·4
0·8219	1	0·8229	10·5·4
0·8165	1	0·8166	884
0·8101§	1	0·8098	14·1·4
0·8069§	2	0·8069	10·7·4
0·8049§	1	0·8048	15·0·4

* All lines except six so marked are satisfied by more than one *hkl* combination (for brevity only the line yielding the best agreement or, if equally good, that with the lowest *hkl* values, is reported).

† May be enhanced by superposition of $K\beta$ radiation from the following exceptionally strong line.

‡ May be enhanced by preferred orientation.

§ Broadened line.

extinction rule does not exist in the hexagonal crystal system. The observation may well be related to a contingent phenomenon (a singular ordered fragmentation of the crystal after the transition).

Of course the assumption of a cell with $c=3{\cdot}59$ Å implies a complete superposition of molecular layers. Allowing for the absence of any condition limiting possible reflexions, the most probable space group accounting for such an arrangement is $P6mm$ (C_{6v}^1) (No. 183) with six molecules at $x,\bar{x},z$; $x, 2x,z$; $2\bar{x},\bar{x},z$; $\bar{x},x,z$; $\bar{x},2\bar{x},z$; $2x,x,z$; three molecules at $\frac{1}{2},0,z$; $0,\frac{1}{2},z$; $\frac{1}{2},\frac{1}{2},z$; two molecules at $\frac{1}{3},\frac{2}{3},z$; $\frac{2}{3},\frac{1}{3},z$; and one molecule at $0,0,z$ (with $z=0$ or $\frac{1}{2}$ these positions are also in agreement with space group $P6/mmm$ (D_{6h}^1) (No. 191), but the presence of a mirror plane perpendicular to the sixfold axis is not compatible with the configuration of the hydrogen atoms in the methyl groups).

The symmetry operations of $P6mm$, remembering that the *ab* plane of the triclinic (Ph. II) cell has nearly hexagonal symmetry ($a=8{\cdot}92$, $b=8{\cdot}86$ Å, $\gamma=119°34'$), necessitate only a 30° rotation of part of the molecules of a layer in their own plane and a sliding of the whole layer with respect to the adjacent one by about 3·8 Å, referring to the original triclinic structure stable at room temperature.

Several trials have also been performed along the lines recently suggested by Prasad, Woodruff & Kopelman (1973) – trigonal symmetry $\bar{3}m$ (D_{3d}) for Ph. III of HMB – but no possible cell was found to be compatible with any of the six space groups of this class. Nevertheless a better packing (type *ABCA*) of molecular layers and a smaller sliding of adjacent ones (about 3·3 Å) was attainable in this case.

Naturally, owing to the high symmetry exhibited and to the numerous lines with high *d* values, it is impossible to find a small cell which will yield a complete indexing of the observed powder pattern. Thus the assumption of Prasad *et al.* (1973), that the unit cell of HMB (Ph. III) contains only one molecule, cannot be justified.

No cell with marked pseudo-hexagonal symmetry has been found which will give a sufficiently good indexing of all observed lines and at the same time satisfy the coordinates of the equivalent positions required by the triclinic and monoclinic space groups. For a systematic search we employed the powder-diagram automatic indexing program devised by Taupin (1973), adapted to a CDC-6600 computer. The smallest calculated cell for which all the observed reflexions could be indexed is a monoclinic one, with $a=10{\cdot}885$, $b=12{\cdot}561$, $c=3{\cdot}590$ Å, $\gamma=99°09'$, $V=485$ Å^3, $Z=2$, $\varrho_x=1{\cdot}11$ g cm^{-3}, but such a cell is clearly not compatible with the symmetry visible in single-crystal photographs. So we were finally obliged to choose the above-mentioned hexagonal cell, even though it appears somewhat surprising that HMB can show at low temperatures a higher crystallographic symmetry than the forms stable at room temperature and above.

Furthermore, to explain the absence from the powder spectrum of *hk*0 lines with smaller *h* and *k* values, we can only assume on the basis of present knowledge that the cut-off towards low θ values is due to the cryostat enclosing the sample. A deeper insight into the many still unanswered questions raised in this research will come only from a complete structural determination.

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