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References

- ABRAHAMS, S. C. (1955). *Acta Cryst.* **8**, 661.
 BAILEY, S. W. & TAYLOR, W. H. (1955). *Acta Cryst.* **8**, 621.
 BERGHUIS, J., HAANAPPEL, I. M., POTTERS, M., LOEPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 BERTAUT, F. & FORRAT, F. (1956). *C. R. Acad. Sci., Paris*, **242**, 382.
 BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344.
 BOND, W. L. (1958). *Acta Cryst.* To be published.
 DELORME, C. (1956). *Acta Cryst.* **9**, 200.
 GELLER, S. (1957). *Acta Cryst.* **10**, 248.
 GELLER, S. & GILLES, M. A. (1957a). *Acta Cryst.* **10**, 239.
 GELLER, S. & GILLES, M. A. (1957b). *J. Phys. Chem.*
Solids, **3**, 30; Fourth International Congress, International Union of Crystallography, Montreal, 10–19 July, 1957, Abstract No. 6·27 (*Acta Cryst.* (1957), **10**, 787).
 HAHN, T. & BUERGER, M. J. (1955). *Z. Kristallogr.* **106**, 308.
 JAMES, R. W. & BRINDLEY, G. W. (1931). *Z. Kristallogr.* **78**, 470.
 MACGILLAVRY, C. H., KORST, W. L., MOORE, E. J. W. & VAN DER PLAS, H. J. (1956). *Acta Cryst.* **9**, 773.
 MENZER, G. (1928). *Z. Kristallogr.* **69**, 300.
 NEUNHAM, R. E. & BRINDLEY, G. W. (1956). *Acta Cryst.* **9**, 759.
 PRINCE, E. (1957). Fourth International Congress, International Union of Crystallography, Montreal, 10–19 July 1957, Abstract No. 6·28 (*Acta Cryst.* (1957), **10**, 787).
 SEEMAN, H. (1956). *Acta Cryst.* **9**, 251.
 SKINNER, B. J. (1956). *Amer. Min.* **41**, 428.
 STEINFINK, H., POST, B. & FANKUCHEN, I. (1955). *Acta Cryst.* **8**, 420.
 TUNELL, G. (1939). *Amer. Min.* **24**, 448.
 YODER, H. S. & KEITH, M. L. (1951). *Amer. Min.* **36**, 519.
 ZUSSMAN, J. (1955). *Acta Cryst.* **8**, 301.

Acta Cryst. (1958). **11**, 441

Thermal Expansion of Hexamethylbenzene

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From X-ray measurements of the thermal expansion of hexamethylbenzene, the principal coefficients of thermal expansion have been determined in magnitude and direction, the values being 2·09, 0·48 and $0\cdot30 \times 10^{-4}$ deg.⁻¹. The increase in distance between molecules linked by van der Waals forces varies from 3·3 to $6\cdot5 \times 10^{-4}$ Å deg.⁻¹.

Although detailed structural investigations such as those of Cruickshank (1956) on anthracene are necessary for a complete description of the thermal movement of the atoms or molecules forming a crystal, some conclusions may, in simple cases, be drawn from the thermal expansion of the crystal lattice.

Hexamethylbenzene affords such a case (Brockway & Robertson, 1939). The molecules constituting this crystal are highly symmetrical ($6/m$) and lie very nearly in close-packed layers in the (001) plane. The stacking of these layers is, however, such that the crystal is triclinic, ($P\bar{1}$), with one molecule per unit cell. Thus the orientation of the expansion ellipsoid is not determined by the symmetry requirements of the crystal.

A sample of hexamethyl benzene kindly supplied by Messrs I. C. I., was purified by Prof. A. R. Ubbe-lohde, to whom the author is indebted for the material

used and also for the following note regarding its preparation:

'The difficulties in the purification of hexamethylbenzene for measurement of the thermal properties arise from its comparatively low lattice energy. This permits the crystals to pack related molecules as impurities in solid solution, and to retain solvent molecules in solid solution unless these have a very different molecular shape. The sample available was therefore purified by two successive chromatographic treatments on a column of activated alumina (Type H, Peter Spence). In the first fractionation the elutrient was 50% benzene and 50% petroleum ether (b.p. 80–100° C.); ten equal fractions were collected. After evaporation of solvent and determination of the melting points, the two best fractions that gave large crystals free from efflorescence and creep (m.p. 163·4–163·6° C.), and that were free from colour, were

chromatographed a second time, using pure petroleum ether as elutrient. The middle fraction was retained for use.

Measurements were made on single crystals obtained by evaporation from petroleum ether and benzene, using a multiple-exposure camera of 14 cm. diameter (Ubbelohde, 1939) and a cold-gas chamber of a type previously described (Ubbelohde & Woodward, 1943). The temperature of the chamber was measured continuously by a thermocouple calibrated at points between room temperature and the boiling point of oxygen. The temperature range used was +20° C. to -70° C., far removed from the transformations at +110° C. and -165° C. associated with the onset of rotation of the molecules and the methyl groups respectively.

Cu $K\alpha$ radiation was used throughout. Although several separate experiments were made for each of the reflexions studied, the number of observations was not sufficient for a statistical assessment of the probable error. All films were measured by two observers, and it was considered that the largest error arose from the shape of the reflexions. As the crystals were easily cleaved, they could not be trimmed to the shape required to give a sharp and narrow reflexion by certain planes.

Six points on the expansion ellipsoid are required for its determination in the case of a triclinic crystal; measurements were made in ten directions, as shown in Table 1. Here $\alpha(hkl)$ denotes the mean coefficient

Table 1. Values of coefficient of thermal expansion per degree Centigrade

hkl	Temperature interval (°C.)	$\alpha(hkl) \times 10^4$ measured	$\alpha(hkl) \times 10^4$ calculated
(1)	(2)	(3)	(4)
{ 003 }	70	1.83	1.78
{ 004 }			
404	48 & 26	1.92	2.00
703	68	0.55	0.56
701	68	1.32	1.29
702	70	1.62	1.61
570	80-85	0.90	0.89
740	85	0.49	0.49
860	85	1.15	1.12
1020	85	1.01	1.06
$\bar{9}, 10, 5$	74	0.43	0.41

of expansion per degree Centigrade normal to the plane (hkl). As slightly differing temperature intervals were used in different experiments on the same reflexion, approximate values of the temperature intervals are quoted.

The principal expansions ($\alpha_1 > \alpha_2 > \alpha_3$) were derived from the measured values of $\alpha(hkl)$ by the following semi-graphical method, which involved a minimum of computation and was considered as accurate as the measurements justified:

(1) The expansion ellipse in the plane of real space normal to the zone axis [010] was calculated from the

five measurements made in this zone, using the method of least squares.

(2) The expansion ellipse in the plane normal to [001] was similarly calculated from the four measurements in this zone.

As a check, the value of $\alpha(100)$ was derived from both these curves. The agreement between the values obtained (0.88 and 0.85×10^{-4}) was considered satisfactory.

(3) The expansion coefficients $\alpha(001)$ and $\alpha(\bar{9}, 10, 0)$ were derived from (1) and (2) respectively. The expansion ellipse in the plane normal to [10,9,0] was then calculated, using these values and the measured value of $\alpha(\bar{9}, 10, 5)$.

(4) The coefficients α in the three planes normal to the zone axes [010], [001] and [10,9,0], respectively, were plotted, at 0.1×10^{-4} intervals, on a 20 cm. diameter stereographic net (see Fig. 1). Circular sections

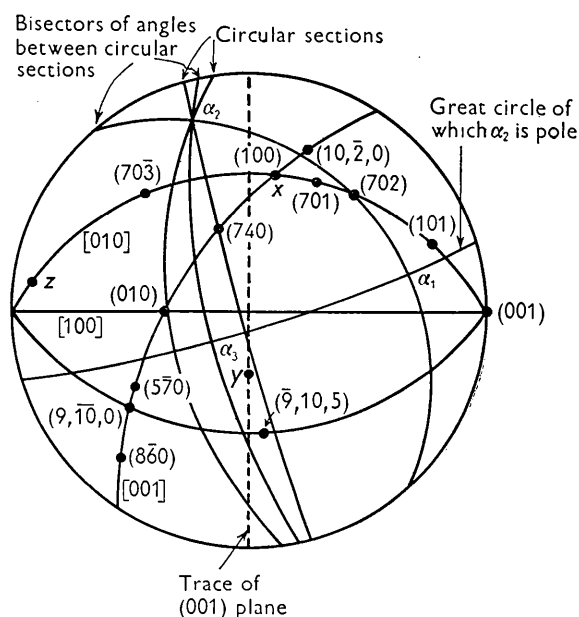


Fig. 1. Stereographic projection illustrating the method of determining the principal coefficients of expansion of hexamethylbenzene from the measured values.

of the expansion ellipsoid were found by trial and error, cutting these zones at points of equal α within an accuracy of about 0.05×10^{-4} .

(5) One principal expansion α_2 lies at the intersection of the circular sections of the expansion ellipsoid. Its value, equal to that of α on the circular sections, and its position were read from the stereographic projection.

(6) The great circle on which α_1 and α_3 lie, with α_2 as pole, was drawn on the projection, and the values of α at its points of intersection with the planes normal to the [010] and [001] zone axes were noted. As α_1 and α_3 also lie midway between the circular sections, their positions were read off and their values could be calculated.

The expansion ellipsoid was now completely defined and the value of the coefficient of expansion $\alpha(hkl)$ in any direction could be derived from it. Such values are listed in Table 1, column (4), for comparison with the measured values, column (3).

The agreement between measured and calculated values of α was considered satisfactory, except in the case of $\alpha(101)$. This observation was thought to be less reliable, on account of the smaller temperature interval, and was accorded a low weight in calculation (1). The discrepancy may however reflect a real variation in the expansion over the range $+20^\circ$ C. to -70° C.

Table 2 defines the expansion ellipsoid. Fig. 1 illustrates the method used. It will be noted that

Table 2. *Principal coefficients of thermal expansion per degree Centigrade*

	$\alpha \times 10^4$	φ ($^\circ$)	ψ ($^\circ$)	ω ($^\circ$)
α_1	2.09	60	70	147
α_2	0.48	32	108	65
α_3	0.30	79	22	70½

α_2 and α_3 lie near the (001) plane, in which the molecules are approximately close-packed.

The orthogonal axes of reference used are:

OX normal to (100) plane,

OZ perpendicular to OX in [010] zone,

OY coincident with b crystal lattice axis,

φ, ψ, ω being the angles with OX, OY, OZ respectively.

Discussion

The figures in Table 2 show that the coefficient of expansion is strongly anisotropic, being largest perpendicular to the plane of the molecule. The increase in distance between the centres of neighbouring molecules does not, however, vary so markedly with direction.

Thus, the maximum and minimum values of the coefficient of expansion in the plane of the molecule are found to be 0.70×10^{-4} and 0.37×10^{-4} deg. $^{-1}$ and the molecules are approximately close packed with a distance of 9 Å between their centres. The increase in this distance therefore varies from 6.3×10^{-4} to 3.3×10^{-4} Å deg. $^{-1}$. Further, the distance between the layers of molecules is the d_{001} spacing 3.66 Å (Brockway & Robertson, 1939) and this increases by $1.78 \times 3.66 \times 10^{-4}$ Å deg. $^{-1} = 6.5 \times 10^{-4}$ Å deg. $^{-1}$. Hence the average increase in the distance between adjacent molecular centres is 5.4×10^{-4} Å deg. $^{-1}$.

In the absence of any explanation of the anisotropy in the (001) plane, which does not appear to bear a

simple relationship to the proximity of the methyl groups in that plane, this average must be regarded as a rough estimate only of the increase to be expected when van der Waals forces are operative in linking the molecules.

It is of interest to compare the thermal increase in distance between molecules in other structures fulfilling such conditions. In *p*-nitroaniline the molecules have now been shown (Donohue & Trueblood, 1956) to be linked by hydrogen bonds in sheets which are themselves connected by van der Waals forces. Taking these sheets as 3.5 Å apart, and the coefficient of thermal expansion normal to them as 1.5×10^{-4} deg. $^{-1}$ (McKeown, Ubbelohde & Woodward, 1951), the increase in intermolecular distance is 5.3×10^{-4} Å deg. $^{-1}$. The close agreement between this figure and the average figure 5.4×10^{-4} Å deg. $^{-1}$ for hexamethylbenzene may be fortuitous, but a considerable measure of agreement would be expected if we consider that, as a first approximation, the expansion of *p*-nitroaniline in this direction is that of a structure held together by van der Waals forces.

Other compounds for which measurements have been made are *p*-dinitrobenzene (McKeown, Ubbelohde & Woodward, 1951) and the phthalocyanines (Ubbelohde & Woodward, 1943).

In these cases, although van der Waals forces only are present, the increase in the distance between the centres of the molecules is widely different in different directions. An extreme case is that of platinum phthalocyanine, where one principal expansion shows a small negative value. If we adopt a static model, we must postulate a small change with temperature of the molecular orientation.

No reliable figure for the increase in intermolecular distances can be derived from the thermal expansion of such crystals. It has been shown (Cruickshank, 1956) that large flat molecules execute anisotropic translational vibrations and angular oscillations. Further discussion must await the results of such studies, and of full structural analyses at different temperatures.

References

- BROCKWAY, L. O. & ROBERTSON, J. M. (1939). *J. Chem. Soc.* p. 1324.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915.
 DONOHUE, J. & TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9** 960.
 MCKEOWN, P. J. A., UBBELOHDE, A. R. & WOODWARD, I. (1951). *Acta Cryst.* **4**, 391.
 UBBELOHDE, A. R. (1939). *J. Sci. Instrum.* **16**, 155.
 UBBELOHDE, A. R. & WOODWARD, I. (1943). *Proc. Roy. Soc. A*, **181**, 415.