

*The Structure of Overcrowded Aromatic Compounds. Part IV.**
The Crystal Structure of Tetrabenzonaphthalene.

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A partial analysis of the crystal structure of tetrabenzonaphthalene has been carried out by two-dimensional Fourier methods. The molecular position and orientation in the $h0l$ zone were determined by the interpretation of the strong high-angle spectra and of the Fourier transform calculated for a planar regular model. The (010) projection was refined by successive $F_o - F_c$ syntheses to an R factor of 0.22. The third set of co-ordinates has not yet been determined.

The projected molecular dimensions rule out a planar centrosymmetric structure; it is suggested that the molecular symmetry is 222, and that the type of distortion of the aromatic nucleus is similar to that found in 3:4-benzophenanthrene.

THE analysis of the crystal structure of tetrabenzonaphthalene (Fig. 1) is part of a research programme outlined in Part I (*J.*, 1954, 3288). The primary aim is to obtain some quantitative measure of the deformation of representative overcrowded molecules caused by the retention of minimum distances of approach between non-bonded atoms. Formally, the nature of overcrowding in tetrabenzonaphthalene and 3:4-benzophenanthrene (Part III *) is very similar, and it is therefore of interest to compare the mechanisms of the relief of overcrowding in the two molecules. However, the crystal structure of tetrabenzonaphthalene is not readily investigated by two-dimensional methods, since only one zone gives a reasonably clear view of the molecule, the other two zones being completely overlapped. As the three-dimensional analysis must be delayed, we present the preliminary results of a partial two-dimensional analysis now, although only the broad outlines of the crystal and molecular structure are available.

The dimensions of the unit cell, and in particular the length of the b axis, suggest that the molecules are arranged in a two-layer structure with the molecular planes inclined at about 25° to the (010) plane. On the assumption that the molecule is approximately planar and has atoms placed at the corners of regular hexagons of side 1.40 Å, one may expect groups of strong spectra at about 120° to one another with interplanar spacings of 1.2 and 2.1 Å, respectively, as these distances correspond to prominent periodicities of the molecule (cf. Robertson and White, *J.*, 1945, 607). Table I lists the strongest high-

TABLE I. *List of strong, high-angle spectra.*

| $h0l$ | d (Å) | $U(h0l)$ | $h0l$ | d (Å) | $U(h0l)$ | $h0l$ | d (Å) | $U(h0l)$ | $h0l$ | d (Å) | $U(h0l)$ |
|-------|---------|----------|----------------|---------|----------|-------|---------|----------|----------------|---------|----------|
| 602 | 2.20 | 0.24 | 205 | 2.33 | 0.28 | 208 | 1.23 | 0.25 | 14,0,II | 1.06 | 0.34 |
| 801 | 2.00 | 0.40 | 804 | 2.37 | 0.23 | 408 | 1.14 | 0.31 | 16,0 $\bar{2}$ | 1.22 | 0.53 |
| | | | 10,0 $\bar{4}$ | 2.00 | 0.46 | 608 | 1.04 | 0.27 | 16,0 $\bar{3}$ | 1.25 | 0.41 |
| | | | | | | | | | 18,0 $\bar{3}$ | 1.10 | 0.38 |

angle spectra together with the values of the interplanar spacings and unitary structure factors. The results limit the possible orientations to the three shown in Fig. 2. A choice among these three orientations was effected by means of the molecular Fourier transform, which was calculated for a planar and centrosymmetric model with atoms placed at the corners of regular hexagons of side 1.40 Å.

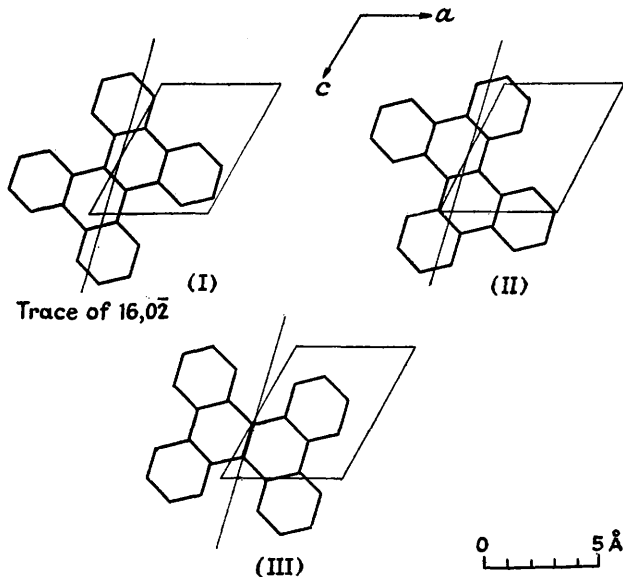
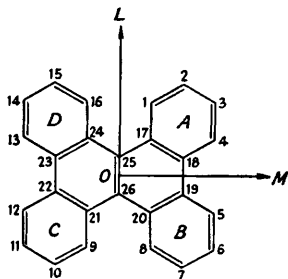
The net of the weighted reciprocal lattice was adjusted to the plot of the Fourier transform in accordance with each of the three molecular orientations deduced from the high-angle spectra. Orientations I and III were eliminated immediately by comparison of the Fourier-transform values with the observed $h00$ structure factors. Values of $u_0 = 0.013$, $w_0 = 0.354$ corresponding to orientation II were calculated by comparison of the measured and the transform values of the geometrical structure factors, after slight adjustment of

* Part III, preceding paper.

the molecular orientation had produced the best agreement between them. With these values the phase factors $\cos 2\pi(hu_0 + lw_0)$ were calculated, and the signs of the $h0l$ structure factors derived. Some of these signs were unreliable because of the small values of their phase factors or because the reciprocal-lattice points lay in regions where the sign of the Fourier transform changed rapidly; however, 108 of the 171 observed terms were considered sufficiently reliable to be incorporated into a first Fourier projection on to the (010) plane. Of these 108 signs actually only 64 were found to be correct when compared with the signs calculated from the final set of atomic co-ordinates. The greater number of signs deduced incorrectly here, as compared for example with α -phenazine (Herbstein and Schmidt, *Nature*, 1952, **169**, 323), is due mainly to errors in the (u_0, w_0) co-ordinates; the final co-ordinates (0.009, 0.383) of the molecular reference point O are in only fair agreement with the original estimate. A further source of error lies in the initial assumptions

FIG. 2. The three possible orientations of the molecule, projected on to (010), as deduced from the high-angle spectra. The trace of 16,0 $\bar{2}$, passing through the subsequently-determined position of the molecular centre, has been inserted to act as reference line.

FIG. 1. The planar model of the tetrabenzonaphthalene molecule, showing the molecular axes and the nomenclature of atoms.



about the molecular shape; the molecule is in fact not planar, regular, or centrosymmetric. However, the error in the $h0l$ structure factors due to the incorrect molecular shape assumed in the calculation of the Fourier transform is reduced by the small inclination of the molecular plane to the plane of projection (cf. the similar situation in dianthronylidene; Harnik and Schmidt, Part II, *J.*, 1954, 3295).

The Fourier projection on to (010) gave a recognisable view of the molecule, although only 13 out of the 26 crystallographically independent atoms were resolved. A first refinement of this projection was carried out by three further Fourier syntheses, the unresolved atoms being placed on the assumption of a regular and planar molecule. Further refinement, without assumptions about molecular shape, was achieved by $F_O - F_C$ syntheses. After four cycles the R factor had been reduced to 0.22, whereupon refinement ceased although there remained 26 terms of uncertain sign, of which 14 had unitary structure factors >0.05 . It is probable that 171 reflections are too few to allow of the complete refinement of a zone where 52 parameters are to be determined. The atomic co-ordinates from the final difference synthesis are listed in Table 2; the signs of the structure factors calculated from these co-ordinates (Table 3) were used in the summation of the Fourier series shown in Fig. 3, in which 145 terms were included.

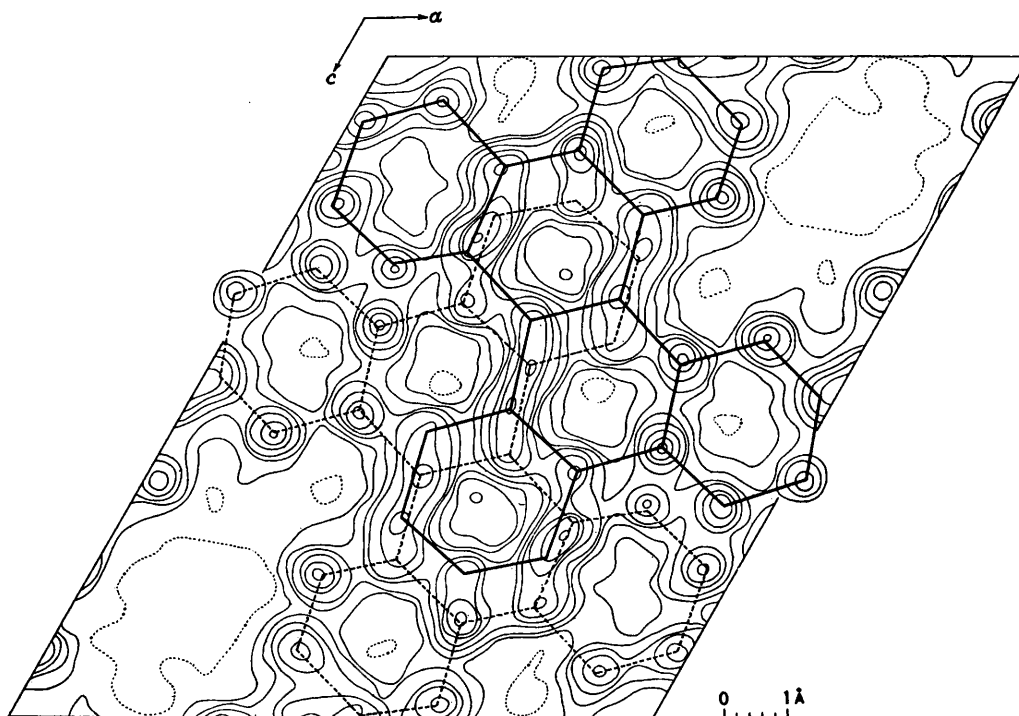
TABLE 2. Experimentally-measured atomic co-ordinates (in Å).

| Atom * | <i>x</i> | <i>z</i> | Atom * | <i>x</i> | <i>z</i> | Atom * | <i>x</i> | <i>z</i> | Atom * | <i>x</i> | <i>z</i> |
|--------|----------|----------|--------|----------|----------|--------|----------|----------|--------|----------|----------|
| 1 | 1.96 | 3.82 | 8 | 6.54 | 2.62 | 15 | 4.40 | 8.48 | 21 | 7.46 | 5.69 |
| 2 | 0.49 | 2.76 | 9 | 8.59 | 5.26 | 16 | 4.01 | 6.92 | 22 | 7.91 | 7.21 |
| 3 | 0.20 | 1.22 | 10 | 9.96 | 6.28 | 17 | 3.05 | 3.61 | 23 | 6.77 | 7.65 |
| 4 | 1.31 | 0.82 | 11 | 10.49 | 7.80 | 18 | 2.88 | 2.03 | 24 | 5.15 | 6.49 |
| 5 | 3.54 | 0.22 | 12 | 9.43 | 8.28 | 19 | 3.91 | 1.75 | 25 | 4.68 | 4.87 |
| 6 | 4.66 | 0.05 | 13 | 7.08 | 9.24 | 20 | 5.52 | 2.92 | 26 | 5.89 | 4.47 |
| 7 | 6.26 | 1.27 | 14 | 5.91 | 9.52 | | | | | | |

* Cf. Fig. 1 and footnote, below.

An objective assessment of the accuracy of the *u* and *w* co-ordinates is not possible in view of their incomplete refinement; however, the mean shift after one refinement cycle was about 0.05 Å, and as it is probable that a single cycle would suffice to complete the

FIG. 3. The electron-density projection on (010). The contours are drawn at intervals of 1 e.Å⁻², with the one-electron contour dotted.



refinement if the remaining signs were known, it is reasonable to estimate the mean errors in co-ordinates at about 0.05 Å.

The molecular dimensions measured from the projection on (010) are shown in Fig. 5: the projected bond lengths vary from 1.20 to 1.50 Å. The molecule is not centrosymmetric nor is the projection consistent with a molecular model in which the carbon atoms are arranged at the corners of regular hexagons. From the variations in the projected interatomic distances it can be deduced that the molecule as a whole is not planar, a conclusion supported by the increase in the distance between atoms 1 and 16* from the value of 2.4 Å appropriate to a planar, regular model to a value, in projection, of 2.75 Å.

It is theoretically possible for a non-planar tetrabenzonaphthalene molecule to exist in

* In this paper the numbers used in references to the carbon atoms are those shown in Fig. 1 and not those strictly related to the name tetrabenzonaphthalene.

TABLE 3. List of observed and calculated structure factors.

| $h0l$ | F_o | F_c | $h0l$ | F_o | F_c | $h0l$ | F_o | F_c | $h0l$ | F_o | F_c |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 200 | 88 † | 108 | 806 | 8 | 9 | 604 | 5 | 15 | 14,12 | 8 | -2 * |
| 4 | 65 | 60 | 7 | 0 | -1 | 5 | 0 | 0 | 13 | 3 | -8 |
| 6 | 53 | -50 | 8 | 3 | 4 | 6 | 15 | -22 | 14 | 7 | -8 |
| 8 | 14 | 2 * | 9 | 5 | -5 | 7 | 7 | 8 | 15 | 7 | 7 |
| 10 | 16 | -18 | 10 | 5 | 1 * | 8 | 5 | -12 | | | |
| 12 | 0 | 4 | | | | 9 | 12 | -13 | 16,01 | 13 | 5 * |
| 14 | 9 | -11 | 10,01 | 9 | 9 | 10 | 3 | -1 * | 2 | 55 | 52 |
| 16 | 0 | -4 | 2 | 0 | 3 | 11 | 8 | -9 | 3 | 44 | -51 |
| 18 | 0 | 1 | 3 | 0 | 3 | 12 | 19 | 14 | 4 | 7 | -14 |
| 20 | 0 | -1 | 4 | 0 | -3 | 13 | 4 | 0 * | 5 | 6 | -1 * |
| 22 | 3 | -1 * | 5 | 4 | 6 | 14 | 0 | 2 | 6 | 0 | -10 |
| | | | 6 | 0 | 3 | 15 | 3 | 5 | 7 | 0 | -4 |
| 001 | 70 | -78 | 7 | 0 | -2 | | | | 8 | 9 | -10 |
| 2 | 14 | -13 | 8 | 0 | -3 | 801 | 9 | 10 | 9 | 0 | -9 |
| 3 | 20 | 15 | 9 | 14 | -12 | 2 | 10 | 7 | 10 | 11 | -8 |
| 4 | 10 | 11 | | | | 3 | 37 | -35 | 11 | 4 | 5 |
| 5 | 15 | 15 | 12,01 | 10 | 3 * | 4 | 59 | 43 | 12 | 10 | -10 |
| 6 | 12 | -7 | 2 | 9 | 13 | 5 | 6 | -1 * | 13 | 6 | -5 |
| 7 | 3 | -3 | 3 | 0 | 4 | 6 | 4 | 0 * | 14 | 0 | -1 |
| 8 | 3 | 6 | 4 | 7 | 5 | 7 | 7 | -7 | 15 | 7 | 8 |
| 9 | 14 | 15 | 5 | 6 | 0 * | 8 | 8 | 12 | | | |
| 10 | 4 | 4 | 6 | 0 | 4 | 9 | 6 | -2 * | 18,01 | 7 | 4 |
| 11 | 0 | -4 | 7 | 0 | -4 | 10 | 0 | 5 | 2 | 0 | -3 |
| 12 | 0 | 0 | 8 | 10 | 5 | 11 | 0 | 2 | 3 | 33 | -36 |
| 13 | 14 | 11 | | | | 12 | 12 | 12 | 4 | 14 | -1 * |
| | | | 14,01 | 0 | 7 | 10,01 | 0 | -2 | 5 | 7 | -10 |
| 201 | 83 | 83 | 2 | 8 | -2 * | 2 | 5 | -13 | 6 | 4 | 3 |
| 2 | 0 | -3 | 3 | 0 | 7 | 3 | 3 | 1 * | 7 | 13 | 11 |
| 3 | 16 | -17 | 4 | 0 | 0 | 4 | 99 | 88 | 8 | 19 | -18 |
| 4 | 30 | 44 | 5 | 8 | 7 | 5 | 23 | -19 | 9 | 6 | 4 |
| 5 | 16 | 23 | | | | 6 | 7 | 14 | 10 | 0 | 1 |
| 6 | 13 | 11 | 16,01 | 3 | 4 | 7 | 12 | 11 | 11 | 0 | -3 |
| 7 | 19 | 18 | 2 | 4 | -3 | 8 | 0 | -1 | 12 | 6 | -5 |
| 8 | 26 | 26 | 3 | 0 | 3 | 9 | 15 | 13 | 13 | 5 | -4 |
| 9 | 7 | 3 * | 4 | 4 | -3 | 10 | 23 | -25 | 14 | 3 | 2 |
| 10 | 0 | 11 | | | | 11 | 6 | 1 * | | | |
| 11 | 0 | 2 | 18,01 | 6 | -10 | 12 | 0 | 3 | 20,01 | 0 | 1 |
| 12 | 14 | -11 | 2 | 4 | 2 | 13 | 3 | 3 | 2 | 7 | 2 * |
| 13 | 9 | 7 | | | | | | | 3 | 0 | 1 |
| | | | 201 | 70 | -80 | 12,01 | 0 | -2 | 4 | 6 | -13 |
| 401 | 29 | -27 | 2 | 27 | -24 | 2 | 13 | 13 | 5 | 0 | 6 |
| 2 | 20 | 13 | 3 | 20 | 20 | 3 | 0 | -7 | 6 | 0 | 4 |
| 3 | 0 | 1 | 4 | 9 | -14 | 4 | 8 | 11 | 7 | 0 | -5 |
| 4 | 17 | -21 | 5 | 71 | 71 | 5 | 13 | 1 * | 8 | 10 | -18 |
| 5 | 14 | -13 | 6 | 26 | -19 | 6 | 16 | -18 | 9 | 0 | -3 |
| 6 | 3 | 8 | 7 | 17 | 20 | 7 | 0 | -1 | 10 | 0 | 1 |
| 7 | 20 | -16 | 8 | 6 | -5 | 8 | 8 | 6 | 11 | 0 | 5 |
| 8 | 28 | 25 | | | | 9 | 10 | 12 | 12 | 0 | -1 |
| 9 | 20 | 17 | 401 | 37 | 28 | 10 | 6 | 4 | 13 | 0 | 1 |
| 10 | 0 | 2 | 2 | 16 | 13 | 11 | 0 | 11 | 14 | 3 | -8 |
| 11 | 7 | 1 * | 3 | 6 | 10 | 12 | 10 | -8 | | | |
| | | | 4 | 41 | 48 | 13 | 0 | 3 | 22,01 | 0 | -8 |
| 601 | 48 | -49 | 5 | 8 | 12 | 14 | 3 | 2 | 2 | 0 | -1 |
| 2 | 56 | 50 | 6 | 19 | -15 | | | | 3 | 0 | -2 |
| 3 | 15 | 17 | 7 | 28 | -26 | 14,01 | 0 | -9 | 4 | 0 | -1 |
| 4 | 0 | 0 | 8 | 10 | -4 * | 2 | 6 | 11 | 5 | 0 | -1 |
| 5 | 9 | 10 | 9 | 8 | -5 | 3 | 3 | -5 | 6 | 0 | 1 |
| 6 | 0 | -5 | 10 | 8 | 6 | 4 | 0 | 0 | 7 | 3 | -10 |
| 7 | 6 | 14 | 11 | 4 | 2 | 5 | 3 | -4 | 8 | 0 | -3 |
| 8 | 21 | -16 | 12 | 3 | -5 | 6 | 12 | 14 | 9 | 3 | 1 * |
| | | | 13 | 5 | 1 * | 7 | 0 | 5 | 10 | 0 | 1 |
| 801 | 86 | -76 | | | | 8 | 7 | 13 | 11 | 0 | 0 |
| 2 | 21 | 11 | 801 | 5 | 6 | 9 | 5 | 9 | 12 | 6 | 4 |
| 3 | 7 | 0 * | 2 | 14 | -7 * | 10 | 4 | 3 | 13 | 0 | -3 |
| 4 | 0 | 3 | | | | 11 | 27 | -23 | 14 | 3 | 4 |
| 5 | 13 | -9 | 3 | 24 | 21 | | | | | | |

* Term omitted from Fourier summations.

† Presumed secondary extinction error.

any of three stereoisomeric forms. There are two geometrical isomers (Fig. 6) differing in the relative inclinations of the four benzo-rings. The symmetries of idealised models of these isomers would be 222 and $\bar{1}$, of which the former can exist in two enantiomorphous forms. As the molecule is not centrosymmetric in projection its actual symmetry cannot be $\bar{1}$ and thus the stereoisomers encountered in the present work are probably those of symmetry 222 . The crystals analysed here are centrosymmetric; thus the two enantiomorphs crystallise together and the crystals are those of the racemate. In this

FIG. 4. *The projection of the unit-cell contents on (010).*

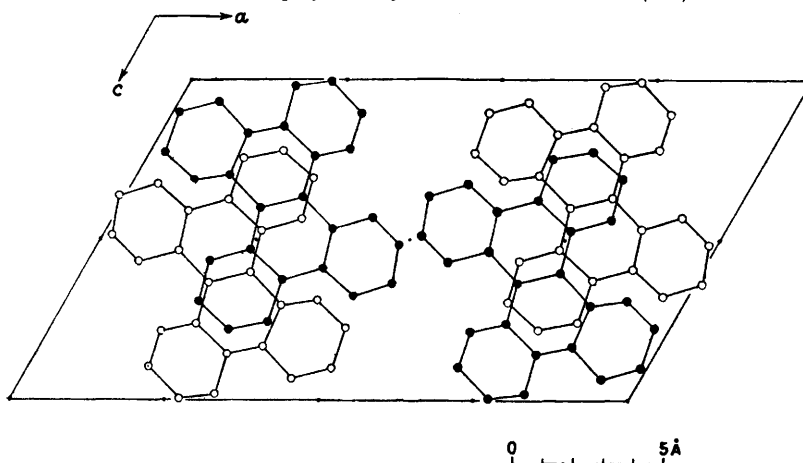


FIG. 5. *Projected bond lengths and intramolecular distances as determined from ρ ($h0l$).*

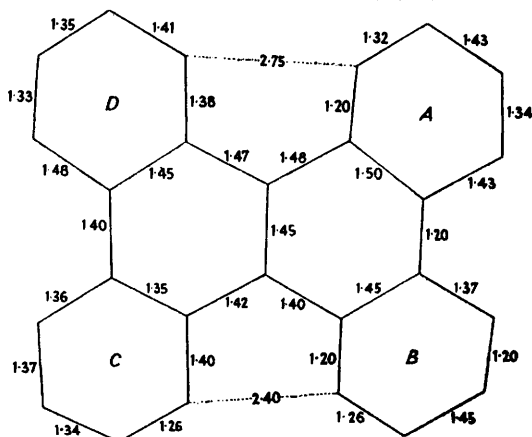
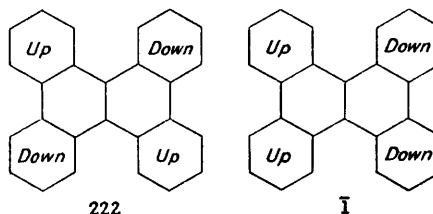


FIG. 6. *Possible configurations providing relief of intramolecular overcrowding.*



respect tetrabenzonaphthalene differs from 3 : 4-benzophenanthrene, where resolution of the optical isomers occurs on crystallisation.

The projection on (010) suggests that rings *A* and *B* are bent out of the mean molecular plane, while it follows from the suggested molecular symmetry that the bending must be in opposite directions. The necessity of relieving the overcrowding between atoms 1 and 16, and between 8 and 9, implies that ring *D* must be bent in the opposite sense to ring *A* and similarly for rings *B* and *C*; if these suggestions are correct the general mechanism of the relief of overcrowding in this molecule may well therefore be similar to that encountered in 3 : 4-benzophenanthrene (see Part III, *loc. cit.*). However, it has not been possible to obtain any further evidence from the projection on (010) about the exact nature of the distortions in the molecule.

The projected distance between atoms 1 and 16 has been increased to 2.75 Å, approaching the distances of 2.9—3.0 Å found between overcrowded carbon atoms in other molecules, and it thus appears not unlikely that the closest intramolecular approach distances in tetrabenzonaphthalene also lie within the above limits.

Experimental.—Good crystals of tetrabenzonaphthalene were grown by slow cooling of solutions in tetralin. The needle-shaped crystals are elongated along [010], showing {100}, {001}, and {20 $\bar{1}$ }.

The cell dimensions were determined from full-rotation and zero-level Weissenberg photographs taken about the [010] axis, the measurements of a and c being extrapolated to $\theta = 90^\circ$ (Buerger, "X-Ray Crystallography," John Wiley and Sons, New York, 1942, Ch. 20). The crystallographic constants are: $a = 20.45 \pm 0.02$, $b = 7.74 \pm 0.02$, $c = 12.18 \pm 0.01$ Å; $\beta = 119^\circ 33' \pm 7'$; d (found) = 1.292, d (calc.) = 1.275, $n = 4$. The space-group, determined from zero- and first-layer Weissenberg photographs about [010] and [001], is $P2_1/a$.

The intensities of the $h0l$ reflections were estimated visually from multiple-film Weissenberg photographs; the F^2 values were placed on an approximately absolute scale by Wilson's statistical method (*Nature*, 1942, 150, 152) and later rescaled by comparison with the calculated values.

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