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# The Crystallography of Anthracene at 95 °K and 290 °K

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X-Ray data, at both 290 °K and 95 °K, of high internal consistency, are reported together with the results of a number of detailed least-squares refinement analyses. The observed bond lengths, with an average estimated standard deviation of 0·008 Å, are compared with those predicted theoretically by a number of procedures and previous comparisons and suggestions are examined critically. The expansion coefficients of the crystal are markedly anisotropic and, together with the X-ray diffuse scattering, are discussed in relation to rigid body molecular vibrations and molecular reorientation in the lattice on cooling; this latter feature also provides an explanation for the temperature dependence of the principal crystal diamagnetic susceptibilities.

## Introduction

Since the original demonstration of the molecular nature of their crystals, naphthalene and anthracene have been intensively studied by X-ray methods. Their recent crystallographic history has been summarized by Cruickshank & Sparks (1960), who were, however, largely concerned with an examination of the bond lengths in anthracene as determined by several refinement analyses of three-dimensional photographic data (Mathieson, Robertson & Sinclair, 1950) and a more limited set of proportional counter data (Phillips, 1957). These latter data were, in part, prompted by the need to confirm the accuracy claimed for the X-ray photographic intensity data of anthracene, naphthalene and a number of aromatic molecules of biological interest (Mason, 1957, 1960) and also to establish an absolute intensity basis in counter diffraction investigations of protein structure. The need for accurate and low-temperature data in 'super-refinement' techniques had also been stressed by Lonsdale, Mason & Wells (1957) in reply to suggestions that any refinement procedures beyond the usual Fourier analysis of the electron density should be regarded as artificial (Kitajgorodskij, 1957); a low-temperature analysis of anthracene and naphthalene was again indicated by the observed temperature variation of the crystal diamagnetic susceptibilities (Lumbroso-Bader, 1958; Leela, 1959).

## Experimental

Anthracene, $C_{14}H_{10}$, $P2_1/a$, $Z = 2$, $F(000) = 188$, $a = 8{\cdot}561$, $b = 6{\cdot}036$, $c = 11{\cdot}163$ Å; $\beta = 124°\,42'$ (Mathieson *et al.*, 1950) compared with

$$a=8{\cdot}562\pm0{\cdot}006,\ b=6{\cdot}038\pm0{\cdot}008\,,$$
$$c=11{\cdot}184\pm0{\cdot}008\ \text{Å};\ \beta=124°\,42'\pm6'\ \text{at}\ 290\ °\text{K}\,,$$

and

$$a=8{\cdot}443\pm0{\cdot}006,\ b=6{\cdot}002\pm0{\cdot}007\,,$$
$$c=11{\cdot}124\pm0{\cdot}008\ \text{Å};$$
$$\beta=125°\,36'\pm8'\ \text{at}\ 95\ °\text{K (this investigation).}$$

Precision measurements on a single film, at different temperatures, show the thermal expansion coefficients to be markedly anisotropic. Values and directions of

$$\bar{\alpha}_{hkl}^{95-290°}=\frac{1}{195}\,\frac{(d_{hkl}^{290°}-d_{hkl}^{95°})}{d_{hkl}^{95°}}\ °\text{K}^{-1}$$

for planes in the three axial zones, ($hk0$), ($h0l$), and ($0kl$), are shown in Fig. 1. The following equations result from a least-squares analysis of the expansion coefficients for high-order reflexions:

$$\bar{\alpha}_{hk0}=(31{\cdot}0+101{\cdot}0\sin^2\psi)\,.\,10^{-6}\ °\text{K}^{-1}$$
$$\bar{\alpha}_{0kl}=(31{\cdot}0+\ \ 50{\cdot}0\sin^2\psi)\,.\,10^{-6}\ °\text{K}^{-1}$$
$$\bar{\alpha}_{h0l}=(34{\cdot}0+\ \ 98{\cdot}0\cos^2\varphi)\,.\,10^{-6}\ °\text{K}^{-1}$$

where $\psi$ is the angle between [010] and the normal to ($hk0$) or ($0kl$) as the case may be, and $\varphi$ is the angle between the normal to ($h0l$) and the projected direction of the large in-plane molecular axis which has direction cosines

$$-0{\cdot}4941,\ -0{\cdot}1274,\ +0{\cdot}8600\ \ \text{at}\ \ 290\ °\text{K}$$

and

$$-0{\cdot}5117,\ -0{\cdot}1311,\ +0{\cdot}8491\ \ \text{at}\ \ 95\ °\text{K}$$

referred to the orthogonal axes $a$, $b$ and $c'$.

These results have been determined from calibrated Weissenberg photographs using Cu $K\alpha$ radiation ($\lambda\,K\alpha_1=1{\cdot}54051$, $\lambda\,K\alpha_2=1{\cdot}54433$ Å). The low-temperature techniques employed were essentially those described by Robertson (1960); X-ray photographs at temperatures intermediate to 95 °K and 290 °K were also taken, a variable cold-nitrogen gas flow controlled by a small electric heater being used,

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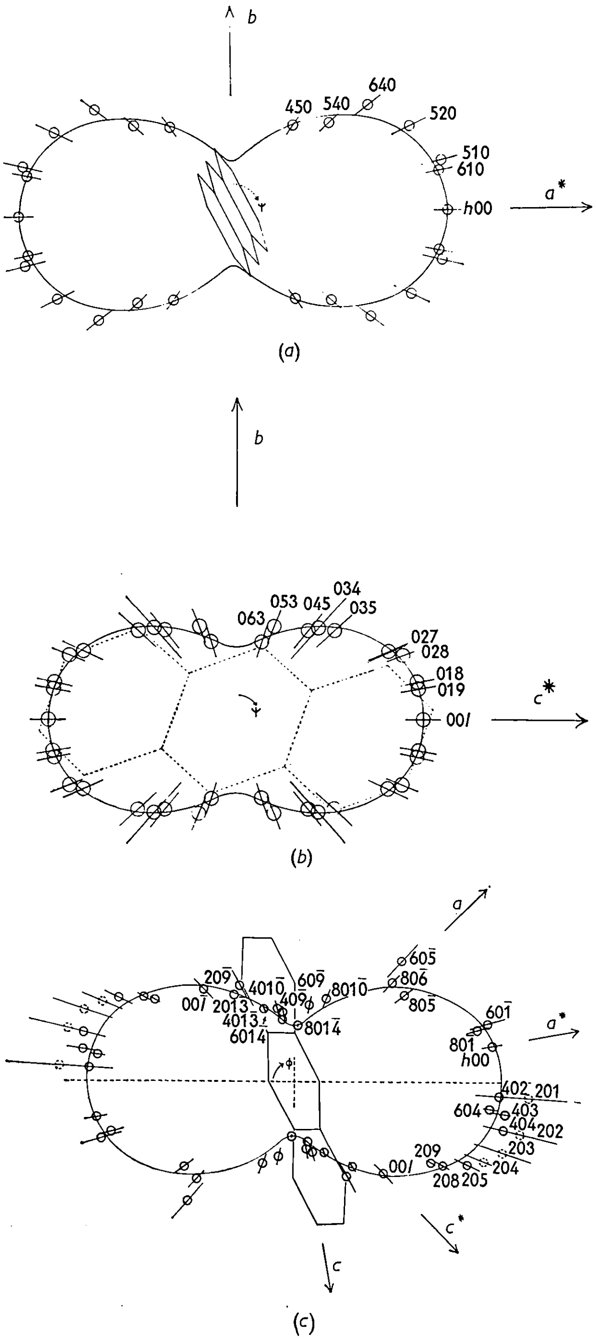


Fig. 1. Values and directions of thermal expansion coefficients for planes (*a*) ($hk0$), (*b*) ($0kl$), (*c*) ($h0l$).

and no discontinuous changes of unit-cell constants with temperature were apparent within this range.

Shock heat treatment and a study of several very small crystals ($<0{\cdot}01$ mm) were used to minimize the effects of primary and secondary extinction. The maximum path-length difference through any crystal examined in detail was about 10% in a crystal of 0·1 mm average dimensions; the effects of absorption can therefore be neglected. All photographic intensity estimates of the complete two-dimensional data were made visually with intensity scales prepared from the crystal under analysis, multiple-film and multiple-exposure techniques providing an approximate intensity range of 20,000 to 1. Film absorption factors were measured for each film pack and the ratio of intensities for different exposure times was measured experimentally; in reproduction of reflexion intensities under several different experimental conditions, slight variations in the processing of the films appear less important than varying film sensitivity.

The probable error of any single visual estimate of intensity is some 10–15% so that the estimation must be placed on a statistical basis if precise amplitudes, accurate to say 2–3%, are required. This is done by treating symmetry-related reflexions as independent (with subsequent averaging) and by the use of several intensity scales so as to avoid systematic errors in the visual range. The reproducibility of 'reading' defined by

$$R_I = \frac{\Sigma|I_0(hkl) - I_0'(hkl)|}{\Sigma I_0(hkl)}$$

where $I_0$ and $I_0'$ represent any two equivalent and averaged sets of intensities from the same crystal, is 3·5%. But intensities from different, although in principle equivalent, crystals were found to differ by an average $R_I' = 5{\cdot}5 - 7{\cdot}0\%$. That is, the overall residual error index $R_F'$ between observed structure factor amplitudes collected from different crystals is of the order 3–4%. The fact that $R' > R$ is largely due to variations in extinction, and other systematic errors, between crystals. It is clear that $R'$ represents a more useful criterion for judging the point beyond which the refinement of any set of data is devoid of physical significance, and that the use of more accurate recording devices may be misleading if highly reproducible intensities are obtained for one crystal only.

The original two-dimensional data (Robertson, 1933) were placed on an absolute scale by comparison with the absolute values of a few of the anthracene reflexions (Robinson, 1932). According to Mathieson *et al.* (1950), their data were placed on the absolute scale of the 1933 investigation; the absolute values for the present investigation result from a least-squares adjustment of the scale of the observed relative amplitudes to the final calculated data; the proportional counter data (Phillips, 1957) have been treated in a similar way.

A summary comparison of all the data shows that, even by the 1933 standard, the scale of the amplitudes of the 1950 and 1956 investigations is in fact some 10% high. In relation to the present measurements, the 1933 scale itself appears to be 4–5% too large, a figure which is probably, however, just within the error of determination of the scale factor. Inclusion of those values liable to extinction does not alter the general lack of agreement between the recorded results. The agreement between the present photographic and counter data is good; the overall consistency is 3·5% and there are no significant differences (<1·5%) between the individual zone scalings. The latter result is useful since the problem of scaling separate photographs and zones together is difficult and is one which is likely to lead to systematic 'patchiness' in the X-ray data with consequent effects on statistical analyses. The difficulties of scaling data collected from a number of crystals of various sizes are, of course, even more pronounced.

The present absolute scale of amplitudes (Table 3) has resulted from a least-squares convergence to the $F_c$'s. It could be suggested that the calculated amplitudes, based on 'non-bonded' atoms, might not provide a reliable criterion for an absolute scale determination. It is therefore worth while noting that the observed amplitude of the 001 reflexion ($F_o=33·1$) agrees to within 0·9% with the experimentally determined value of 32·8 (Robinson, 1932).

The results now suggest that one of the methods of determining the absolute scale, namely, that of ensuring that the integrated 'difference' density is zero within a reasonable molecular volume, has little value in any precise structure investigation. In Cruickshank's (1956) investigation this criterion suggested that the scale should be increased by about 2–3%, whereas the scale factor was, apparently, already some 10–15% too high; the correct determination of an absolute scale obviously depends upon the detection and elimination of systematic errors.

## The refinement analysis

The analysis of the crystal structure at 290 °K was based on the coordinates of Sinclair, Robertson & Mathieson (1950) and an isotropic temperature factor

Table 1. *Anthracene*: *atomic coordinates at* 290 °K

(i) Diagonal least-squares–two-dimensional data

| Atom | $x/a$ | $y/b$ | $z/c$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| *A* | 0·08791 | 0·02567 | 0·36586 | 0·00059 | 0·00121 | 0·00042 |
| *B* | 0·11884 | 0·15919 | 0·28056 | 0·00051 | 0·00095 | 0·00040 |
| *C* | 0·05924 | 0·08071 | 0·13847 | 0·00047 | 0·00087 | 0·00038 |
| *D* | 0·08746 | 0·20859 | 0·04774 | 0·00046 | 0·00092 | 0·00038 |
| *E* | 0·03078 | 0·13350 | −0·08965 | 0·00046 | 0·00084 | 0·00038 |
| *F* | 0·05932 | 0·26272 | −0·18324 | 0·00051 | 0·00138 | 0·00037 |
| *G* | 0·00226 | 0·18177 | −0·31641 | 0·00058 | 0·00109 | 0·00041 |
| *a* | 0·12873 | 0·11472 | 0·46914 | 0·00522 | 0·00957 | 0·00430 |
| *b* | 0·19607 | 0·33121 | 0·31814 | 0·00525 | 0·00924 | 0·00394 |
| *d* | 0·15501 | 0·38180 | 0·08483 | 0·00518 | 0·00936 | 0·00410 |
| *f* | 0·11839 | 0·43631 | −0·14303 | 0·00525 | 0·00987 | 0·00406 |
| *g* | 0·02089 | 0·33677 | −0·38126 | 0·00556 | 0·00971 | 0·00414 |

(ii) Diagonal least-squares–three-dimensional data

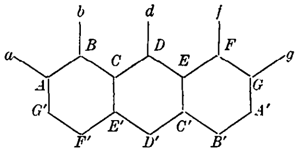
| Atom | $x/a$ | $y/b$ | $z/c$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| *A* | 0·08728 | 0·02712 | 0·36562 | 0·00060 | 0·00095 | 0·00045 |
| *B* | 0·11875 | 0·15775 | 0·28072 | 0·00059 | 0·00084 | 0·00043 |
| *C* | 0·05864 | 0·08030 | 0·13816 | 0·00049 | 0·00071 | 0·00040 |
| *D* | 0·08786 | 0·20936 | 0·04738 | 0·00051 | 0·00081 | 0·00041 |
| *E* | 0·03038 | 0·13067 | −0·08990 | 0·00050 | 0·00073 | 0·00040 |
| *F* | 0·06055 | 0·25943 | −0·18346 | 0·00055 | 0·00083 | 0·00042 |
| *G* | 0·00336 | 0·18060 | −0·31659 | 0·00064 | 0·00092 | 0·00046 |
| *a* | 0·13078 | 0·10834 | 0·47185 | 0·00596 | 0·00841 | 0·00416 |
| *b* | 0·19592 | 0·32463 | 0·31666 | 0·00555 | 0·00799 | 0·00432 |
| *d* | 0·15459 | 0·37636 | 0·08519 | 0·00578 | 0·00766 | 0·00404 |
| *f* | 0·12072 | 0·43044 | −0·14316 | 0·00560 | 0·00833 | 0·00422 |
| *g* | 0·02393 | 0·32391 | −0·37912 | 0·00579 | 0·00892 | 0·00424 |

(iii) 'Complete' least-squares–two-dimensional data

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| *A* | 0·08893 | 0·02818 | 0·36586 |
| *B* | 0·11849 | 0·15836 | 0·28041 |
| *C* | 0·05878 | 0·08054 | 0·13804 |
| *D* | 0·08712 | 0·20829 | 0·04766 |
| *E* | 0·03077 | 0·13087 | −0·08990 |
| *F* | 0·05911 | 0·26461 | −0·18260 |
| *G* | 0·00260 | 0·18099 | −0·31673 |
| *a** | 0·126 | 0·093 | 0·472 |
| *b** | 0·186 | 0·317 | 0·315 |
| *d** | 0·151 | 0·358 | 0·084 |
| *f** | 0·129 | 0·413 | −0·145 |
| *g** | 0·029 | 0·276 | −0·379 |

* These atoms not refined from values reported by Sparks (1958).

$B=3$ Å$^2$, the original refinement of the coordinates and anisotropic Debye factors being accomplished through diagonal least-squares methods, no account being taken of any cross-terms involving coordinates, temperature factors and scale factor. In this refinement analysis all observed reflexions were given unit weighting to correspond to the observed independence of $\sigma(F_o)$ on the magnitude of $|F_o|$. The directions of the axes of the individual thermal vibration ellipsoids were also specified to be identical with those of the molecular symmetry axes; only twelve thermal parameters, three each for atoms *A*–*D* in formula (I), were then needed to describe the vibrations of the carbon atoms if the molecule were also imagined to have *mmm* symmetry in the crystal. All twenty-one thermal parameters (three each for atoms *A*–*G*) were, however, included in the refinement and subsequently averaged.



(I)

After preliminary calculations and comparison with the counter data had shown no evidence of scale errors between the zones, the two-dimensional data were treated as a single three-dimensional set. The hydrogen atoms were included in the coordinate refinement with fractional shifts. McWeeny (1951) valence state atomic scattering curves were used for carbon. Anisotropic temperature factors, equal in magnitude and direction to those of the carbon atom to which the respective atoms were bonded, were applied to the hydrogen atoms but not refined since it was thought, at the time, that such an assumption would not much affect the general progress of the refinement. (Actually recent work on other structures suggests that in the penultimate stages of a refinement analysis this is not true.) The results of each cycle were inspected for any evidence of oscillation in the coordinates and Debye factors, varying fractional shifts being applied depending on the amplitude of oscillation and rate of convergence. Owing to a programming error in the original anisotropic temperature-factor routine, convergence was apparently slow, some ten cycles being necessary to reduce the reliability factor from 0·120 to 0·058. The corrected program gave $R=0{\cdot}070$ for these parameters and then converged to $R=0{\cdot}055$ in two cycles. These final results from the two-dimensional photographic data refinement gave $R=0{\cdot}055$ for the three-dimensional counter data which were in turn reduced to the present value of 0·044 in two cycles. For optimum convergence in the counter data analysis, the Debye factors required fractional shifts of only one quarter of those recommended by the least-squares procedure; this, of course, is a purely empirical way of taking into account what must be quite large off-diagonal terms in the diagonal least-squares refinement of data having a small $(\sin\theta/\lambda)_{\max}$.

Parallel to this work, refinements were also carried out by a complete least-squares routine devised by Curtis (1959), all nine positional and vibrational

Table 2. *Anthracene*: *atomic coordinates at* 95 °K

(i) Diagonal least-squares

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | σ(*x*) | σ(*y*) | σ(*z*) |
|---|---|---|---|---|---|---|
| *A* | 0·08617 | 0·02613 | 0·36813 | 0·00064 | 0·00127 | 0·00047 |
| *B* | 0·11793 | 0·15850 | 0·28352 | 0·00060 | 0·00121 | 0·00047 |
| *C* | 0·05886 | 0·07899 | 0·14027 | 0·00060 | 0·00108 | 0·00047 |
| *D* | 0·08783 | 0·20916 | 0·05076 | 0·00058 | 0·00106 | 0·00046 |
| *E* | −0·03011 | −0·13488 | 0·08974 | 0·00059 | 0·00102 | 0·00046 |
| *F* | −0·06123 | −0·26634 | 0·18215 | 0·00060 | 0·00153 | 0·00044 |
| *G* | −0·00391 | −0·18761 | 0·31834 | 0·00063 | 0·00113 | 0·00047 |
| *a* | 0·14055 | 0·09695 | 0·47524 | 0·00767 | 0·01447 | 0·00628 |
| *b* | 0·18064 | 0·31937 | 0·31510 | 0·00816 | 0·01458 | 0·00599 |
| *d* | 0·14645 | 0·38503 | 0·06789 | 0·00789 | 0·01455 | 0·00619 |
| *f* | −0·12817 | −0·44830 | 0·14122 | 0·00810 | 0·01558 | 0·00616 |
| *g* | −0·02216 | −0·34492 | 0·38234 | 0·00813 | 0·01431 | 0·00612 |

(ii) ‘Complete’ least-squares

| Atom | *x*/*a* | *y*/*b* | *z*/*c* | σ(*x*) | σ(*y*) | σ(*z*) |
|---|---|---|---|---|---|---|
| *A* | 0·08600 | 0·02361 | 0·36797 | — | — | — |
| *B* | 0·11750 | 0·15677 | 0·28348 | — | — | — |
| *C* | 0·05888 | 0·07961 | 0·13963 | — | — | — |
| *D* | 0·08835 | 0·20949 | 0·05174 | — | — | — |
| *E* | −0·02972 | −0·13458 | 0·09030 | — | — | — |
| *F* | −0·06056 | −0·26109 | 0·18263 | — | — | — |
| *G* | −0·00399 | −0·18707 | 0·31804 | — | — | — |
| *a* | 0·13910 | 0·10355 | 0·47509 | — | — | — |
| *b* | 0·17991 | 0·26345 | 0·31379 | — | — | — |
| *d* | 0·14576 | 0·37683 | 0·03799 | — | — | — |
| *f* | −0·12657 | −0·44004 | 0·14368 | — | — | — |
| *g* | −0·01874 | −0·26397 | 0·38137 | — | — | — |

Table 3. *The observed and calculated structure factor amplitudes at* 290 °K *and* 95 °K

| | 290°K | | | 95°K | | |
|---|---|---|---|---|---|---|
| Reflexion | $\|F_o\|$ | $F_c$ | $F_c$(Diagonal) | $\|F_o\|$ | $F_c$ | $F_c$(D) |
| 2 0 0 | 73.64 | 72.72 | 73.20 | 76.04 | 75.88 | 76.72 |
| 4 0 0 | 3.84 | -3.84 | -4.00 | 4.76 | -4.78 | -4.84 |
| 6 0 0 | 8.02 | -6.70 | -7.08 | 11.58 | -11.76 | -11.52 |
| 8 0 0 | 2.54 | -2.28 | -2.24 | 4.48 | -3.58 | -3.12 |
| 0 2 0 | 23.84 | -24.14 | -23.60 | 24.88 | -26.62 | -24.88 |
| 0 4 0 | 2.72 | -2.76 | -2.48 | 0.95 | | -0.80 |
| 0 6 0 | <0.23 | | 0.20 | 2.65 | 2.70 | 2.64 |
| 0 0 1 | 33.06 | 33.90 | 33.72 | 33.82 | 33.26 | 33.00 |
| 0 0 2 | 23.14 | -22.82 | -22.92 | 23.78 | -22.18 | -22.60 |
| 0 0 3 | 14.40 | 14.16 | 14.28 | 16.18 | 16.12 | 15.52 |
| 0 0 4 | 21.24 | -21.00 | -21.00 | 24.60 | -24.42 | -25.32 |
| 0 0 5 | 15.10 | -14.62 | -14.16 | 17.00 | -16.70 | -17.04 |
| 0 0 6 | 4.90 | 4.92 | 4.64 | 7.48 | 7.70 | 7.00 |
| 0 0 7 | 0.68 | -0.42 | -0.60 | 1.70 | -1.62 | -1.68 |
| 0 0 8 | 3.32 | -3.24 | -3.68 | 6.74 | -6.90 | -7.64 |
| 0 0 9 | 4.46 | -4.54 | -4.32 | 9.14 | -9.44 | -9.56 |
| 0 0 10 | 0.90 | -0.50 | -0.32 | 1.22 | -0.62 | -0.52 |
| 0 0 11 | 1.46 | 1.08 | 1.00 | 3.22 | 2.40 | 2.48 |
| 1 1 0 | 59.08 | 60.50 | 59.28 | 58.96 | 61.68 | 59.84 |
| 1 2 0 | 17.36 | -17.56 | -17.72 | 18.90 | -20.24 | -19.24 |
| 1 3 0 | 17.16 | -17.02 | -17.48 | 19.85 | -20.28 | -19.20 |
| 1 4 0 | 0.76 | 0.80 | 1.52 | 1.20 | 1.25 | 1.16 |
| 1 5 0 | 1.26 | 0.54 | 1.04 | 4.40 | 5.14 | 3.92 |
| 1 6 0 | 0.98 | -0.74 | -0.72 | 2.92 | -1.70 | -1.92 |
| 1 7 0 | <0.60 | | 0.36 | <0.75 | | 0.84 |
| 2 1 0 | 52.60 | -53.24 | -53.28 | 56.92 | -55.30 | -56.12 |
| 2 2 0 | 11.98 | -12.08 | -11.60 | 14.72 | -14.60 | -13.88 |
| 2 3 0 | 2.96 | -2.92 | -2.70 | 4.72 | -2.60 | -3.68 |
| 2 4 0 | 1.50 | -1.54 | -1.64 | 2.44 | -0.74 | -0.96 |
| 2 5 0 | 1.18 | -1.36 | -1.44 | 3.58 | -3.14 | -3.44 |
| 2 6 0 | 1.38 | -0.92 | -1.12 | <0.65 | | -0.20 |
| 2 7 0 | <0.30 | | -0.20 | 2.02 | -1.90 | -2.52 |
| 3 1 0 | 11.00 | 11.02 | 10.80 | 11.96 | 11.30 | 11.48 |
| 3 2 0 | 23.02 | -23.04 | -23.04 | 25.74 | -26.40 | -26.20 |
| 3 3 0 | 5.90 | -5.82 | -5.92 | 8.82 | -6.86 | -7.00 |
| 3 4 0 | 0.94 | 0.20 | 0.36 | 2.56 | 0.18 | -1.12 |
| 3 5 0 | 1.66 | -2.26 | -2.28 | 2.68 | -1.76 | -2.04 |
| 3 6 0 | 1.26 | -0.90 | -0.40 | 3.38 | -3.48 | -2.92 |
| 3 7 0 | <0.35 | | 0.36 | <0.51 | | 0.00 |
| 4 1 0 | 23.46 | -23.02 | -22.12 | 25.58 | -27.28 | -26.68 |
| 4 2 0 | 1.94 | -1.96 | -1.20 | 4.88 | -4.62 | -3.60 |
| 4 3 0 | 1.54 | -1.16 | -1.32 | <2.50 | | -2.00 |
| 4 4 0 | 2.84 | -2.68 | -3.04 | 3.30 | -3.60 | -4.76 |
| 4 5 0 | 2.80 | -3.20 | -3.00 | 7.16 | -7.22 | -6.76 |
| 4 6 0 | 0.64 | -0.60 | -0.56 | <1.20 | | -1.08 |
| 4 7 0 | <0.45 | | 1.12 | | | |
| 5 1 0 | 4.86 | -4.82 | -4.64 | 7.32 | -7.22 | -7.12 |
| 5 2 0 | 7.04 | -7.20 | -6.92 | 10.32 | -9.38 | -9.12 |
| 5 3 0 | 1.06 | -1.42 | -0.80 | 4.22 | -4.34 | -4.16 |
| 5 4 0 | 3.04 | -3.30 | -3.04 | 6.10 | -6.02 | -6.56 |
| 5 5 0 | 2.06 | -2.06 | -1.96 | 4.02 | -4.18 | -3.00 |
| 5 6 0 | <0.60 | | 0.76 | <1.56 | | 1.32 |
| 6 1 0 | 4.12 | -4.18 | -3.64 | 6.74 | -5.88 | -5.24 |
| 6 2 0 | <0.75 | | 0.56 | <2.16 | | -1.84 |
| 6 3 0 | 1.34 | -1.48 | -1.96 | <2.60 | | -2.56 |
| 6 4 0 | 3.32 | -3.64 | -3.36 | 8.94 | -6.58 | -8.08 |
| 6 5 0 | 1.46 | -1.40 | -1.20 | 5.12 | -5.16 | -3.56 |
| 7 1 0 | 2.14 | -2.22 | -2.20 | 6.14 | -4.60 | -4.20 |
| 7 2 0 | 0.84 | -0.84 | -0.96 | <1.80 | | -0.80 |
| 7 3 0 | 1.98 | -2.58 | -2.04 | 8.42 | -8.32 | -8.28 |
| 7 4 0 | 2.14 | -2.38 | -2.16 | 4.76 | -4.88 | -4.52 |
| 7 5 0 | <0.38 | | 0.64 | | | |
| 8 1 0 | <0.60 | | 0.36 | <1.05 | | 0.92 |
| 8 2 0 | <0.55 | | -0.40 | 3.14 | -2.54 | -2.52 |
| 8 3 0 | 1.86 | -1.92 | -1.96 | 3.74 | -3.78 | -3.56 |
| 0 1 1 | 8.94 | 9.32 | 9.30 | 9.22 | 10.08 | 9.68 |
| 0 1 2 | 2.96 | 2.70 | 3.04 | 2.52 | 2.84 | 2.96 |
| 0 1 3 | 3.32 | -2.88 | -3.28 | 3.46 | -2.76 | -3.16 |
| 0 1 4 | 11.46 | -10.98 | -10.40 | 14.20 | -12.74 | -12.64 |
| 0 1 5 | 13.24 | -12.58 | -12.20 | 17.48 | 15.90 | -15.72 |
| 0 1 6 | 0.60 | 0.70 | 0.52 | 1.20 | | 0.66 |
| 0 1 7 | 2.58 | 2.58 | 2.48 | 4.64 | 3.54 | 3.80 |
| 0 1 8 | 7.28 | 7.20 | -7.36 | 13.66 | -12.18 | -12.12 |
| 0 1 9 | 7.12 | 7.10 | -7.16 | 13.34 | -12.50 | -12.28 |
| 0 1 10 | <0.44 | | -0.52 | <0.85 | | 0.36 |
| 0 1 11 | <0.25 | | -0.12 | <0.75 | | -0.56 |
| 0 2 1 | 15.50 | -16.10 | -16.04 | 16.50 | -16.84 | -17.30 |
| 0 2 2 | 6.40 | 6.72 | 6.68 | 7.92 | 8.00 | 8.36 |
| 0 2 3 | 4.00 | -4.12 | -3.36 | 6.06 | -5.14 | -5.08 |
| 0 2 4 | 14.12 | 14.02 | -14.12 | 16.26 | -15.66 | -15.72 |
| 0 2 5 | 1.26 | 1.54 | 1.68 | 4.02 | 4.84 | 4.72 |
| 0 2 6 | <0.77 | | -1.12 | 2.40 | -1.68 | -2.00 |
| 0 2 7 | <0.20 | | 0.04 | 1.03 | | 0.28 |
| 0 2 8 | 8.82 | 9.32 | 9.36 | 18.78 | 19.28 | 18.20 |
| 0 2 9 | 2.76 | 2.80 | 2.52 | 5.12 | 4.50 | 3.80 |
| 0 2 10 | 1.54 | -1.52 | -1.68 | 3.74 | 4.22 | -4.00 |
| 0 2 11 | <0.35 | | 0.20 | <1.75 | | 1.52 |
| 0 3 1 | 15.34 | -15.80 | -16.00 | 19.56 | -19.30 | -20.04 |
| 0 3 2 | 0.76 | 0.82 | -0.80 | <0.75 | | 0.48 |
| 0 3 3 | 6.06 | 5.90 | 5.92 | 7.80 | 7.20 | 7.24 |
| 0 3 4 | 11.12 | 11.24 | 11.72 | 15.46 | 14.82 | 14.52 |
| 0 3 5 | 11.58 | 12.14 | 12.16 | 16.84 | 17.28 | 18.44 |
| 0 3 6 | 3.60 | 3.32 | 3.20 | 5.12 | 4.18 | 4.76 |
| 0 3 7 | 1.66 | -1.70 | -1.60 | 4.10 | -4.00 | -4.08 |
| 0 3 8 | 2.62 | -2.32 | -2.16 | 5.04 | -5.00 | -4.24 |
| 0 3 9 | 1.38 | -1.26 | -1.44 | 3.46 | 2.84 | -3.24 |
| 0 3 10 | <0.15 | | 0.08 | <0.65 | | 0.20 |
| 0 4 1 | 3.84 | -3.82 | -3.08 | 5.52 | -4.52 | -4.72 |
| 0 4 2 | <0.45 | | -0.36 | <0.95 | | -0.84 |
| 0 4 3 | <0.47 | | 0.20 | <0.96 | | 0.92 |
| 0 4 4 | 1.62 | 1.66 | 0.88 | 3.10 | -2.42 | -0.56 |
| 0 4 5 | 10.88 | 10.64 | 10.20 | 15.66 | 15.94 | 16.16 |
| 0 4 6 | 4.78 | 4.90 | 5.16 | 8.34 | 8.92 | 9.16 |
| 0 4 7 | 2.80 | -2.42 | -2.96 | 7.52 | -6.66 | -6.36 |
| 0 4 8 | 1.26 | -1.24 | -1.64 | 3.50 | -3.08 | -2.68 |
| 0 4 9 | 2.06 | -1.80 | -1.52 | 5.70 | -5.12 | -4.04 |
| 0 4 10 | 1.34 | -1.20 | -1.24 | 3.96 | -4.00 | -4.20 |
| 0 5 1 | <0.35 | | -0.20 | <1.80 | | -1.60 |
| 0 5 2 | 1.22 | -1.60 | -1.76 | <2.55 | | -2.36 |
| 0 5 3 | 8.26 | -8.30 | -8.88 | 13.86 | -13.76 | -15.24 |
| 0 5 4 | 2.78 | 4.02 | -4.32 | 6.34 | -6.40 | -6.68 |
| 0 5 5 | 2.14 | 2.10 | 1.72 | 3.66 | 3.20 | 4.08 |
| 0 5 6 | 0.64 | 0.64 | | 3.34 | -3.20 | -1.72 |
| 0 5 7 | 1.50 | 1.18 | 2.20 | 4.14 | 4.32 | 4.96 |
| 0 5 8 | 2.58 | 2.42 | 2.36 | 8.10 | 7.44 | 6.28 |
| 0 5 9 | 1.06 | -1.08 | -0.84 | | | |
| 0 6 1 | 3.28 | -3.20 | -3.64 | 5.94 | -6.86 | -7.28 |
| 0 6 2 | 0.64 | -0.78 | -0.84 | <2.50 | | -2.24 |
| 0 6 3 | 6.40 | 6.14 | 6.76 | 13.22 | 13.18 | 14.44 |
| 0 6 4 | 2.72 | 2.26 | 2.36 | 3.22 | 3.46 | 3.36 |
| 0 6 5 | 3.24 | -2.42 | -2.80 | 7.96 | -6.14 | -6.96 |
| 0 6 6 | 2.84 | -1.92 | -2.00 | 6.14 | -5.24 | -4.56 |
| 0 6 7 | 1.14 | -1.06 | -0.76 | 2.52 | -2.62 | -2.32 |
| 0 7 1 | 2.06 | 1.74 | -1.80 | 4.66 | -5.12 | -4.04 |
| 0 7 2 | 1.26 | 0.92 | -0.48 | <1.25 | | -0.60 |
| 0 7 3 | 0.56 | 0.58 | -0.08 | <1.55 | | -1.44 |
| 0 7 4 | 0.25 | | -0.08 | <1.59 | | 0.80 |
| 0 7 5 | 1.02 | -0.74 | -0.76 | | | |
| 2 0 13 | 2.92 | 3.18 | -3.08 | 9.36 | -10.06 | -10.12 |
| 2 0 12 | 0.75 | | -0.60 | 2.64 | -2.56 | -2.32 |
| 2 0 11 | 0.90 | | 0.80 | 1.96 | 2.14 | 2.08 |
| 2 0 10 | 0.65 | | 0.12 | 1.62 | -1.66 | -1.52 |
| 2 0 9 | 7.88 | 8.10 | 8.08 | 10.58 | 11.64 | 10.64 |
| 2 0 8 | 2.54 | 2.76 | 2.60 | 3.66 | 4.14 | 3.76 |
| 2 0 7 | 3.52 | -3.88 | -3.88 | 5.20 | -5.30 | -5.20 |
| 2 0 6 | 4.74 | 5.12 | 5.24 | 5.62 | 7.00 | 6.88 |

parameters for all the carbon atoms being refined. Convergence from the original $R=0.120$ to $R=0.040$ required only four cycles. Unfortunately, the calculated values of the thermal parameters could scarcely be compared with those from the diagonal analysis since the two programs use different routines for the atomic scattering factors. The results from the complete analysis were therefore recalculated and refined with a program, devised by Rollett (1959), using scattering factors identical with those of the diagonal least-squares analysis. From $R=0.059$, the refinement proceeded to a minimization of $\Sigma w\Delta^2$,

Table 3 (*cont.*)

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 0 $\bar{5}$ | 4.62 | -5.24 | -5.08 | 4.68 | -5.56 | -5.08 |
| 2 0 $\bar{4}$ | 2.84 | 3.22 | 3.00 | 2.56 | 1.76 | 2.38 |
| 2 0 $\bar{3}$ | 14.08 | 13.52 | 13.72 | 15.78 | 15.20 | 15.92 |
| 2 0 $\bar{2}$ | 29.54 | -28.60 | -29.08 | 31.30 | -31.90 | -31.36 |
| 2 0 $\bar{1}$ | 52.92 | 51.74 | 52.32 | 53.68 | 51.64 | 52.56 |
| 2 0 1 | 5.02 | -4.84 | -4.36 | 6.18 | -6.02 | -6.12 |
| 2 0 2 | 4.62 | 4.44 | 4.28 | 5.78 | 4.72 | 4.92 |
| 2 0 3 | 4.62 | -4.42 | -4.76 | 5.82 | -5.42 | -4.92 |
| 2 0 4 | 22.26 | -23.62 | -22.32 | 30.90 | -31.68 | -30.36 |
| 2 0 5 | 8.18 | -7.54 | -7.20 | 10.32 | -10.12 | -9.92 |
| 2 0 6 | 3.08 | 3.30 | 2.96 | 5.70 | 5.20 | 5.04 |
| 2 0 7 | 0.85 | | -0.72 | 1.16 | | -1.44 |
| 2 0 8 | 5.78 | -5.86 | -5.96 | 11.62 | -12.06 | -12.64 |
| 2 0 9 | 4.78 | -4.34 | -4.32 | 10.08 | -9.76 | -9.60 |
| 2 0 10 | <0.52 | | 0.28 | | | |
| 4 0 $\overline{14}$ | 2.22 | -2.82 | -2.84 | 8.94 | -8.80 | -8.88 |
| 4 0 $\overline{13}$ | 3.04 | -2.34 | -2.28 | 10.04 | -8.60 | -8.32 |
| 4 0 $\overline{12}$ | 2.14 | 1.48 | 1.40 | 3.94 | 3.46 | 3.12 |
| 4 0 $\overline{11}$ | 3.24 | -2.86 | -2.80 | 5.16 | -5.40 | -5.08 |
| 4 0 $\overline{10}$ | 8.66 | 8.48 | 8.64 | 11.22 | 11.26 | 11.36 |
| 4 0 $\bar{9}$ | 22.74 | 22.98 | 22.92 | 34.44 | 35.98 | 35.68 |
| 4 0 $\bar{8}$ | 1.42 | 1.18 | 1.40 | 4.22 | 3.42 | 4.12 |
| 4 0 $\bar{7}$ | 4.46 | -4.26 | -4.52 | 7.16 | -8.16 | -7.56 |
| 4 0 $\bar{6}$ | 4.32 | 4.54 | 4.80 | 6.26 | 5.90 | 6.56 |
| 4 0 $\bar{5}$ | 10.52 | -10.36 | -10.08 | 10.58 | -12.00 | -11.20 |
| 4 0 $\bar{4}$ | 1.78 | -1.08 | -1.36 | 2.52 | -1.90 | -1.64 |
| 4 0 $\bar{3}$ | 5.62 | 5.64 | 5.48 | 7.40 | 7.12 | 7.32 |
| 4 0 $\bar{2}$ | 5.90 | -6.08 | -5.76 | 7.56 | -7.42 | -7.00 |
| 4 0 $\bar{1}$ | 3.28 | 3.96 | 3.40 | 4.64 | 4.84 | 4.56 |
| 4 0 1 | <0.25 | | 0.08 | 0.98 | -0.90 | -0.80 |
| 4 0 2 | 3.36 | 2.96 | 2.92 | 5.16 | 4.40 | 4.52 |
| 4 0 3 | 7.20 | -7.20 | -6.76 | 10.16 | -10.70 | -9.92 |
| 4 0 4 | 7.24 | -7.14 | -6.80 | 10.50 | -11.10 | -10.76 |
| 4 0 5 | 1.18 | -1.20 | -1.12 | 2.48 | -1.58 | -2.16 |
| 4 0 6 | <0.81 | | 0.64 | <1.16 | | 1.32 |
| 4 0 7 | <0.86 | | -0.92 | <1.20 | | -0.24 |
| 4 0 8 | 2.42 | -3.04 | -2.96 | 8.06 | -7.88 | -7.76 |
| 6 0 $\overline{14}$ | 2.88 | -2.18 | -2.24 | 8.34 | -7.36 | -6.84 |
| 6 0 $\overline{13}$ | 1.50 | 1.10 | 1.20 | 1.62 | 1.78 | 1.80 |
| 6 0 $\overline{12}$ | | | | 2.44 | 2.26 | 1.76 |
| 6 0 $\overline{11}$ | 3.16 | -3.10 | -2.96 | 8.10 | -7.90 | -7.56 |
| 6 0 $\overline{10}$ | 15.06 | 15.02 | 15.00 | 23.98 | 24.44 | 24.24 |
| 6 0 $\bar{9}$ | 15.34 | 15.84 | 15.40 | 28.86 | 29.34 | 29.28 |
| 6 0 $\bar{8}$ | 2.50 | -2.44 | -2.24 | 3.30 | -2.98 | -3.24 |
| 6 0 $\bar{7}$ | 1.74 | 1.66 | 1.36 | 1.50 | 1.76 | 1.28 |
| 6 0 $\bar{6}$ | 5.02 | -4.70 | -4.76 | 4.64 | -3.54 | -3.88 |
| 6 0 $\bar{5}$ | 17.44 | -17.42 | -16.72 | 24.42 | -23.14 | [illegible] |
| 6 0 $\bar{4}$ | 3.76 | -3.46 | -3.48 | 5.44 | [illegible] | [illegible] |
| 6 0 $\bar{3}$ | 4.08 | 3.66 | 3.60 | 6.14 | 5.96 | 5.72 |
| 6 0 $\bar{2}$ | 3.12 | -2.66 | -2.36 | 3.00 | -2.54 | -2.32 |
| 6 0 $\bar{1}$ | 12.06 | -12.56 | -12.00 | 17.08 | -17.28 | -17.12 |
| 6 0 1 | 2.06 | 1.94 | 1.44 | 4.22 | 4.08 | 3.72 |
| 6 0 2 | 0.84 | -0.74 | -0.36 | 1.92 | -0.40 | -1.20 |
| 6 0 3 | <0.62 | | 0.48 | 1.42 | 1.42 | 1.36 |
| 6 0 4 | 3.80 | 3.04 | 2.80 | 8.22 | 8.40 | [illegible] |
| 6 0 5 | <0.51 | | 0.36 | 1.50 | -1.36 | -1.76 |
| 8 0 $\overline{14}$ | 1.26 | -1.18 | -1.08 | 4.06 | -2.92 | -2.92 |
| 8 0 $\overline{13}$ | 1.78 | 1.60 | 1.60 | 6.26 | 5.90 | 5.06 |
| 8 0 $\overline{12}$ | 0.68 | -0.92 | -0.92 | <1.32 | | -1.40 |
| 8 0 $\overline{11}$ | <0.31 | | 0.04 | 2.52 | -1.76 | -1.92 |
| 8 0 $\overline{10}$ | 6.80 | 6.94 | 6.60 | 15.12 | 15.36 | 14.88 |
| 8 0 $\bar{9}$ | 2.42 | 2.04 | 1.64 | 5.86 | 5.92 | 5.32 |
| 8 0 $\bar{8}$ | <0.41 | | -0.12 | <1.30 | | -1.24 |
| 8 0 $\bar{7}$ | 1.22 | 1.40 | 1.40 | 4.44 | 4.96 | 4.52 |
| 8 0 $\bar{6}$ | 7.20 | -7.40 | -7.52 | 11.54 | -11.76 | -11.68 |
| 8 0 $\bar{5}$ | 8.90 | -8.94 | -8.68 | 16.58 | -16.06 | -15.60 |
| 8 0 $\bar{4}$ | 1.46 | -1.46 | -1.28 | 2.88 | -2.96 | -2.76 |
| 8 0 $\bar{3}$ | 2.10 | 2.00 | 1.96 | 4.18 | 4.02 | 4.08 |
| 8 0 $\bar{2}$ | 3.48 | -3.40 | -3.52 | 4.56 | -4.42 | -4.48 |
| 8 0 $\bar{1}$ | 7.64 | -8.36 | -7.36 | 15.54 | -15.82 | -15.32 |
| 8 0 1 | <0.66 | | -0.20 | <1.25 | | 0.84 |
| 8 0 2 | <0.67 | | 0.72 | <1.20 | | -1.24 |
| 8 0 3 | 5.62 | 5.24 | 6.64 | 14.44 | 15.54 | 14.84 |
| 10 0 $\overline{11}$ | 1.02 | -0.60 | -0.32 | 0.98 | -0.86 | -0.36 |
| 10 0 $\overline{10}$ | 2.22 | -1.82 | -2.12 | 4.26 | -3.60 | -3.56 |
| 10 0 $\bar{9}$ | 2.14 | -1.66 | -2.20 | 6.02 | -5.38 | -5.44 |
| 10 0 $\bar{8}$ | 0.90 | 0.82 | 0.92 | 3.58 | 2.96 | 2.88 |
| 10 0 $\bar{7}$ | 0.64 | -0.32 | -0.36 | <0.75 | | -0.20 |
| 10 0 $\bar{6}$ | 1.18 | -1.48 | -2.00 | 5.40 | -5.40 | -5.36 |
| 10 0 $\bar{5}$ | <0.60 | | -0.56 | 1.96 | -2.46 | -2.16 |
| 10 0 $\bar{4}$ | <0.52 | | -0.04 | 2.60 | -2.44 | -2.20 |
| 10 0 $\bar{3}$ | <0.47 | | -0.20 | | | |
| 10 0 $\bar{1}$ | | | | 5.04 | -5.82 | -4.92 |

corresponding to $R=0·049$, in three cycles. At this stage it was then clear that a number of parameters, both positional and thermal, differed significantly from those reported by Sparks (1958) who, using a comprehensive least-squares routine, refined the three-dimensional counter data to $R=0·036$. His results were therefore used as a starting point in the refinement of the two-dimensional photographic data; again, from $R=0·059$ the refinement converged to the final value of 0·043 in three cycles. The agreement between our results and those of Sparks was, in general, reasonable. It was, however, surprising at the time of the analysis (1959) that the 'final' results depended on the starting point in the refinement; it is now obvious that the refinement should have been pursued beyond the stage where the indicated maximum shifts from the least squares were not greater than one-third to one-half the estimated standard deviation; recent experience suggests that the criterion (Sparks, 1961) of stopping at that point where indicated shifts do not exceed $\frac{1}{6}$ to $\frac{1}{10}\sigma$ is more satisfactory.

The final atomic coordinates at 290 °K are given in Table 1; a preliminary report on the thermal parameters has already been given by Lonsdale & Milledge (1961).

The starting point of the low-temperature analysis was the refined room-temperature coordinates and an isotropic temperature factor $B=1·5$ Å$^2$. The refinement procedure was similar to that described for the room-temperature analysis although it should be mentioned that oscillation in successive refinement cycles of the Debye factor analysis was more difficult to control; this may be due to the fact that no anisotropic atomic scattering factors were used in this analysis, a shortcoming which will be more important the lower the average atomic $B$ factor. The atomic coordinates at 95 °K are listed in Table 2.

## Discussion

In comparing the observed bond lengths (Table 4) with those predicted theoretically by various quantum mechanical models, we should remember that any apparently significant differences which exist may be due to (i) systematic errors in the diffraction data leading to unrealistic estimates of the accuracy of

Table 4. *Bond lengths and bond angles*

(*a*) Bond lengths at 290 °K and 95 °K

| | | | $r_{ij}$, 290 °K | | | | $r_{ij}$, 95 °K | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Bond | Diagonal L.S. (2D) | | Diagonal L.S. (3D) | | Complete L.S. (2D) | | Diagonal L.S. (2D) | | Complete L.S. (2D) | |
| $G'A$ | 1·4087 Å | | 1·4112 Å | | 1·4216 Å | | 1·4285 Å | | 1·4119 Å | |
| $AB$ ($FG$) | 1·3848 | 1·3665 | 1·3739 | 1·3612 | 1·3677 | 1·3831 | 1·3722 | 1·3781 | 1·3725 | 1·3526 |
| $BC$ ($EF$) | 1·4446 | 1·4336 | 1·4461 | 1·4401 | 1·4459 | 1·4395 | 1·4458 | 1·4362 | 1·4484 | 1·4272 |
| $CE'$ | 1·4443 | | 1·4235 | | 1·4273 | | 1·4270 | | 1·4267 | |
| $CD$ ($DE$) | 1·4012 | 1·3975 | 1·4106 | 1·4017 | 1·3982 | 1·4047 | 1·3947 | 1·4115 | 1·3815 | 1·4259 |
| $Aa$ ($Gg$) | 1·13 | 1·25 | 1·13 | 1·19 | 1·11 | 1·02 | 1·08 | 1·24 | 1·11 | 0·91 |
| $Bb$ ($Ff$) | 1·17 | 1·14 | 1·15 | 1·13 | 1·07 | 1·03 | 1·06 | 1·19 | 0·77 | 1·17 |
| $Dd$ | 1·15 | | 1·12 | | 1·01 | | 1·13 | | 1·16 | |

(*b*) Averaged bond lengths

| Bond | Diagonal values only | | 'Complete' values only | | Unweighted mean | |
|---|---|---|---|---|---|---|
| | 290 °K | 95 °K | 290 °K | 95 °K | 290 °K | 95 °K |
| $G'A$ | 1·4099 Å | 1·4285 Å | 1·4216 Å | 1·4119 Å | 1·4157 Å | 1·4202 Å |
| $AB$ | 1·3716 | 1·3752 | 1·3754 | 1·3625 | 1·3735 | 1·3688 |
| $BC$ | 1·4411 | 1·4410 | 1·4427 | 1·4378 | 1·4419 | 1·4394 |
| $CE'$ | 1·4339 | 1·4270 | 1·4273 | 1·4267 | 1·4306 | 1·4268 |
| $CD$ | 1·4028 | 1·4031 | 1·4014 | 1·4037 | 1·4021 | 1·4034 |
| $Aa$ | 1·17 | 1·16 | 1·07 | 1·01 | 1·16 | 1·15 |
| $Bb$ | 1·15 | 1·13 | 1·05 | 0·97 | 1·14 | 1·12 |
| $Dd$ | 1·13 | 1·13 | 1·01 | 1·16 | 1·14 | 1·13 |

(*c*) Average carbon–carbon bond lengths corrected for rotational effects

| Bond | 290 °K | 95 °K |
|---|---|---|
| $G'A$ | 1·418 Å | 1·421 Å |
| $AB$ | 1·375 | 1·370 |
| $BC$ | 1·444 | 1·440 |
| $CE'$ | 1·433 | 1·428 |
| $CD$ | 1·405 | 1·405 |

$\bar{l}_{\mathrm{C-C}}$ (290 °K) = 1·415 Å

$\bar{l}_{\mathrm{C-C}}$ (95 °K) = 1·413 Å

(*d*) Averaged carbon–carbon bond angles (uncorrected for rotational effects)

| Angle | 290 °K | 95 °K |
|---|---|---|
| $G'$–$A$–$B$ | 121° 19′ | 120° 43′ |
| $A$–$B$–$C$ | 119° 21′ | 120° 0′ |
| $B$–$C$–$E'$ | 119° 15′ | 119° 1′ |
| $B$–$C$–$D$ | 121° 13′ | 121° 38′ |
| $E'$–$C$–$D$ | 119° 31′ | 119° 20′ |
| $C$–$D$–$E$ | 120° 58′ | 121° 19′ |

r.m.s. deviation 290 °K and 95 °K = 0° 13′.

individual bond lengths, (ii) modification of molecular geometry through intermolecular forces in the crystal and (iii) the possibility that theoretical predictions, based on models of varying approximation, may not closely represent the real situation in the molecules and cannot be adequately allowed for in the empirical bond order–bond length curve.

There are certainly systematic errors present in the three-dimensional X-ray data of Mathieson *et al.* (1950); but these appear to have produced systematic errors in the atomic Debye factors rather than in the atomic positional coordinates. The r.m.s. deviations between the present lengths at 290 °K and 95 °K respectively, and those of Cruickshank (1956) are 0·007 and 0·006 Å; 0·006 Å and 0·004 Å are r.m.s. deviations referred to those determined by Sparks (1958).

Within experimental error, the molecule considered as an isolated unit has *mmm* symmetry in spite of the fact that its packing in the crystal unit is only centrosymmetrical. Thus a least-squares determination of the best plane in the molecule shows the r.m.s. deviation of the atoms to vary from 0·004 Å in the diagonal refinement of the two-dimensional data (290 °K) to 0·007 Å in the case of the 'complete' refinement of the same data. The maximum deviation of any atom is 0·012 Å (*G*, in formula (I), in the 'complete' analysis at 290 °K) and this result is not significant. It seems generally true from a number of recent accurate analyses that, unless intramolecular 'overcrowding' occurs, bond lengths measured by X-ray methods are identical with those measured in the vapour phase, always bearing in mind that such techniques as X-ray, neutron, and electron diffraction, and infrared and Raman spectroscopy, measure quantities which correspond to different definitions of the interatomic separation. As the diffraction techniques improve in accuracy, any real differences which become apparent would prove of considerable theoretical interest.

Cruickshank & Sparks (1960) have summarized the bond lengths predicted by a number of authors (Coulson, Daudel & Robertson, 1951; Pritchard & Sumner, 1955; Pariser, 1956). The apparent conclusion — that no particular model offers any considerable advantage over another in accounting for the present results — is, however, one that needs some explanation. A number of the theoretically predicted bond lengths are based on order–length relationships which are inconsistent with more recent data on carbon–carbon bond lengths in a variety of molecules. Pritchard & Sumner (1955) found that with the then available bond lengths in naphthalene and anthracene the choice of order–length curves was not important.

Mason (1957) later showed that the usual equation

$$R_{ij} = S - \frac{S-D}{1+K(1-O_{ij})/O_{ij}}$$

(in which $R_{ij}$, the calculated bond length between atoms $i$ and $j$, corresponds to a $\pi$ bond order $O_{ij}$ and $S$ and $D$ are the single and double bond distances respectively between trigonally hybridized carbon atom) was not completely useful in representing the bond lengths in 1,2:8,9-dibenzacridine, even when $S$ was given the more realistic value of 1·50 Å. It does seem quite clear from six separate analyses of aromatic molecules that we have completed that a judicious choice of bond order–bond length relationship is capable of disguising the shortcomings of the various theoretical models. With this point in mind we may examine some of the arguments set out by Cruickshank & Sparks (1960) for preferring the simple valence bond model of conjugated systems to that provided by the molecular orbital approach. These authors do show that valence bond theory in the Pauling approximation may be an excellent empirical basis for a bond order–bond length curve-fitting procedure. But this result cannot be then extended to any conclusion which imagines that the electronic conditions in, say, biphenyl are *really* as this form of the valence bond theory assumes. It seems likely in the first place that bond length is a quite insensitive criterion of conjugation in regions of $\pi$ bond order 0·1 to 0·3, that is a total bond order of 1·1 to 1·3. The simple molecular orbital bond order of 0·37 for the central bond in biphenyl decreases considerably if the variation of $\beta$, the resonance integral, with bond length is considered in detail. Both valence bond and molecular orbital methods, used in the correct way, give a very low bond order in biphenyl in that region of weak dependence of length on order. Cruickshank & Sparks (1960) suggest that 'direct evidence of the $\pi$ electron distribution' in biphenyl would be of great interest, but it seems irrelevant in discussing the relative merits of what are nothing more than two extreme approximations. The case for a great deal of more careful investigation of bond lengths in the ground states of aromatic hydrocarbons seems unproven; the point seems quite clear — any given model is capable of predicting bond lengths in such conjugated systems to better than some 0·02 Å in so far as we recognize that order–length curves can absorb the shortcomings in the various approximations which must of course converge to one picture in the most sophisticated theoretical approaches (valence bond with configuration interaction and so on; S.C.F. molecular orbital model); a more systematic, self-contained and rigorous order–length relation in the region of interatomic separations of 1·36 to 1·51 Å would of course be of considerable help.

### *Atomic vibrations, diffuse scattering and thermal expansion*

The results of our least-squares analysis of the atomic thermal parameters have been discussed by Lonsdale & Milledge (1961), who point out some of the problems involved in determining the details of the vibrational characteristics of anthracene. We shall not be interested here, however, in the details of the determination of the librational and translational molecular vibrations but rather in correlating some of the broader features of these results with the diffuse scattering and expansion coefficients of the crystal. As for benzene (Cox, 1957) and naphthalene (Mason, unpublished) the maximum coefficient of thermal expansion lies approximately in the direction of $N$, the molecular axis normal to the molecular plane. Fig. 1 clearly indicates that $\alpha_{\max}$ is roughly along $a^*$ but more accurately at right angles to $(40\bar{9})$. Annaka & Amoros (1960) have examined the diffuse scattering of anthracene and shown it to be composed of sharp planes, streaks and weak continuous regions; the diffuse scattering domains, extended again more or less along $a^*$, are due in considerable part to uncoupled molecular motions in the crystal and owe a good deal of their intensities to contributions from the optical branch of the vibrational spectrum. As Lonsdale (1959) has pointed out, it is such high-frequency vibrations which lead to large expansion coefficients provided, of course, that they have sufficiently large amplitude. We should therefore look for a correlation between librational modes and expansion coefficients. Cruickshank's original and elegant calculation of the torsional oscillations about $L$, $M$ and $N$ gave the values of 3·8°, 2·2° and 3·1° respectively; these may be compared with the present values of 3·6°, 2·7° and 3·1° respectively. The translational vibrations are a good deal more isotropic having $\sqrt{(\overline{u^2})}$ values of 0·20, 0·16 and 0·16 Å (Cruickshank, 1956) and 0·22, 0·17 and 0·16 Å (this investigation). At 95 °K the calculated libration amplitudes are 0·9°, 0·9° and 1·6° respectively with translational amplitudes of 0·13, 0·07 and 0·09 Å.

The most important factor affecting the expansion coefficient is that the molecules have changed their relative orientation so that $L$ is now more nearly parallel to $a$. The direction cosines of the molecular axes are

| | | 290 °K | |
|---|---|---|---|
| $L$ | −0·49409 | −0·12738 | +0·86003 |
| $M$ | −0·31752 | −0·89444 | −0·31490 |
| $N$ | +0·80935 | −0·42867 | +0·40149 |
| | | 95 °K | |
| $L$ | −0·51171 | −0·13109 | +0·84910 |
| $M$ | −0·30351 | −0·89699 | −0·32140 |
| $N$ | +0·80376 | −0·42218 | +0·41920 |

referred to the orthogonal axes $a$, $b$ and $c'$ of the crystal. The molecular reorientation implies more symmetrical interactions at 95 °K than at 300 °K, a feature which will be of interest in relation to the crystal structures of the aromatic hydrocarbons (Mason, 1961). It also affords an explanation of the temperature dependence of the crystal susceptibilities; the calculated *molecular* susceptibilities are found, as could be intuitively expected, to be temperature independent (Leela, 1962).

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# The Crystal Structure of $UF_4$*

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The crystal structure of $UF_4$ has been determined from single-crystal X-ray data. The monoclinic unit cell has the dimensions $a = 12{\cdot}73$, $b = 10{\cdot}75$, $c = 8{\cdot}43$ Å and $\beta = 126° 20'$; space group $C2/c$. It contains twelve formula units per unit cell. These cell dimensions are identical with those of Shankar, Khubchandani & Padmanabhan (1957). In the least-squares refinement of the structure a secondary extinction parameter and the real and imaginary portions of the anomalous dispersion corrections were used. Normal interatomic distances were observed. Uranium atoms have as neighbors eight fluorine atoms arranged in a slightly distorted antiprism configuration.

## Introduction

Two items have renewed our interest in the structure of $UF_4$; first, the determination of the crystal structure of $ZrF_4$ by Burbank & Bensey (1956) in which fluorine atom positions are given and, second, a single crystal fragment of $UF_4$ given to us by W. P. Ellis of this Laboratory for structure analysis. The fragment selected for structure analysis yielded the best optical extinction figure of several score examined and therefore was the most strain-free sample available.

## Crystallographic data

The crystal structure of $UF_4$ was first described by Zachariasen (1949). A monoclinic unit cell containing twelve formula units, isostructural with $ZrF_4$ and $HfF_4$, was proposed. Only the uranium atom positions were given and these only approximately (see Table 1). Shankar, Khubchandani & Padmanabhan (1957) used

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