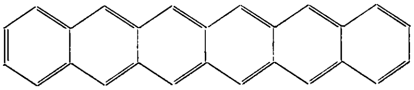
number of rings, preclude the preparation of heptacene and higher benzologues (Clar, 1952). The following paragraphs describe an investigation of the hexacene structure.



(I)

All the crystals of hexacene which we obtained were small, extremely thin, almost-black plates, with (001) developed; they were invariably twinned. The unit-cell dimensions, determined from various rotation and Weissenberg photographs, and the density, measured by flotation in aqueous potassium iodide solution, are compared in Table 1 with the revised data for the other members of the series; the comparison indicates that hexacene has a crystal structure very similar to the lower benzologues, the only significant difference in cell dimensions being a further increase of 2·4 Å in the *c*-axis to accommodate the extra ring.

As a preliminary to complete structure analysis the intensities of the 0*kl* and *h*0*l* reflexions were recorded on Weissenberg films with Cu $K\alpha$ radiation. As a result of the rather poor quality of the crystal specimens the proportion of the possible reflexions observed was even smaller than for tetracene and pentacene; only 17 independent 0*kl* reflexions and 16 *h*0*l* reflexions were measurable. Since there are 78 carbon atom positional parameters the data were clearly insufficient for any detailed analysis of the structure. Comparison of the Weissenberg photographs with the corresponding films for tetracene and pentacene showed marked similarities, the strong reflexions being in the same regions of reciprocal space in each case. The orientations of the hexacene molecules in the unit cell are therefore very similar to those in the other members of the series, but no detailed determination of the molecular dimensions is possible.

We thank Dr E. Clar for the crystal sample. One of us (R. B. C.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

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# The unit cell dimensions and crystal structure of KBaPO$_4$.

By C. W. Struck and J. G. White,
*RCA Laboratories, Princeton. New Jersey, U.S.A.*

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The low temperature form of KBaPO$_4$ has been reported to be orthorhombic (Klement & Uffelmann, 1941), with

$$a=5{\cdot}61_5,\ b=11{\cdot}09,\ c=7{\cdot}62\ \text{Å}\ .$$

Several polycrystalline samples of this phase have been made here recently, using for raw materials either KNO$_3$ + BaHPO$_4$ or $\frac{1}{2}$ K$_2$CO$_3$ + BaHPO$_4$, and firing in N$_2$ at temperatures from 900 to 1250 °C. for 3–24 hours. We have annealed the phase for one week at 600 °C.

All samples prepared in these ways have given identical X-ray diffraction patterns, which can be indexed on the basis of an orthorhombic unit cell, with

$$a=5{\cdot}66_6\pm0{\cdot}005,\ b=9{\cdot}95_9\pm0{\cdot}010,\ c=7{\cdot}69_7\pm0{\cdot}008\ \text{Å}\ .$$

Our *a* and *c* axes are quite close to the dimensions of Klement & Uffelmann but *b* is appreciably different.

Table 1. *Coordinates of the atoms in* KBaPO$_4$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| K | 0·250 | 0·415 | −0·330 |
| Ba | 0·250 | −0·312 | 0·000 |
| P | 0·250 | 0·425 | 0·267 |
| O$_1$ | 0·250 | 0·432 | 0·046 |
| O$_2$ | 0·250 | −0·417 | 0·350 |
| O$_3$ | 0·005 | 0·343 | 0·337 |

In our data, the unobserved reflections are consistent with the space group *Pmcn* ($D_{2h}^{16}$). The cell dimensions and space group are highly suggestive of the $\beta$-K$_2$SO$_4$ structure (Ehrenberg & Hermann, 1929). This structure requires four formula units per unit cell with 4K, 4Ba, 4P, and 8O atoms in positions (*c*) $\frac{1}{4}, y, z;\ \frac{1}{4}, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{3}{4}, \bar{y}, \bar{z};\ \frac{3}{4}, \frac{1}{2}+y, \frac{1}{2}-z$ and 8O atoms in (*d*) $\pm x, y, z;\ \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}+x, \bar{y}, \bar{z};\ \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ with the parameters as given in Table 1. The intensities of the first 56 lines recorded on a powder diffraction photograph (Cu $K\alpha$ radiation) were estimated visually using a multiple film technique. Of these lines 31 are separately resolved reflections and 25 may be composed of overlapping reflections. A Patterson section at $x=0$ showed clearly the barium and potassium atom positions and several electron density maps of the plane $x=\frac{1}{4}$ were computed, in which the intensities of overlapping lines were divided in the ratio of the calculated contributions, and an artificial temperature factor was used for convergence of the rather short series. The oxygen parameters were obtained by assuming a regular tetrahedron for the phosphate group and rotating about the *P* position to obtain the best fit with the observed electron density.

The observed and calculated values of the lattice spacings and intensities are listed in Table 2. For the calculated intensities the scattering factors given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. II (1935) have been used. The observed intensities have been modified by a cylindrical absorption correction chosen to give the best fit with the calculated data and since the latter are for atoms at rest the tem-

Table 2. *Measured and calculated values of the lattice spacings and reflection intensities in* KBaPO$_4$

| *hkl* | $d_c$ (Å) | $d_o$ (Å) | $I_c$ | $I_o$ |
|---|---|---|---|---|
| 011 | 6·09 | 6·06 | 12 | 19 |
| 020 | 4·98 | 4·94 | 101 | 103 |
| 110 | 4·93 | | | |
| 111 | 4·15 | 4·15 | 4 | 15 |
| 002 | 3·85 | 3·85 | 18 | 15 |
| 012 | 3·59 | 3·59 | 0 | 5 |
| 121 | 3·36 | 3·36 | 72 | 79 |
| 031 | 3·05 | 3·04 | 231 | 212 |
| 022 | 3·04 | | | |
| 112 | 3·03 | | | |
| 130 | 2·864 | 2·848 | 106 | 113 |
| 200 | 2·833 | | | |
| 131 | 2·685 | 2·682 | 1 | 7 |
| 122 | 2·682 | | | |
| 211 | 2·569 | 2·567 | 9 | 9 |
| 032 | 2·513 | 2·514 | 4 | 4 |
| 013 | 2·484 | 2·484 | 33 | 38 |
| 041 | 2·369 | 2·373 | 2 | 4 |
| 221 | 2·345 | 2·340 | 5 | 5 |
| 202 | 2·281 | 2·279 | 17 | 28 |
| 023 | 2·280 | | | |
| 212 | 2·224 | 2·220 | 6 | 12 |
| 141 | 2·186 | 2·183 | 55 | 53 |
| 123 | 2·115 | 2·112 | 7 | 5 |
| 231 | 2·075 | 2·070 | 71 | 67 |
| 222 | 2·074 | | | |
| 033 | 2·030 | 2·030 | 25 | 22 |
| 142 | 1·961 | 1·958 | 0 | 2 |
| 051 | 1·929 | 1·929 | 19 | 26 |
| 240 | 1·871 | 1·868 | 16 | 17 |
| 213 | 1·867 | | | |
| 104 | 1·822 | 1·821 | 3 | 2 |
| 241 | 1·818 | | | |
| 024 | 1·795 | 1·792 | 25 | 24 |
| 114 | 1·792 | | | |
| 321 | 1·722 | 1·719 | 12 | 6 |
| 143 | 1·704 | 1·704 | 35 | 26 |
| 312 | 1·671 | 1·670 | 20 | 19 |
| 233 | 1·650 | 1·650 | 13 | 7 |
| 330 | 1·642 | 1·639 | 7 | 7 |
| 134 | 1·597 | 1·595 | 28 | 29 |
| 251 | 1·594 | | | |
| 053 | 1·573 | 1·572 | 4 | 5 |
| 214 | 1·571 | | | |
| 161 | 1·560 | 1·559 | 8 | 10 |
| 062 | 1·524 | 1·521 | 6 | 5 |
| 044 | 1·523 | | | |
| 224 | 1·516 | 1·513 | 7 | 7 |
| 243 | 1·511 | | | |
| 341 | 1·477 | 1·473 | 14 | 14 |
| 162 | 1·472 | | | |
| 323 | 1·455 | 1·454 | 3 | 2 |
| 234 | 1·435 | 1·434 | 0 | 1 |
| 125 | 1·423 | 1·421 | 14 | 3 |
| 400 | 1·416 | 1·415 | 11 | 7 |
| 342 | 1·402 | 1·399 | 2 | 5 |
| 071 | 1·399 | | | |
| 170 | 1·380 | 1·377 | 10 | 10 |
| 411 | 1·380 | | | |
| 253 | 1·376 | | | |
| 163 | 1·353 | 1·352 | 5 | 7 |
| 154 | 1·345 | 1·343 | 14 | 7 |
| 262 | 1·342 | | | |
| 215 | 1·340 | | | |
| 314 | 1·336 | 1·337 | 7 | 6 |
| 072 | 1·335 | | | |
| 343 | 1·298 | 1·298 | 15 | 12 |
| 431 | 1·284 | 1·283 | 16 | 10 |
| 422 | 1·284 | | | |
| 006 | 1·283 | | | |
| 145 | 1·276 | 1·276 | 5 | 9 |
| 235 | 1·252 | 1·251 | 8 | 9 |
| 106 | 1·251 | | | |
| 263 | 1·250 | | | |
| 026 | 1·242 | 1·241 | 8 | 9 |
| 116 | 1·241 | | | |
| 440 | 1·231 | 1·229 | 9 | 7 |
| 361 | 1·231 | | | |
| 413 | 1·230 | | | |
| 081 | 1·228 | | | |
| 055 | 1·217 | 1·217 | 5 | 3 |
| 245 | 1·188 | 1·187 | 1 | 4 |
| 442 | 1·173 | 1·170 | 4 | 3 |
| 136 | 1·170 | | | |
| 206 | 1·168 | | | |
| 433 | 1·161 | 1·160 | 12 | 6 |
| 216 | 1·160 | | | |
| 325 | 1·160 | | | |
| 451 | 1·141 | 1·139 | 21 | 19 |
| 404 | 1·140 | | | |
| 046 | 1·140 | | | |
| 280 | 1·140 | | | |
| 273 | 1·139 | | | |

perature factor has also been approximately removed. For all the observed diffraction lines $R=\Sigma|I_o-I_c|/\Sigma I_0$ is 0·173. Clearly no high accuracy of coordinates can be expected from the very limited X-ray data available but it is established that the atomic arrangement in KBaPO$_4$ is very close to that in $\beta$-$K_2SO_4$. Displacements of the atoms in positions (*c*) from the planes $x=\frac{1}{4}, \frac{3}{4}$ could lower the symmetry to the space group $P2_1cn$ which has the same systematic absences as *Pmcn*. However, the agreement between the calculated and observed intensities suggests that if any such displacements exist they must be quite small. The very high coordination of the cations by oxygen atoms in this structure would also favor the higher symmetry space group.

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