Although in the active BPG modification the neighboring monomers are stacked along **c** in an arrangement which should be most favorable for solid-state reactivity, the conversion to polymer is never complete. The residual monomer can be extracted leaving very disordered almost fiber-like crystals of the pure polymer. The low reactivity of BPG can be attributed to the fact that the phenyl rings are fixed directly to the diyne system. This restricts the mobility of the side groups which seems to be necessary for a fast and complete polymerization.

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# The Neutron Crystal Structure at −75 °C of Polymorph II of 5,5-Diethylbarbituric Acid (Barbital)

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Polymorph II of barbital ($C_8H_{12}N_2O_3$) at −75 °C is monoclinic, space group $C2/c$ with X-ray (Mo $K\alpha$) lattice parameters $a$ = 7·113 (2), $b$ = 14·103 (3), $c$ = 9·745 (1) Å, $\beta$ = 88·86 (3)° and with four molecules in the unit cell. Intensities for 1369 neutron reflections with $\sin\theta/\lambda < 0{\cdot}71$ Å$^{-1}$ ($\lambda$ = 1·0470 Å) were used in a structure refinement which converged at $R(F^2)$ = 0·053. The room-temperature X-ray structure is confirmed. In the –CO–NH–CO– system, 0·015 Å differences within pairs of CO and CN bond lengths become significant because of the better precision in the neutron structure. There is intramolecular motion in the ethyl groups where r.m.s. amplitudes up to 0·4 Å are observed for the H atoms.

## Indroduction

The crystal structure determination of polymorph II of 5,5-diethylbarbituric acid (barbital) using neutron and X-ray diffraction has been undertaken in order to analyze the electronic charge-density distribution. Barbital is chemically the simplest drug-active barbiturate. Of the three polymorphs of barbital for which the crystal structures have been reported (Craven, Vizzini & Rodrigues, 1969; Craven & Vizzini, 1971), polymorph II is most suitable for charge-density analysis because this structure is centrosymmetric with space group $C2/c$ and only four molecules in the unit cell. The barbital molecule makes use of a crystallographic twofold axis of rotation (Fig. 1) so that parameters need to be determined for only 14 of the 25 atoms (including H).

To obtain greater accuracy in a charge-density analysis, it is important not only to keep the number of independent atoms small, but also to collect the intensity data at a low temperature. In the case of barbital II, there was no difficulty in cooling the small crystal which was used for X-ray diffraction. However, when the larger crystals needed for neutron diffraction were cooled to about −100°C, they fractured, even when the rate of cooling was slow (3 h from room temperature). It was suspected that the crystal fracture might be due to a phase transition, but from X-ray diffraction there was no discontinuity in the lattice parameters or diffracted intensities when a small crystal was examined in the temperature range near −100°C. The crystal data were collected at −75°C when it was found that the larger crystals were stable at this temperature.

The present paper is concerned with the nuclear configuration in barbital II as determined by neutron diffraction.

## Experimental

Crystals of barbital II were grown during a week by evaporation of a saturated ethanol solution at room temperature. The neutron diffraction data were collected using a crystal with dimensions $1{\cdot}60 \times 1{\cdot}50 \times 2{\cdot}34$ mm and a volume of $5{\cdot}36$ mm$^3$ which was formed by $(11\bar{1})$ cleavage.* The crystal was measured and described in terms of seven faces from the forms $\{11\bar{1}\}$, $\{021\}$ and $\{110\}$.

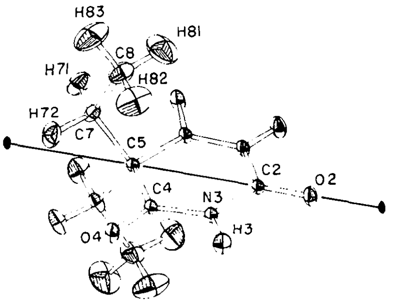

Fig. 1. Barbital II. Atomic nomenclature and thermal motion. Ellipsoids are shown with 25% probability of enclosing each nucleus.

The neutron data were collected with a four-circle automated diffractometer at the High Flux Beam Reactor of the Brookhaven National Laboratory. A monochromatic beam was obtained by reflection from the (002) plane of a beryllium crystal. The neutron wavelength, 1·04703 (16) Å, was determined by measurement of the lattice parameter ($a_o = 6{\cdot}5966$ Å) of a standard KBr crystal at room temperature.

The barbital II crystal was glued on an aluminum pin and sealed under a quartz dome. The assembly was cooled and maintained at −75 ± 1 °C inside a closed cycle helium refrigerator* constructed of aluminum which was mounted within the diffractometer $\chi$ circle. The crystal scattering vector $0\bar{2}\bar{1}$ was within a few degrees of the diffractometer $\varphi$ axis.

Lattice parameters for barbital II (Table 1) were obtained by a least-squares fitting procedure from the observed diffractometer angles for 27 reflections.

Corresponding X-ray parameters were obtained from 15 reflections, measured at $\pm\theta$ with a four-circle diffractometer (Enraf–Nonius CAD-4) and graphite-monochromated Mo $K\alpha$ radiation. The crystal was cooled by a stream of nitrogen gas. The X-ray values for $c$, and possibly $a$, may be significantly larger than the neutron values, indicating that the X-ray measurements may have been at a temperature slightly higher than −75 °C. The X-ray cell parameters were used in both the neutron and X-ray structure refinements.

The neutron integrated intensities were measured using $\omega/2\theta$ step scans. Scan widths were 3·6° in $2\theta$ for reflections with $\sin\theta/\lambda \le 0{\cdot}404$ Å$^{-1}$ and were varied according to the dispersion formula $\Delta(2\theta) = 1{\cdot}64 + 3{\cdot}25\tan\theta$ for reflections with $0{\cdot}40 < \sin\theta/\lambda \le 0{\cdot}71$ Å$^{-1}$. So as to observe neutron scattering from the cryostat and quartz surrounding the crystal, scans were made for the entire $2\theta$ range at $\chi = 0$, 45 and 90°. The $\varphi$-angles were chosen to avoid Bragg reflections from barbital. The features in these scans were so broad that it was considered unnecessary to take them into account in estimating backgrounds. The background for each barbital reflection was subtracted as a linear function of the intensities calculated from the first and last tenth of the total scan. The variance in an intensity was assumed to be $\sigma^2(I) = I + 5B + (0{\cdot}02I)^2$. Neutron-absorption corrections were applied using an

Table 1. *Lattice parameters for barbital* II

| | Neutron (−75° C) | X-ray (−75° C) | X-ray (20° C)* |
|---|---|---|---|
| $a$ | 7·098 (4) Å | 7·113 (2) Å | 7·120 (5) Å |
| $b$ | 14·096 (6) | 14·103 (3) | 14·162 (10) |
| $c$ | 9·717 (6) | 9·745 (1) | 9·810 (7) |
| $\beta$ | 88·94 (4)° | 88·86 (3)° | 89·23 (3)° |
| $\lambda$ | 1·04703 (16) Å | 0·7107 Å | 1·5418 Å |

* Craven, Vizzini & Rodrigues (1969).

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* The cleavage was incorrectly given as $(10\bar{1})$ by Craven, Vizzini & Rodrigues (1969).

* Air Products and Chemicals, Inc. DISPLEX® Model CS-202.

analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient ($\mu$ = 0·196 mm$^{-1}$) calculated from the assumed mass-absorption coefficient for chemically bonded H (23·9 mm$^3$ mg$^{-1}$) agreed with the value 0·200 (6) mm$^{-1}$ measured from the attenuation of a finely collimated beam of neutrons which was passed through a crystal of barbital II of known uniform thickness.

When average values of 3812 intensities were taken, there were 1369 non-symmetry-related reflections with $\sin\theta/\lambda < 0{\cdot}714$ Å$^{-1}$. The agreement factor $\sum_H |\langle F^2\rangle - F^2|/\sum_H F^2$ summed over all equivalent reflections was 0·043.

Full-matrix least-squares refinement of the structure was carried out with a modified version of the computer program *ORFLS* by Busing, Martin & Levy (1962) so as to minimize $\sum_H w_H \Delta_H^2$ where $\Delta_H = (F_{\text{obs}})_H^2 - (F_{\text{calc}})_H^2$ and $w_H = 1/\sigma^2(F^2)$. The neutron-scattering lengths ($\times 10^{-11}$ mm) were assumed to be 0·6648 for C, 0·5803 for O and −0·374 for H (Shull, 1972). The value for N determined in the refinement was found to be 0·9237 (5). Initial parameter values were those of Craven, Vizzini & Rodrigues (1969) for the atomic positions, and an assumed overall isotropic temperature factor with $U$ = 0·019 Å$^2$. After three cycles of refinement, it became apparent that there was a severe neutron extinction effect. An isotropic extinction correction of type I was applied, assuming a Lorentzian distribution of mosaicity (Becker & Coppens, 1974). Anisotropic temperature factors were also introduced.

Table 2. *Atomic parameters with their e.s.d.'s*

Positional parameters are fractional coordinates ×10$^4$ referred to the crystal axes. E.s.d.'s in brackets refer to the least significant digit in the parameter.

| | *x* | *y* | *z* |
|---|---|---|---|
| O(2) | 0 | 4088 (1) | 2500 |
| O(4) | −1934 (2) | 1363 (1) | 546 (1) |
| N(3) | −980 (1) | 2713 (1) | 1545 (1) |
| C(2) | 0 | 3232 (1) | 2500 |
| C(4) | −1048 (1) | 1744 (1) | 1454 (1) |
| C(5) | 0 | 1158 (1) | 2500 |
| C(7) | 1445 (1) | 524 (1) | 1726 (1) |
| C(8) | 2887 (2) | 1061 (1) | 863 (1) |
| H(3) | −1706 (3) | 3098 (1) | 825 (2) |
| H(71) | 2151 (3) | 96 (2) | 2497 (2) |
| H(72) | 648 (4) | 38 (2) | 1083 (2) |
| H(81) | 3705 (6) | 1548 (4) | 1466 (5) |
| H(82) | 2239 (6) | 1484 (3) | 64 (4) |
| H(83) | 3853 (6) | 585 (3) | 358 (5) |

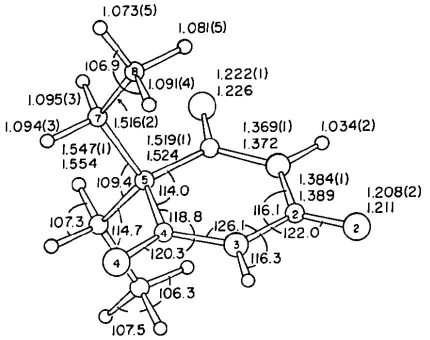

Fig. 2. Barbital II, bond lengths (Å) and angles (°). The e.s.d.'s in bond lengths are in parentheses. Librationally corrected bond lengths are given under each observed value. The e.s.d.'s in bond angles (not shown) were 0·1° in the ring and 0·3° in the ethyl groups. The angle librational corrections (not shown) were all less than 0·1°. Angles C(4)—C(5)—C(7), C(4)—C(5)—C(7′) are 108·5°, 108·1°.

The refinement converged with $R(F^2)$ = 0·053 and $R_w(F^2)$ = 0·074, and QME = 1·41.* The extinction parameter was $g$ = 1·48 (4) × 10$^4$, giving the most severe correction (0·20 $F^2_{\text{calc}}$) for the reflection $\bar{1}11$. The largest correlation factor for refined variables was 0·82 between the scale factor and the extinction parameter. Atomic positional parameters are in Table 2.†

## Discussion

Bond lengths and angles are shown in Fig. 2. These agree with the room-temperature X-ray values (Craven, Vizzini & Rodrigues, 1969), within the experimental errors. With the greater precision of the neutron determination, the small differences (0·015 Å) became significant in the pairs of bond lengths C(2)—N(3), C(4)—N(3) and C(2)—O(2) and C(4)—O(4). These differences show a conjugative effect since the longer of the C—O bonds is adjacent to the shorter C—N bond and *vice versa*. The longer carbonyl bond involves oxygen O(4) which forms a hydrogen bond, N(3)H(3)···O(4) with N(3)···O(4) distance 2·86 Å, H(3)···O(4) distance 1·83 Å and N—H···O angle 173°. The shorter carbonyl bond involves oxygen O(2) which is not hydrogen bonded. In other barbiturate crystal structures, small bond-length differences (0·01 Å) in the chemically equivalent halves of the ring have been attributed to hydrogen bonding (Craven, Cusatis, Gartland & Vizzini, 1973). Hydrogen-bonding effects probably contribute to the bond-length variations noted in barbital II, although in this structure the bonds involved are chemically different.

The ethyl groups have a conformation which is almost *trans* or fully extended, with the best least-

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* $R(F^2) = \sum_H \Delta_H^2/\sum_H F_H^2$; $R_w(F^2) = (\sum_H w_H \Delta_H^2/\sum_H w_H F_H^4)^{1/2}$; QME $= [\sum_H w_H \Delta_H^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33874 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Best least-squares planes through selected atoms*

Planes were calculated with respect to the crystal axes, using fractional coordinates ($x,y,z$) and coefficients in Å. Planes are constrained to pass through the crystallographic and molecular twofold axis.

(1) The eleven-atom trioxopyrimidine ring system: $-5{\cdot}6831x + 5{\cdot}7076z = 1{\cdot}4269$.

(2) The ethyl C atoms: $4{\cdot}3741x + 7{\cdot}8023z = 1{\cdot}9506$

Distances of atoms from planes (Å)

| (1) | | (2) | |
|---|---|---|---|
| C(2) | 0 | C(5) | 0 |
| O(2) | 0 | C(7) | 0·029 |
| C(5) | 0 | C(8) | −0·014 |
| N(3) | 0·012 | | |
| H(3) | 0·013 | | |
| C(4) | −0·002 | | |
| O(4) | −0·016 | | |

squares plane through the ethyl C atoms and C(5) almost perpendicular (91·0°) to the ring plane (Table 3). The torsion angle C(7′)—C(5)—C(7)—C(8) is 177·0 (1)°. In the projection down the C(7)—C(8) bond, the five ethyl C—H bonds and C(7)—C(5) are almost ideally staggered, with torsion angles ranging between 58·8 (3) and 61·8 (3)°. Bonds C(8)—H(81) and C(8)—H(82) are nearly parallel to the two ring bonds at C(5) with H···C(4) nonbonded intramolecular distances of 2·70, 2·76 Å. However, any H···C(4) repulsive interaction would appear to be weak, since the three bond angles C(7)—C(8)—H are almost equal at 112·4, 112·2, 111·2° (e.s.d. 0·3°), for the angles involving H(81), H(82) and H(83) respectively.

The ellipsoids (Johnson, 1976) in Fig. 1 which show the nuclear thermal motion at −75 °C are similar in shape and orientation to those derived from the X-ray room-temperature data (Fig. 8*b* in Craven, Vizzini & Rodrigues, 1969). Although the vibrational amplitudes are smaller at −75 °C, there is still considerable thermal motion, particularly in the ethyl groups. The neutron thermal parameters for the complete molecule gave a very poor fit to rigid-body behavior (Schomaker & Trueblood, 1968). However, the fit was greatly improved (Table 4) by omitting all H atoms and the terminal C atoms, C(8). From inspection of Fig. 1, there could be torsional motion about the bonds C(5)—C(7) and C(7)—C(8). The largest r.m.s. amplitudes of nuclear vibration are 0·4 Å for the H atoms H(81), H(82), H(83) in directions nearly tangential to the circle on which they lie.

Table 4. *Rigid-body thermal parameters*

The r.m.s. difference between observed $U_{ij}$ values and those for the best fit to a rigid body is 0·0131 Å$^2$ for all atoms, or 0·0010 Å$^2$ for the fragment with H atoms and C(8) excluded. Tensor components for this fragment are with respect to the Cartesian crystal axial system, *a*, *b*, *c**.

(1) Translational motion (Å$^2$)

$$\mathbf{T} = \begin{pmatrix} 0{\cdot}0160\ (6) & 0 & -0{\cdot}0034\ (5) \\ & 0{\cdot}0183\ (4) & 0 \\ & & 0{\cdot}0143\ (5) \end{pmatrix}$$

R.m.s. principal values: 0·137, 0·135, 0·108 Å.

(2) Librational motion (deg$^2$)

$$\boldsymbol{\omega} = \begin{pmatrix} 6{\cdot}4\ (4) & 0 & 5{\cdot}1\ (3) \\ & 23{\cdot}4\ (7) & 0 \\ & & 9{\cdot}1\ (5) \end{pmatrix}$$

R.m.s. principal values: 4·8, 3·6, 1·6°.

(3) Cross tensor (deg Å)

$$\mathbf{S} = \begin{pmatrix} 0{\cdot}047 & 0 & 0{\cdot}016 \\ 0 & -0{\cdot}164 & 0 \\ 0{\cdot}035 & 0 & 0{\cdot}107 \end{pmatrix}$$

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