ment Statistician, J. V. T. Baker, in providing time on the IBM 1620 computer is gratefully acknowledged.

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The Crystal Structure of
2α-Bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane*

BY THOMAS A. BEINEKE†

Ames Laboratory (U.S. Atomic Energy Commission), Iowa State University, Ames, Iowa 50010, *U.S.A.*

The crystal structure of 2α-bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane has been determined by three-dimensional single-crystal X-ray diffraction techniques. The crystals are orthorhombic, space group $P2_12_12_1$ with unit-cell dimensions $a=13\cdot415$, $b=11\cdot407$, $c=6\cdot215$ Å and four molecules per unit cell. The final R for 478 reflections is 0·045. The molecular conformation is a distorted chair with the bromo and bromomethyl groups in axial positions. The interior O–P–O angle is 104·9° which is similar to the corresponding angle in acyclic phosphate esters and explains the similarity in the rates of hydrolysis of six-membered cyclic and acyclic phosphate esters as opposed to the strained five-membered cyclic esters.

Introduction

In the course of nuclear magnetic resonance studies on the mechanism of long range phosphorus–hydrogen spin–spin interactions, 2α-bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane (II, hereafter referred to as BBMOD) was prepared by reaction in benzene of the bicyclic phosphite ester (I) with bromine (Bertrand, Verkade & McEwen, 1968). Prior to the present work neither the conformation of BBMOD nor the mechanism of the reaction had been established. The dipole moment of BBMOD in dioxane is 6·59D which agrees favorably with the 6·40D moment calculated for conformation II from individual bond moments. An identical treatment of individual bond moments for the other, sterically more favorable chair conformation (III) yielded a calculated moment of 1·57 D.
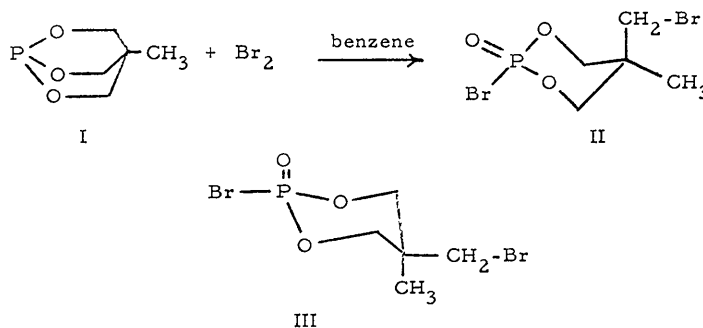
In order to provide the structural parameters necessary for the interpretation of both the ^{31}P and the proton spectra of BBMOD, and to confirm the conformation tentatively assigned on the basis of the dipole

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moment, the crystal structure of BBMOD was investigated by single-crystal X-ray diffraction techniques. A preliminary report on this work has been published elsewhere (Beineke, 1966).

Experimental

A sample of BBMOD, m.p. 81–82°C, which had been recrystallized from hexane was kindly supplied by Professor Verkade. Because BBMOD reacts slowly with water vapor in the atmosphere, all crystals used in this investigation were sealed under vacuum in thin-walled glass capillaries. The crystals are colorless needles.

Crystal data

BBMOD = $C_5H_9PO_3Br_2$, $M = 307.9$. Orthorhombic, $a = 13.415 \pm 0.003$, $b = 11.407 \pm 0.004$, $c = 6.215 \pm 0.005$Å. These data were obtained from oscillation and Weissenberg photographs about the needle (c) axis. The photographs taken with Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, were corrected for film shrinkage by calibration with aluminum powder patterns ($a = 4.0331$ Å at 22°C). The systematic absences are: $h00$ when h is odd; $0k0$ when k is odd; $00l$ when l is odd. The space group is $P2_12_12_1$. BBMOD is soluble in all of the organic solvents in which flotation was initially attempted. The reaction with water, however, was found to proceed slowly enough to permit flotation in an aqueous silver nitrate solution. $\varrho_m = 2.00$ g.cm^{-3}; $\varrho_x(z = 4) = 2.15$ g.cm^{-3}. The linear absorption coefficient for Mo $K\alpha$ radiation is 87.9cm^{-1}.

A needle 0.10×0.15 mm in cross section and 0.5 mm long was used for the measurement of intensity data. A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with Mo $K\alpha$ radiation in the moving crystal-moving-counter mode (θ, 2θ coupling) to measure intensities. A 100 sec scan covering 3.33° was used for each reflection. Backgrounds were obtained from a curve based on about 60 background measurements which were made at various values of 2θ with ω offset by 1.8°. Strong peaks were corrected for non-linearity

of the counting system by assuming a dead time of 10^{-5} sec. The intensity of a reference reflection decreased linearly by fourteen per cent during the process of intensity measurement. A linear decomposition correction was therefore applied to all intensity data. One octant of data was collected out to $2\theta = 45°$ (sin $\theta/\lambda = 0.558$) beyond which few reflections could be distinguished above the background. A total of 755 reflections were recorded. A streak correction (Williams & Rundle, 1964) was applied to 60 reflections which occurred along densely packed radial reciprocal lattice rows. The approximate crystal dimensions were used to compute absorption corrections (Busing & Levy, 1957), and the resulting transmission factors which ranged from 0.286 to 0.401 were applied along with the usual Lorentz–polarization corrections to reduce the intensities to structure factors.

A standard deviation was computed for each intensity by means of the expression:

$$\sigma(I) = \frac{1}{A}[C_T + C_B + C_S + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2 + (K_A I)^2]^{\frac{1}{2}},$$

where C_T, C_B, C_S, I, and A are, respectively, the total counts, background counts, streak counts, intensity corrected for Lorentz–polarization and absorption effects, and the transmission factor. K_T, K_B, K_S, and K_A are, respectively, the estimated systematic errors in the total counts, background counts, streak counts, and the transmission factor. Based on experience in this laboratory K_T was assigned a value of 0.02; K_B and K_S, 0.10; and K_A, 0.03. $\sigma(F)$ was computed from $\sigma(I)$ for each reflection by the method of finite differences (Williams & Rundle, 1964):

$$\sigma(F) = (\text{Lp})^{-\frac{1}{2}}([I + \sigma(I)]^{\frac{1}{2}} - I^{\frac{1}{2}}).$$

Reflections were considered observed if in addition to giving a definite peak on the recorder trace, $F_o > 3\sigma(F_o)$. It was felt that the latter criterion was not too severe since even at this level a number of reflections with $F_o > 3\sigma(F_o)$ were classed as unobserved because of the absence of a clearly defined peak on the recorder trace.
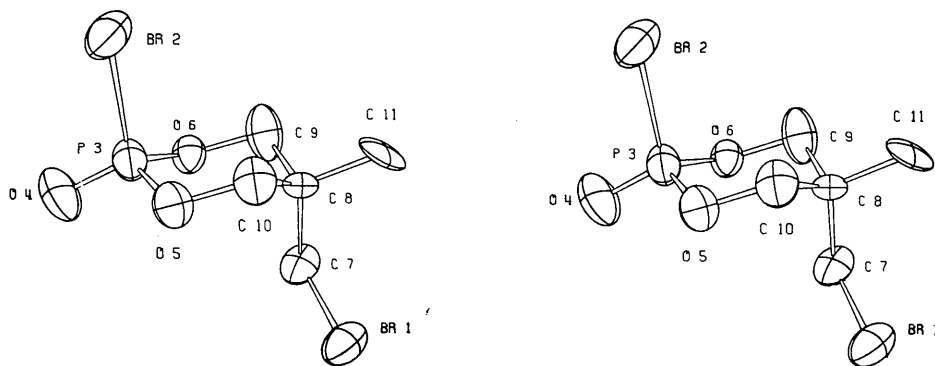

Fig. 1. Stereoscopic (Johnson, 1965) illustration of the BBMOD molecule. Anisotropic thermal vibration is indicated by 50% probability ellipsoids.

Of the 755 reflections only 470 were considered observed. Unobserved reflections were assigned a threshold value of $3\sigma(F_o)$ or F_o, whichever was the larger, and were included in the least-squares refinement only if this threshold value was exceeded by F_c. Only eight unobserved reflections had $F_c > F_o$ and were included in the final cycle of refinement.

Determination and refinement of the structure

The bromine positions were located directly from a sharpened three-dimensional Patterson synthesis. Successive structure-factor Fourier syntheses yielded the remaining atoms. The structure which resulted is illustrated in Fig. 1. All of the calculations were performed on an IBM 360 model 50 computer with the crystallographic programs of the National Research Council of Canada (Ahmed, Hall, Pippy, & Saunderson, 1966) unless otherwise noted. The structure was refined by block-diagonal least-squares minimization of the function $\Sigma\, w(|F_o| - |F_c|)^2$. Two blocks were used for each anisotropic atom. The first was a 3×3 block of positional parameters; the second, a 6×6 block of anisotropic temperature factors. The weighting scheme was $\sqrt{w} =$
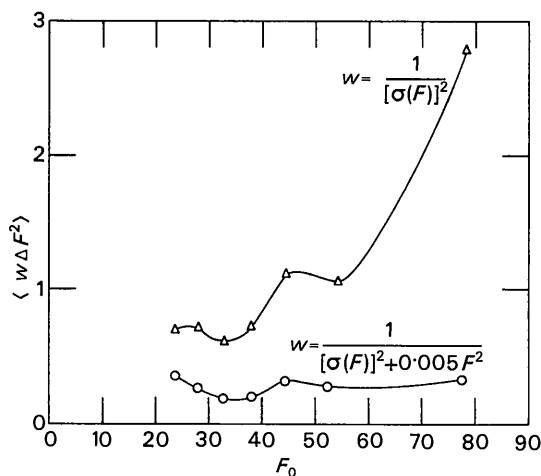
Fig. 2. Plot of $\langle w(|F_o| - |F_c|)^2 \rangle$ vs. $|F_o|$. Between 75 and 127 reflections are averaged for each point. $-\triangle-$: the unmodified weighting scheme; $-\bigcirc-$: the modified weighting scheme.

$\sigma(F)^{-1}$. Unobserved reflections were weighted in exactly the same way as observed reflections if $F_c \geq F_o$. They were, however, given weights of zero if $F_c < F_o$. The scattering factors which were used are those of Hanson, Herman, Lea & Skillman (1964). The real and imaginary anomalous dispersion corrections from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962) were included for both bromines and the phosphorus. Since the space group is acentric, both enantimorphs were tried. After convergence with all atoms given anisotropic temperature factors, the conventional R index $R_1 = \Sigma\, (|F_o| - |F_c|)/\Sigma\, |F_o|$ was 0·055 and 0·050 for the two enantimorphs. The enantiomorph which yielded the lower R_1 was selected; however, since the only difference between the two enantiomorphs is rotation of the C(7)–Br(1) bond by 120° about the C(7)–C(8) bond, no effort was made rigorously to establish absolute configuration. An attempt was made to locate the hydrogens in a difference-Fourier synthesis computed with low-angle data, but the noise level, ± 0.4 e.Å^{-3}, was too high.

The standard deviation of a reflection of unit weight was 1·14 which indicated that the weights were properly scaled. However, when average values of $w(F_o| - |F_c|)^2$ were plotted as a function of $|F_o|$ as in Fig. 2, a striking dependence on $|F_o|$ was observed. In constructing this plot, overlapping regions containing from 75 to 127 reflections were used for each point. A modified weighting scheme, $\sqrt{w} = [\sigma(F)^2 + PF_o^2]^{-\frac{1}{2}}$, was subsequently used with the value of P chosen to minimize the dependence of $\langle w(|F_o| - |F_c|)^2 \rangle$ on $|F_o|$. In this case independence was achieved with a value of 0·005 for P as illustrated in Fig. 2. In the final least-squares cycle, the the average shift was 0·05σ with the maximum shift, 0·17σ. The final weighted R, $R_2 = (\Sigma\, w(|F_o| - |F_c|)^2/ \Sigma\, wF_o^2)^{\frac{1}{2}}$ was 0·057 with $R_1 = 0.045$. The standard deviation of a reflection of unit weight was 0·59. Apparently the modified weights are not on an absolute scale, but this is of little consequence since they have been made independent of $|F_o|$.

The final positional and thermal parameters along with their estimated standard deviations are listed in Table 1. Experience in this laboratory indicates that the block-diagonal approximation leads to standard

Table 1. *Final parameters and standard deviations (in parentheses)*

All values have been multiplied by 10^4. The temperature factor expression is:
$$\exp\,[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)].$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Br(1)	8268 (2)	8797 (2)	7509 (4)	68 (1)	85 (2)	419 (8)	−36 (3)	−52 (8)	112 (9)
Br(2)	5528 (2)	4224 (2)	9602 (4)	86 (2)	69 (2)	455 (8)	−41 (3)	−61 (8)	56 (8)
P(3)	5715 (4)	5656 (4)	7338 (9)	62 (3)	66 (4)	230 (16)	2 (7)	−36 (17)	−32 (19·
O(4)	5326 (12)	5360 (14)	5243 (22)	104 (13)	144 (17)	241 (46)	8 (26)	−93 (45)	−74 (50)
O(5)	6863 (8)	5907 (11)	7353 (21)	65 (8)	83 (12)	277 (41)	7 (17)	1 (40)	−42 (52)
O(6)	5242 (9)	6730 (11)	8447 (20)	56 (9)	58 (10)	253 (40)	8 (16)	−17 (34)	−13 (36)
C(7)	6891 (14)	8426 (17)	8243 (33)	66 (15)	50 (16)	336 (72)	10 (26)	−94 (60)	106 (58)
C(8)	6837 (14)	7467 (16)	10008 (31)	54 (12)	61 (14)	153 (49)	−26 (24)	35 (48)	50 (47)
C(9)	5686 (16)	7240 (19)	10429 (37)	82 (16)	96 (20)	381 (77)	51 (34)	−49 (75)	−174 (79)
C(10)	7342 (14)	6358 (18)	9314 (34)	63 (14)	68 (17)	300 (67)	30 (29)	−46 (55)	9 (68)
C(11)	7331 (21)	7843 (22)	12200 (30)	158 (23)	122 (25)	101 (62)	−44 (44)	−58 (71)	152 (75)

deviations which are consistently underestimated by a factor of 0·8. Consequently the standard deviations listed in Table 1, as well as all estimated errors derived from them, should be multiplied by 1·2 to correspond with values derived from the more conventional full-matrix least-squares techniques. The structure factors computed from these parameters are compared with the observed values in Table 2. An examination of the

Table 2. *Observed and calculated structure factors*

Each group of data is headed with values for h and k. Within each group of data are listed l, $10F_o$, $10\sigma(F_o)$, and $10F_c$ respectively. Reflections for which F_o is negative are unobserved.

* These reflections were omitted from the refinement because $F_c < F_o$ (threshold).

observed and calculated F's for the more intense re-
flections indicated the absence of extinction effects.
Consequently, no extinction correction was made.

Results

Prior to this work, conformation III with the bulky
bromo and bromomethyl groups in equatorial posi-
tions, was considered to be sterically more favorable
than II. The actual conformation of BBMOD, however,
is best described as II in agreement with the dipole
moment measurements. Bond distances and angles are
listed in Table 3 along with their standard deviations.
The interior C–O–P angles which are larger by nine de-
grees than the ring angles in cyclohexane (Davis &
Hassel, 1963) cause the phosphate end of the ring to
assume a somewhat planar configuration with the re-
sultant loss of distinction between equatorial and axial
positions at P(3). This is best illustrated by considering
the angle between the normal to the least-squares plane
through O(5), O(6), C(9), and C(10) (from which the
atoms deviate by ±0·01 Å) and the normal to the plane
defined by O(5), P(3), and O(6). It is 36·7°, whereas
the corresponding angle with the plane of C(8), C(9),
and C(10) is 52·5°. The net result is a reduction of the
steric interactions between Br(2) and the hydrogens of
C(9) and C(10). The intramolecular interactions of
Br(1) also involve the methylene groups C(9) and C(10),
but because of the tetrahedral arrangement of bonds
about C(8), these interactions are independent of the
conformation of the ring. Thus, there is very little, if
any, preference for either conformation on the basis of
steric considerations. By way of comparison, it should
be noted that axial halogens have been observed in a
number of *trans*-dihalodioxanes (Altona, Knobler, &
Romers, 1963*a* and *b*; Altona & Romers, 1963). The
torsion angles about the ring bonds are listed in Table
4. When each bond is viewed in Newman projection in
the direction indicated, a clockwise rotation of the ring
atom farthest from the viewer has arbitrarily been
given a positive sign; a counterclockwise rotation, a
negative sign.

Table 3. *Bond distances and angles*

Distances (Å)
Standard deviations (× 10³) are given in parentheses.

P(3)–Br(2)	2·171 (6)	C(9)—O(6)	1·487 (25)
O(4)–P(3)	1·443 (16)	C(9)—C(8)	1·588 (29)
O(5)–P(3)	1·566 (13)	C(10)–O(5)	1·471 (24)
O(6)–P(3)	1·543 (13)	C(10)–C(8)	1·498 (27)
C(7)–Br(1)	1·949 (20)	C(11)–C(8)	1·575 (30)
C(8)–C(7)	1·551 (27)		

Angles (°)
Standard deviations in degrees are given in parentheses.

Br(2)–P(3)–O(4)	111·5 (0·7)	C(7)—C(8)—C(9)	106·1 (1·5)
O(5) –P(3)–Br(2)	104·4 (0·5)	C(7)—C(8)—C(10)	111·8 (1·6)
O(5) –P(3)–O(4)	113·8 (0·8)	C(7)—C(8)—C(11)	113·6 (1·6)
O(5) –P(3)–O(6)	104·9 (0·7)	C(9)—C(8)—C(10)	110·5 (1·6)
O(6) –P(3)–Br(2)	105·1 (0·5)	C(9)—C(8)—C(11)	108·1 (1·6)
O(6) –P(3)–O(4)	116·1 (0·8)	C(10)–C(8)—C(11)	106·8 (1·6)
C(10)-O(5)–P(3)	119·9 (1·1)	C(8)—C(9)—O(6)	108·5 (1·6)
C(9) –O(6)–P(3)	121·0 (1·2)	C(8)—C(10)–O(5)	109·6 (1·5)
Br(1)–C(7)–C(8)	111·3 (1·3)		

Table 4. *Torsion angles in the ring*

See text for sign convention.

Bond	Torsion angle
O(6)--→P(3)	−43·2°
P(3)--→O(5)	+44·6
O(5)--→C(10)	−56·1
C(10)--→C(8)	+58·4
C(8)--→C(9)	−63·1
C(9)--→O(6)	+55·8

The way in which BBMOD packs is illustrated in
Fig. 3. All intermolecular distances less than the sum
of the pertinent van der Waals radii (Pauling, 1960) are
listed in Table 5. All of these short distances involve
methylene or methyl groups for which reliable van der
Waals radii are not available. In the absence of accu-
rate positions for the hydrogens, little can be said about
these distances.

Discussion

Five-membered cyclic phosphate esters exhibit anom-
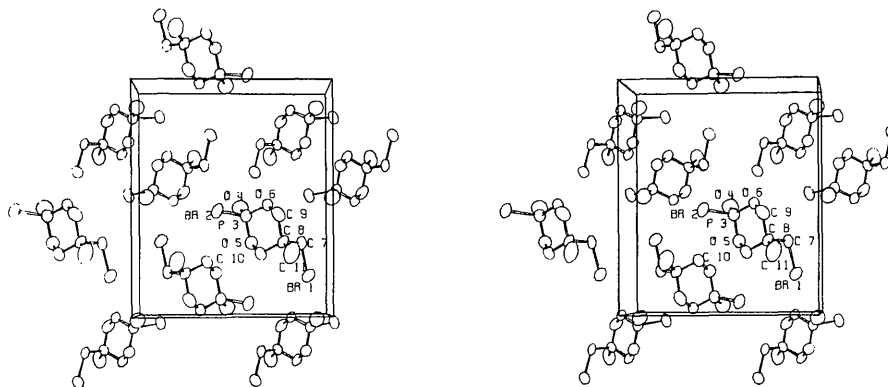alously high rates of hydrolysis when compared with

Fig. 3. Packing diagram. The c axis points out of the plane of the paper; the a axis, from top to bottom; and the b axis from left to right.

Table 5. *Short intermolecular distances*

Listed below are all distances which are less than the sum of the van der Waals radii (Pauling, 1960).

From	to	in molecule at	Distance
Br(1)	C(9)	$\frac{1}{4}+x, \frac{3}{2}-y, 2-z$	3·683Å
Br(1)	C(11)	$x, y, z-1$	3·695
Br(1)	C(11)	$\frac{3}{2}-x, 2-y, z-\frac{1}{2}$	3·920
Br(2)	C(7)	$1-x, y-\frac{1}{2}, \frac{3}{2}-z$	3·806
O(5)	C(10)	$\frac{3}{2}-x, 1-y, z-\frac{1}{2}$	3·373
C(7)	C(11)	$x, y, z-1$	3·859

their six-membered and cyclic analogues (Kumamoto, Cox, & Westheimer. 1956; Khorana, Tener, Wright, & Moffat, 1957). It has been suggested (Westheimer, 1957; Cox, Wall, & Westheimer, 1959) that a major factor in this rate enhancement is strain in the five-membered ring. According to this proposal, these hydrolysis reactions proceed through a trigonal-bipyramidal activated complex (Haake & Westheimer, 1961) in which one ring oxygen occupies an axial position and the other, an equatorial position. This trigonal-bipyramidal geometry has been observed in 2,2,2-triisopropropoxy-4,5-(2',2''-biphenyleno)-1,3,2-dioxaphospholene (Hamilton, La Placa, Ramirez, & Smith, 1967; Spratley, Hamilton, & Ladell, 1967) in which the internal O–P–O bond angle is 89·3°. One would therefore expect the energy of activation for hydrolysis to be directly related to the deviation of the O–P–O angle in phospate esters from the ideal of 90°. In Table 6 the pertinent molecular dimensions are compared for the three kinds of phosphates. It is immediately evident that the O–P–O angle in the five-membered ring is much closer to 90° than in either the six-membered cyclic or acyclic phosphate. The similar reactivity of these latter compounds is, therefore, attributable to their equal O–P–O bond angles.

A theoretical interpretation of the relationship between ring strain and chemical reactivity in phosphate esters has been given by Collin (1966). In that study π-electron energies which arise from 2p–3d orbital

interactions were calculated from the known geometries of acyclic and five-membered cyclic phosphate esters, by a self-consistent molecular orbital method. In the absence of structural data for six-membered cyclic phosphate esters estimates were made from molecular models. That the geometry of the BBMOD ring is almost exactly that used for these calculations lends credence to this interpretation. The π-electron energies of acyclic and six-membered cyclic phosphates were seen to be very nearly the same, while that of the five-membered ring was significantly higher. Assuming a similar energy level for the activated complex in the hydrolyses of all three types of phosphates, the energy of activation is clearly smaller in the case of the five-membered cyclic phosphate which explains its enhanced rate of reaction.

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Table 6. *Comparison of molecular dimensions*

The values in parentheses are the standard deviations in the last significant digit.

	BBMOD	Methyl ethylene phosphate (Steitz & Lipscomb, 1965)	Dibenzyl-phosphoric acid (Dunitz & Rollett, 1956)
Bond distances (Å)			
P=O	1·44 (2)	1·44 (1)	1·469 (4)
P–O (ring)*	1·57 (1)	1·57 (1)	1·545 (4)
	1·54 (1)	1·57 (1)	1·566 (4)
Bond angles (°)			
O–P–O (ring)*	104·9 (7)	99·1 (6)	103·8 (2)
O=P–O	113·8 (8)	116·0 (6)	112·8 (2)
	116·1 (8)	117·3 (6)	108·3 (2)
C–O–P (ring)*	120 (1)	112·0 (9)	118·8 (3)
	121 (1)	112·0 (9)	122·3 (3)

* These dimensions refer to the distances and angles within the five and six-membered rings and the analogous dimensions in the acyclic compound.

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Structures Cristallines des Dérivés 2 et 2,3 de la Naphtoquinone-1,4. IX. Amino-3-naphtoquinone-1,4

PAR JACQUES GAULTIER ET CHRISTIAN HAUW

Laboratoire de Cristallographie et Minéralogie associé au C.N.R.S., Faculté des Sciences de Bordeaux, Bordeaux, France

The crystalline structure of 3-amino-1,4-naphthoquinone has been determined by X-ray diffraction methods. The crystals are monoclinic ($P2_1/c$). Three-dimensional integrated intensity data were collected on retigrams and operated by computers. The hydrogen bonds were deduced both from the location of the hydrogen atoms and from the distance between possible acceptors and donors. The distances between N(3) and the nearest oxygen atoms are $2·89_9$ Å and $3·05_2$ Å. The structure consists of piles of parallel molecules; the interplanar spacing within the column is short (3·49 Å).

Données experimentales

Nous avons utilisé l'amino-3-naphtoquinone-1,4 pure des laboratoires Eastman Kodak. Cristallisé par sublimation très lente au voisinage de sa température de fusion ($F=210°$) ce composé forme de belles aiguilles rouge-orangées de section propre à une étude radiocristallographique (0,1 mm²).

Le groupe spatial et les dimensions de la maille ont été déterminés respectivement sur diagrammes de De Jong et de Bragg, la rotation du cristal s'effectuant autour de l'axe d'allongement *b*.

Données cristallographiques

Système monoclinique.

$a = 17,03 \pm 0,02$ Å,

$b = 3,96 \pm 0,01$,

$c = 14,72 \pm 0,02$.

$\beta = 125° 30'$.

Volume de la maille: 808 Å³,

Groupe spatial: $P2_1/c$,

Nombre de molécule par maille: 4,

Densité calculée: 1,42 g.cm⁻³,

$F(000) = 360$.

Nous avons obtenu au moyen du rétigraphe de De Jong (radiation Cu *K*α) les quatre plans réciproques contenus dans la sphère de résolution et portant les réflexions *h*0*l*, *h*1*l*, *h*2*l*, *h*3*l*. Les intensités de 953 réflexions ont été retenues et mesurées par comparaison visuelle avec une échelle étalon. Ce nombre représente 50% environ du nombre total de réflexions contenues dans la sphère de rayon $2/\lambda_{Cu\ K\alpha}$.

Les facteurs de diffusion atomiques employés ont été calculés à partir des coefficients donnés par Brusentsev (1963).

Détermination de la structure

La détermination a pu être effectuée uniquement à partir des projections de la fonction de Patterson réalisées au moyen du photosommateur harmonique de von Eller.

Etude de la projection (010)

La projection (010) est de type *P*2 et contient deux molécules centrosymétriques dans la demi maille *a*, *c*/2.

La projection de la fonction de Patterson 'sur ponctualisée' par l'application des fonctions modifiées* fait apparaître au voisinage de l'origine quelques pseudo

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* James (1948), Abrahamson & Maslen (1963), Waser & Schomaker (1953).