

Table 4. *Torsion angles in the heteroatomic ring (°)*

C(2)—C(7)—B—N(1)	33.8 (3)	C(10)—N(1)—B—C(7)	-179.1 (2)
C(7)—B—N(1)—N(2)	-52.9 (3)	H(N1)—N(1)—B—C(8)	-59 (2)
B—N(1)—N(2)—C(1)	39.4 (3)	H(N1)—N(1)—B—C(9)	179 (2)
N(1)—N(2)—C(1)—C(2)	-1.0 (4)	H(N1)—N(1)—B—C(7)	61 (2)
N(2)—C(1)—C(2)—C(7)	-17.8 (4)	C(2)—C(7)—B—C(8)	148.8 (3)
C(1)—C(2)—C(7)—B	-4.0 (4)	C(2)—C(7)—B—C(9)	-82.2 (3)
C(10)—N(1)—N(2)—C(1)	169.7 (2)	N(2)—N(1)—B—C(8)	-172.7 (2)
C(10)—N(1)—B—C(8)	61.2 (3)	N(2)—N(1)—B—C(9)	64.7 (3)
C(10)—N(1)—B—C(9)	-61.4 (3)		

ably longer than those found in addition compounds between boron trihalides and amines, *e.g.* 1.575 (11) Å in (CH₃)₃NBCl₃ (Hess, 1969). A cyclization similar to that in the title compound is found in *B,B*-diphenylboroxazolidine (Rettig & Trotter, 1973) with a five-membered ring. Its two B—C distances average 1.611 (2) and the B—N distance is 1.653 (3), while the fourth distance, to O, is 1.484 (3) Å. These distances agree well with those in the present compound. C(7)—B—N(1) is only 102.0 (2)° which can be compared to the small O—B—N angle 99.7 (1)° in the boroxazolidine.

N(1)—C(10), 1.485 (4) Å, is normal for four-coordinated N. N(1)—N(2), 1.463 (3), and C(1)—N(2), 1.282 (3) Å, correspond closely to an N—N single bond and a C—N double bond. These bonds are coplanar with C(1)—C(2) (Table 4). The heteroatomic ring seems to be strained as C(2)—C(1)—N(2) and C(1)—N(2)—N(1) deviate considerably from the expected 120°.

The packing of the molecules is shown in Fig. 2. Weak hydrogen bonds N(1)—H...N(2) link the molecules to form chains along *c*. N(1)—N(2) and N(2)—H are 3.058 (3) and 2.19 (3) Å and N(1)—H—N(2) is 164 (3)°. Most likely, the hydrogen bonds N—H...N are also present in (I) as shown by the high melting point, 97°C, compared with that for the corresponding 3,4-dimethyl compound, 20°C (Dewar & Dougherty, 1964).

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A Monoclinic High-Temperature Modification of Potassium Carbonate

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Abstract. β -K₂CO₃, monoclinic, *C*2/*c*; *a* = 5.675 (3), *b* = 9.920 (4), *c* = 7.018 (4) Å, β = 96.8 (1)° at 310°C from powder photographs, *V* = 392.3 Å³, *Z* = 4, *D_x* = 2.34 g cm⁻³; final *R* = 0.077 for 170 reflexions on precession and powder photographs. Crystals were taken from the melt. The main difference from the hexagonal

high-temperature form is that the CO₃ groups are rotated around one of the C—O bonds. Upon cooling, the room-temperature structure (*P*2₁/*c*) is formed at 250°C. It is a superstructure of the present one.

Introduction. Little is known of the structure of the anhydrous alkali carbonates. Crystals of these substances are highly hygroscopic and easily twinned.

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Above 420°C K_2CO_3 crystallizes in a hexagonal structure (Schneider & Levin, 1973; Papin, 1973). In their X-ray and DTA investigations of samples under a CO_2 atmosphere, these authors did not find the transition at 622°C reported by Makarov & Shulgina (1940).

The unit-cell parameters of this hexagonal phase are close to those of α - Na_2CO_3 , the structure of which is described by Eysel (1971). The supposition that the two phases are isostructural is supported by preliminary work in our laboratory. Between the monoclinic phase at room temperature (Gatehouse & Lloyd, 1973) and the hexagonal phase exists an intermediate structure, which has been briefly mentioned elsewhere in relation to the structural transformations of Na_2CO_3 (van Aalst, Becht, den Hollander, Peterse, Struikmans & de Wolff, 1975), and this is described here. This phase is in agreement with the two polymorphic transitions at 250 and 428°C found by Makarov & Shulgina (1940) from their DTA data.

We first saw an intermediate phase on photographs taken with a Guinier-Lenné camera (Nonius, Delft): the weak lines with $h+k$ odd of the room-temperature phase disappear gradually at about 250°C, indicating a new phase with a C -centred monoclinic lattice. This conclusion was confirmed by $h0$ - $3l$ precession photographs taken at 165 and 310°C. Above about 250°C there is a distinct broadening of all powder lines except the $hk0$ and $00l$, possibly due to microtwinning.

Attempts to obtain crystals from a saturated methanol solution did not succeed. We grew crystals from the melt by cooling slowly and then immersing the polycrystalline material in paraffin oil in order to avoid hydration. It was possible to separate small crystals from the product. For our single-crystal photographs we used a small block $0.15 \times 0.19 \times 0.23$ mm. The cell parameters were calculated from high-temperature powder photographs ($Cu K\alpha$).

Systematic absences hkl , $h+k$ odd, and $h0l$, l odd, indicated space groups Cc or $C2/c$. We chose the latter because it contains $P2_1/c$ of the room-temperature form as a subgroup.

We measured a series of $h0$ - $3l$ precession photographs (taken at 310°C with Zr-filtered Mo radiation), integrated and non-integrated, with a densitometer. The r.m.s. error in the intensities was estimated to be 10%, with a minimum corresponding to the smallest observable peak. The capillary containing the crystal was heated in a stream of air. Temperatures were measured and controlled with a Pt-Pt10Rh thermo-

couple. The uncertainty in the temperature measurement was estimated to be 10°C.

High-temperature powder photographs ($Cu K\alpha$), taken with different exposure times, were used for

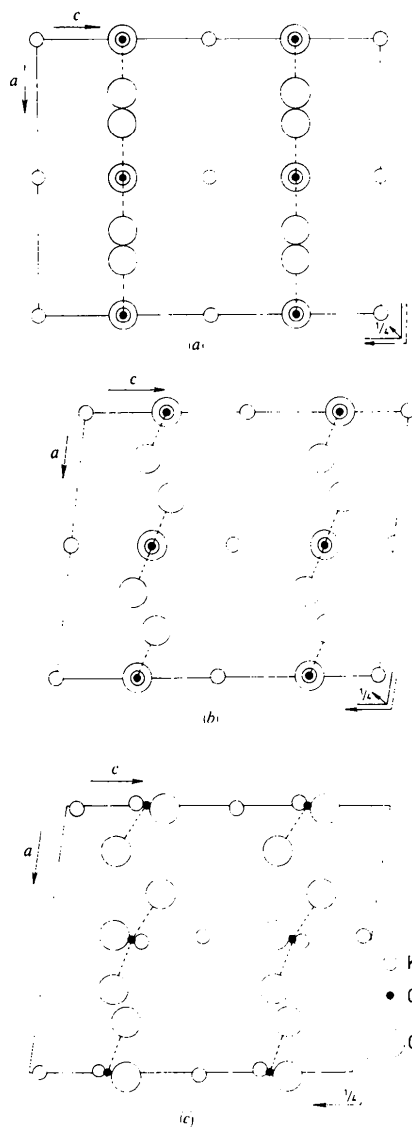


Fig. 1. The structure of K_2CO_3 viewed along b : (a) hexagonal α -form, (b) monoclinic β -form, described in the text, and (c) γ -form, stable at room temperature.

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations in parentheses

Thermal parameters are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \times 10^{-2}]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	7.0 (5)	11.1 (10)	10.3 (6)	0.5 (6)	2.7 (4)	-0.2 (8)
K(2)	0	0.332 (1)	$\frac{1}{2}$	5.0 (4)	11.3 (12)	18.9 (10)	0	2.4 (5)	0
C	0	0.333 (6)	$\frac{3}{4}$	5.0 (16)	4.0 (40)	7.3 (22)	0	-0.3 (15)	0
O(1)	$\frac{1}{2}$	0.702 (3)	$\frac{3}{4}$	6.3 (14)	4.0 (23)	19.5 (30)	0	3.4 (15)	0
O(2)	0.678 (2)	0.895 (2)	0.707 (3)	7.0 (10)	9.5 (19)	21.0 (20)	-0.9 (11)	5.5 (11)	7.1 (18)

intensity scaling. In this way we obtained 17 additional reflexions not visible with the precession technique. Lorentz and polarization corrections were applied and overall temperature and scaling factors computed. Use was made of *DATRDN* and *DATFIX* of the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970). No absorption correction was made, since this correction was estimated to be less than 10% in the measured intensities ($\mu = 22.1 \text{ cm}^{-1}$ for Mo $K\alpha$). From a Patterson map (program *FOURR*) the coordinates of the K atoms were derived, after which a difference map indicated the position of the CO_3 groups. After one cycle of refinement, with estimated isotropic temperature factors and 114 observed and 56 non-observed reflexions, we obtained an $R [\sum w(|F_o| - |F_c|)^2 / \sum (F_o)^2]$ of 0.209. Use was made of the full-matrix least-squares program *CRYLSQ* of the X-RAY 70 system. Throughout the refinement unit weights were used. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Two more cycles, with an increasing number of anisotropic thermal parameters (12 and 22 variables respectively), resulted in an R of 0.135. A last fully anisotropic refinement introducing nine new variables converged to $R = 0.077$.

Application of Hamilton's \mathcal{R} test (*International Tables for X-ray Crystallography*, 1974) to the last step showed that this was significant at better than the 99.5% confidence level.

A final difference map indicated no peaks greater than $0.57 \text{ e } \text{\AA}^{-3}$. The positional and thermal parameters are listed in Table 1.*

Discussion. In Fig. 1 the three structures, stable at high, intermediate and room temperature respectively, are shown projected along **b**. It is seen that the β phase arises from small displacements in the structure of α , while γ is formed by further small distortions in β . The symmetry decreases correspondingly, each lower phase retaining some of the symmetry operations of the one above. Bond lengths and angles of K_2CO_3 at $310 \pm 10^\circ\text{C}$ are given in Table 2. K(1) has a somewhat distorted octahedral environment of six O atoms with K-O distances of 2.66, 2.68 and 2.79 \AA and O-K-O

angles between 81 and 99° . K(2) is coordinated by ten O atoms within a sphere of radius 3.75 \AA .

Table 2. Bond lengths (\AA) and angles ($^\circ$) of $\beta\text{-K}_2\text{CO}_3$ with estimated standard deviations in parentheses

K(1)-K(1 ^{iv})	3.51 (1)	O(1)---K(1)-O(2 ^v)	98.8 (5)
K(1)-K(2)	3.57 (1)	O(1 ⁱⁱⁱ)-K(1)-O(2 ^{iv})	96.8 (5)
K(1)-K(2 ^{iv})	3.73 (1)	O(1 ⁱⁱⁱ)-K(1)-O(2 ^v)	81.2 (5)
K(1)-O(1)	2.66 (2)	O(2 ^{iv})-K(1)-O(2 ^{vi})	83.3 (5)
K(1)-O(2 ^{iv})	2.68 (2)	O(2 ^{iv})-K(1)-O(2 ^v)	96.7 (5)
K(1)-O(2 ^v)	2.79 (2)	O(1 ⁱⁱⁱ)-K(2)-O(1 ^{iv})	94.0 (2)
K(2)-O(1 ⁱⁱⁱ)	2.86 (1)	O(1 ⁱⁱⁱ)-K(2)-O(2 ^{iv})	80.4 (3)
K(2)-O(2 ^{iv})	3.31 (2)	O(1 ⁱⁱⁱ)-K(2)-O(2 ^v)	75.7 (7)
K(2)-O(2 ^v)	2.92 (2)	O(1 ^{iv})-K(2)-O(2 ^{vi})	72.8 (5)
C—O(1 ^{iv})	1.30 (7)	O(1 ^{iv})-K(2)-O(2 ^v)	117.1 (6)
C—O(2 ^{iv})	1.25 (3)	O(2 ^{iv})-K(2)-O(2 ^v)	81.7 (5)
O(1)-K(1)-O(2 ^{iv})	83.2 (5)	O(1 ^{iv})-C—O(2 ^{iv})	119 (3)
		O(2 ^{iv})-C—O(2 ^{vi})	121 (5)

Symmetry code

(i)	$x,$	$1-y,$	$\frac{1}{2}-z$	(v)	$x-\frac{1}{2},$	$\frac{3}{2}-y,$	$z-\frac{1}{2}$
(ii)	$x+\frac{1}{2},$	$y+\frac{1}{2},$	z	(vi)	$\frac{3}{2}-x,$	$y-\frac{1}{2},$	$\frac{3}{2}-z$
(iii)	$x,$	$1-y,$	$z-\frac{1}{2}$	(vii)	$1-x,$	$1-y,$	$1-z$
(iv)	$x-\frac{1}{2},$	$y-\frac{1}{2},$	z	(viii)	$\frac{1}{2}-x,$	$y-\frac{1}{2},$	$\frac{3}{2}-z$

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31944 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.