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The Structures of the Aluminum Carbonitrides

By G. A. Jeffrey and Victor Y. Wu

The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh 13, *Pa., U.S.A.*

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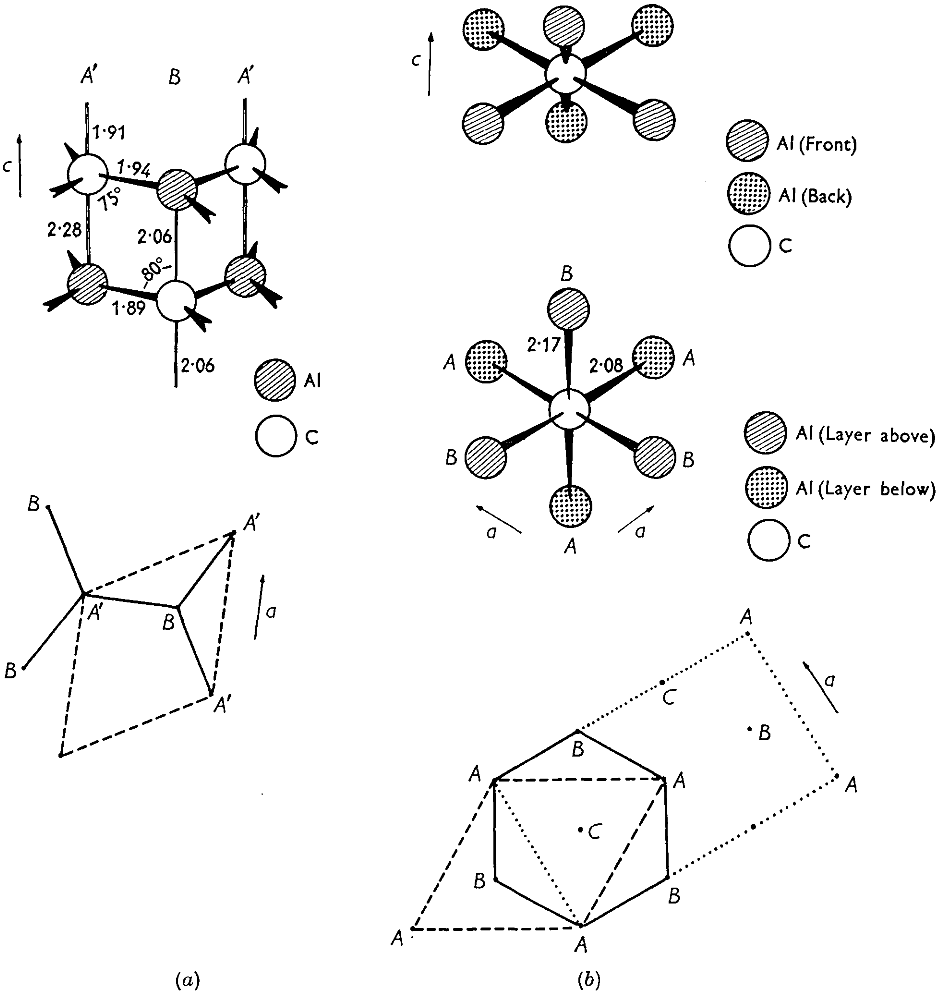
Three new aluminum carbonitrides have been identified by single-crystal X-ray analysis. These are $Al_6C_3N_2$, $Al_7C_3N_3$, $Al_8C_3N_4$. These compounds, together with AlN, Al_4C_3, and Al_5C_3N form two structurally related polytypic series based on hexagonal packing with similar basal spacings and different c axis periodicities. A complete three-dimensional crystal structure analysis is reported for the $Al_7C_3N_3$ compound.

Introduction

In some previous work by Amma & Jeffrey (1961), the X-ray single-crystal diffraction data of Al_2CO were interpreted in terms of a disordered structure based on the inversion of adjacent atomic rows in a wurtzite-type lattice. The corresponding short-range ordered structure contained a structural configuration with a short Al–Al distance of about 2·5 Å, and a 75° valence-bond angle at the non-metal atoms. Because of the diffuse X-ray spectra associated with the short range order, a conclusive proof of the existence of



(*a*) (*b*)

Fig. 1. Structural features in $Al_7C_3N_3$. (*a*) The structural unit of Al_2C_2. (*b*) The structural unit of the Al_2C.

Table 1. *Crystal data for the aluminum carbonitrides* $(AlN)_n . Al_4C_3$

$n = 0–6$

Formula	Z	Laue class	Space group	Cell dimensions a	c	c/a	Strongest $00l$	Mean layer distance	D_x g.cm^{-3}	D_m g.cm^{-3}
AlN	2	$6m$	$P6_3mc$	3·111	4·978	1·600	002	2·489	3·262	3·20
Al_4C_3	3	$\bar{3}m$	$R\bar{3}m$	3·330	24·89	7·474	0012	2·074	3·000	2·93
Al_5C_3N	2	$6m$	$P6_3mc$	3·281	21·67	6·005	0010	2·167	3·039	2·99
$Al_6C_3N_2$	3	$\bar{3}m$	$R\bar{3}m$	3·248	40·03	12·33	0018	2·224	3·076	3·04
$Al_7C_3N_3$	2	$6m$	$P6_3mc$	3·226	31·70	9·826	0014	2·264	3·102	3·046
$Al_8C_3N_4$	3	$\bar{3}m$	$R\bar{3}m$	3·211	55·08	17·15	0024	2·295	3·133	3·05
*$Al_9C_3N_5$	2	$6m$	$P6_3mc$	(3·197)	(41·69)	(13·04)	(0018)	(2·316)	(3·141)	(3·06)
*$Al_{10}C_3N_6$	3	$\bar{3}m$	$R\bar{3}m$	(3·186)	(70·00)	(21·97)	(0030)	(2·333)	(3·157)	(3·07)

* Hypothetical compounds

this configuration was not possible from the Al_2CO structural data alone. However, related structural features have been reported for the minerals cubanite, $CuFeS_2$, by Azaroff & Buerger (1955), and sulvanite, Cu_3VS_4, by Pauling (1960) and for the carbide and carbonitride of aluminum, Al_4C_3 and Al_5C_3N (von Stackelberg *et al.*, 1934, 1935). This prompted a reinvestigation of the aluminum compounds, in the course of which three new aluminum carbonitrides were discovered. These compounds are $Al_6C_3N_2$, $Al_7C_3N_3$, $Al_8C_3N_4$. With the additional crystal data obtained from these materials, it is possible to recognize a structural relationship throughout the whole series of carbide, nitride and the four carbonitrides. The series can also be extrapolated to predict the crystal data for further members, the crystals of which have not yet been discovered.

The crystal structures of Al_4C_3 and Al_5C_3N are related and are based on similar hexagonal layers of aluminum atoms interspersed with layers of the nonmetal atoms in regular stacking sequences. There are two particular features of these structures that are interesting from the point of view of the nature of the interatomic binding forces. One is the lozenge shaped configuration similar to that postulated to exist in Al_2CO and shown in Fig. 1(*a*), in which the carbon atoms have five coordination with a distorted trigonal bipyramid distribution of C–Al bonds. The second, shown in Fig. 1(*b*), is the octahedral coordination of the carbon atoms when the metal lattice switches from a hexagonal to a cubic close-packing stacking sequence. Although the aluminum atoms are tetrahedrally four coordinated, nowhere in the carbide or carbonitride structures do the carbon atoms form the four sp^3 tetrahedral bonds which are normally associated with the valence state of this element. These compounds appear to be an interesting example of a structural principle proposed by Pauling (1960), that an electron-deficient atom, in this case Al, causes adjacent atoms to increase their ligancy to a value greater than their orbital number.

Crystal data

The aluminum carbide and carbonitrides were indistinguishable in appearance and could all be found from samples similarly prepared. They form thin hexagonal translucent plates varying in color, for the same compound, from brown to bright yellow. The crystals cleave easily on the basal plane and for this reason tend to form leaflets. The least stable crystals are the carbide, which decompose to a yellow-brown powder, which may be the amorphous form reported by Wohler & Hofer (1933), or a product of decomposition in moist air.

The crystal data for the new compounds are shown in Table 1, together with the data for AlN, Al_4C_3, Al_5C_3N, for comparison purposes, and the predicted data for $Al_9C_3N_5$, $Al_{10}C_3N_6$ to illustrate the logical extension of the series.

The crystals in the even series with the rhombohedral symmetry were frequently twinned, but no twins were observed in the odd series.

The ideal stoichiometry of the three new carbonitrides was deduced from the crystal data and the structural relationships discussed later. This stoichiometry was confirmed in the case of the $Al_7C_3N_3$ by a complete crystal structure analysis. The density of the crystals of a particular compound varied by several per cent and was always less than that calculated, often by as much as 5%.

The observed values given in Table 1 are the highest obtained from different crystals of the same compound. With crystals of Al_4C_3, densities as low as 20% less than the X-ray value were observed. We believe that this may be associated with carbon vacancies in the structure due to the decomposition in the presence of moist air. The nature of the structures is such that they might be expected to permit non-stoichiometry particularly with respect to the non-metallic atoms.

Experimental

The specimens from which the crystals were obtained were kindly supplied by Dr L. M. Foster of the ALCOA Research Laboratories. They were prepared by heating AlN in a carbon crucible with nitrogen environment at about 2000 °C, and formed on the walls of the vessel.

The crystals were identified by single-crystal Weissenberg photographs about one of the edges of

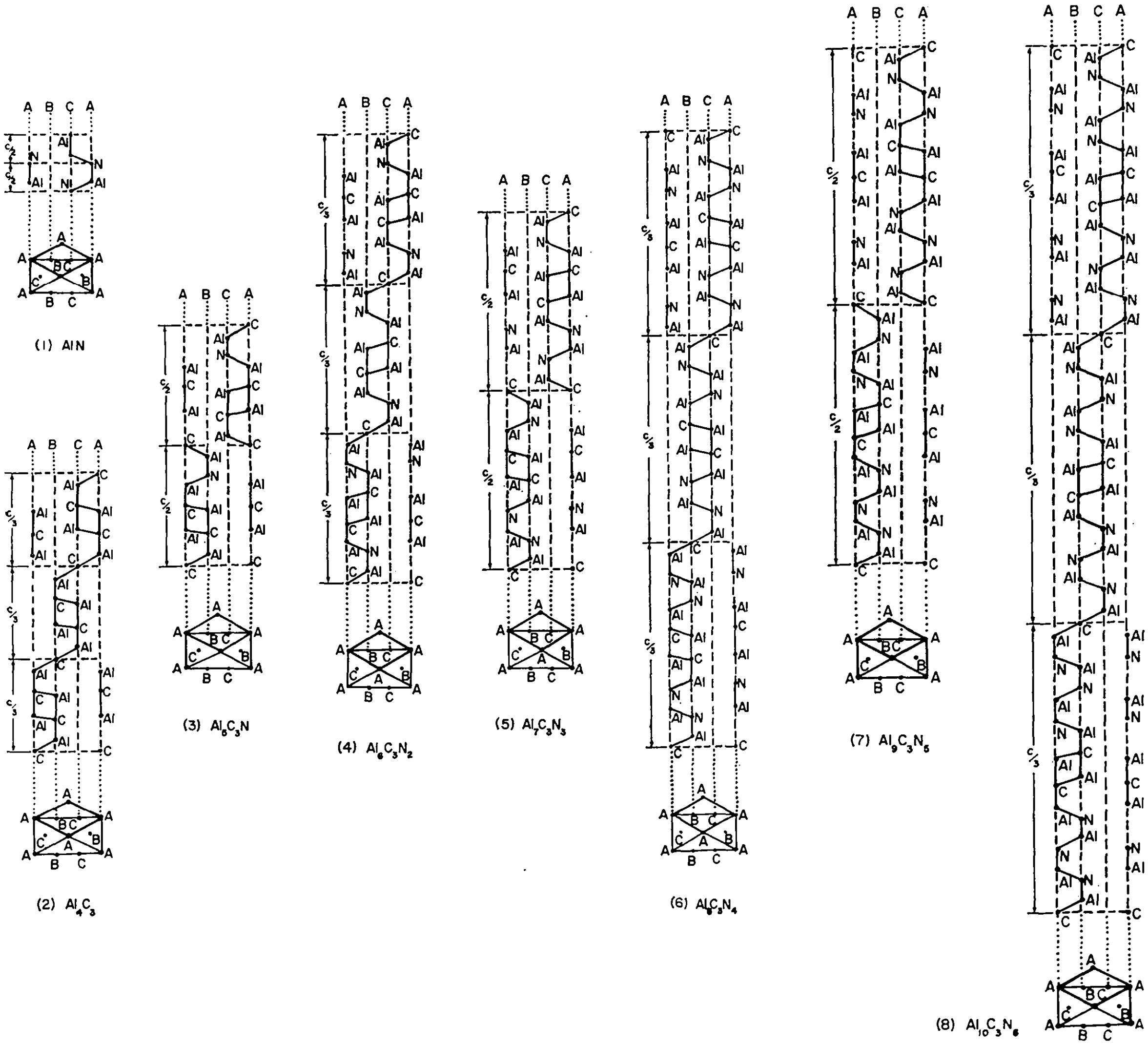


Fig. 2. The structures of aluminium nitride, carbide and the carbonitrides.

the hexagonal plates, the spacings of the 00*l* reflections being the most easily recognized of the diffraction characteristics. Owing to the inhomogeneity of polycrystalline specimens and the similarity in their basal lattice spacings, powder diffraction data would not provide a satisfactory means of identification.

The Laue symmetry, systematic extinctions and approximate unit cell dimensions were obtained from Cu *K* Weissenberg photographs. More precise lattice spacings were measured from single crystals using the G. E. goniostat on an XRD-3 unit with a proportional counter.

The densities were measured by flotation in mixtures of bromoform and methylene iodide. Each crystal, the density of which was measured, was subsequently identified by means of an X-ray photograph.

The three-dimensional intensity data for the $Al_7C_3N_3$ were obtained by eye-estimation from multifilm equi-inclination Weissenberg Cu *K* photographs. The data were recorded from small triangular platy crystals about 0·3 mm in edge and 0·05 mm thick, on four layers about the *a* axis. The intensities were corrected for L. P. factors using Shiono's (1957) IBM 650 program and the layers were correlated through the common reflexions. No corrections were made for absorption or extinction.

The structural relationships

The structures of the eight compounds listed in Table 1 are illustrated in Fig. 2. The atomic rows *ABC* refer to the usual close packing nomenclature, so that atoms in a layer sequence *ABAB*... have an h.c.p. arrangement and *ABCA*... is c.c.p. The order of the strongest 00*l* reflections given in Table 1 correspond with the number of layers in the structure.

As clearly shown in Fig. 2, these structures can be described in terms of three structural segments or blocks in different stacking sequences. These blocks are $[AlN]_n$, $[Al_2C_2]_n$ and $[Al_2C]_n$. The [AlN] block is as in the normal wurtzite structure of AlN. The $[Al_2C_2]_n$ block consists of two adjacent layers of metal atoms with carbon atoms occupying the tetrahedral interstices immediately above and below the double metallic layer forming the structure shown in Fig. 1(*a*). The $[Al_2C]$ block consists of two metallic layers with the carbon atoms between them in the six-fold octahedrally coordinated sites. In terms of these units, the sequential description of Al_5C_3N is $Al_2C_2.AlN.Al_2C.Al_2C_2.AlN.Al_2C$, giving two formula units of Al_5C_3N per unit cell. This arrangement changes the symmetry of the structure from rhombohedral as in Al_4C_3 to hexagonal as for AlN. The aluminum layer stacking sequence is *BABABCACAC*... with the switch from h.c.p. to c.c.p. at $z=0$ and $\frac{1}{2}$.

In $Al_6C_3N_2$, additional blocks of AlN are inserted, so that the stacking sequence is $Al_2C_2.AlN.Al_2C.AlN.Al_2C_2.AlN.Al_2C.AlN.Al_2C_2.AlN.Al_2C.AlN$ corresponding to three formula units of $Al_6C_3N_2$ per unit cell. The aluminum layer sequence is

BABABACBCBCBACACAC .

The switch to c.c.p. occurs at $z=0, \frac{1}{3}, \frac{2}{3}$ and the symmetry reverts to rhombohedral again.

In $Al_7C_3N_3$, the structure sequence is $Al_2C_2.AlN.AlN.Al_2C.AlN.Al_2C_2.AlN.AlN.Al_2C.AlN$, with two formula units per cell and hexagonal symmetry. Similarly in $Al_8C_3N_4$, the structure is rhombohedral with the sequence $[Al_2C_2.AlN.AlN.Al_2C.AlN.AlN]_3$. Fig. 2 illustrates the extension to the hypothetical compounds $Al_9C_3N_5$ and $Al_{10}C_3N_6$.

Not only is the separation into the hexagonal and rhombohedral series explained on this basis, but also some other aspects of the data shown in Table 1. AlN and Al_4C_3 being the extreme members of the series, have respectively the smallest and largest basal periodicities, and the *a* axis lengths decrease regularly in the carbonitrides with increase of AlN content. This is paralleled by the densities which also increase with AlN content. The increase in *c*/*a* ratio per mole of AlN added to the formula unit is 0·810 for the first and tends to converge to the AlN value of 0·800. There is a related trend in the average value of the layer separations. It is therefore possible to predict the crystal data for further members of the series and the predicted values for the hypothetical $Al_9C_3N_5$ and $Al_{10}C_3N_6$ are given in parenthesis in Table 1.

This description of these structures is consistent with the crystal data and with the reported structures for Al_4C_3 and Al_5C_3N, except for the interchange of a carbon and nitrogen positions which were indistinguishable in the original structure analysis. For further verification and to obtain more detailed information concerning the stereochemistry, a complete crystal structure analysis of the $Al_7C_3N_3$ was carried out and is reported below.

The structure analysis of $Al_7C_3N_3$

The structure was solved from the three-dimensional Patterson synthesis and refined by three-dimensional Fourier and differential syntheses. The computations associated with the analysis were carried out on an IBM 650 and IBM 7070 using programs written by Shiono (1957, 1962), McMullan & Chu (1962). For computational convenience the orthorhombic cell was used with $a=3{\cdot}226$, $b=5{\cdot}589$, $c=31{\cdot}70$ Å, containing four $Al_7C_3N_3$ formula units. The orthorhombic space groups consistent with the observed systematic extinctions, (*hkl*) absent for $(h+k)$ odd, (*h*0*l*) absent for *l* odd, are *C*2*cm*, $Cmc2_1$, *Cmcm*.

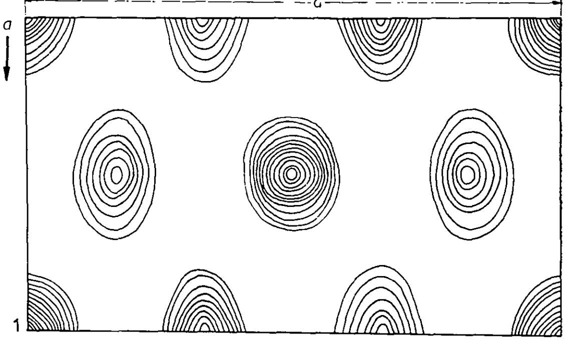


Fig. 3. Two dimensional Patterson projection down [*c*] axis.

A two dimensional Patterson projection down the *c* axis was computed by means of the Beevers–Lipson strips. This is shown in Fig. 3. It confirms a structure based on hexagonal packing. The three-dimensional Patterson section at (*ovw*) was computed on the IBM 650 and is shown in Fig. 4, together with the interpretation, which was arrived at both directly and by vector convergence.

The coordinates of the 28 aluminum atoms were deduced as $0, 0, u$; $\frac{1}{2}, \frac{1}{2}, u$; $0, 0, \frac{1}{2}+u$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u$;

Table 2. *Fractional atomic coordinates and isotropic temperature factors, with standard deviations (in parenthesis)*

Atom	X_n	Y_n	Z_n	B (Å²)
Al_1	0·000	0·334 (0·001)	0·0299 (0·0002)	1·0 (0·4)
Al_2	0·000	0·000 (0·001)	0·1085 (0·0002)	1·1 (0·4)
Al_3	0·000	0·333 (0·001)	0·1844 (0·0002)	1·0 (0·4)
Al_4	0·000	0·001 (0·001)	0·2615 (0·0002)	1·1 (0·4)
Al_5	0·000	0·333 (0·001)	0·3166 (0·0002)	1·3 (0·4)
Al_6	0·000	0·001 (0·001)	0·3915 (0·0002)	1·4 (0·5)
Al_7	0·000	0·333 (0·001)	0·4659 (0·0002)	1·0 (0·4)
N_1	0·000	0·333 (0·002)	0·0939 (0·0004)	1·0 (0·8)
N_2	0·000	0·005 (0·002)	0·1686 (0·0004)	1·0 (0·8)
N_3	0·000	0·333 (0·002)	0·4069 (0·0004)	1·4 (0·8)
C_1	0·000	0·000 (0·002)	0·0009 (0·0006)	1·3 (1·0)
C_2	0·000	0·333 (0·002)	0·2448 (0·0006)	0·5 (1·0)
C_3	0·000	0·001 (0·002)	0·3267 (0·0006)	0·8 (1·0)

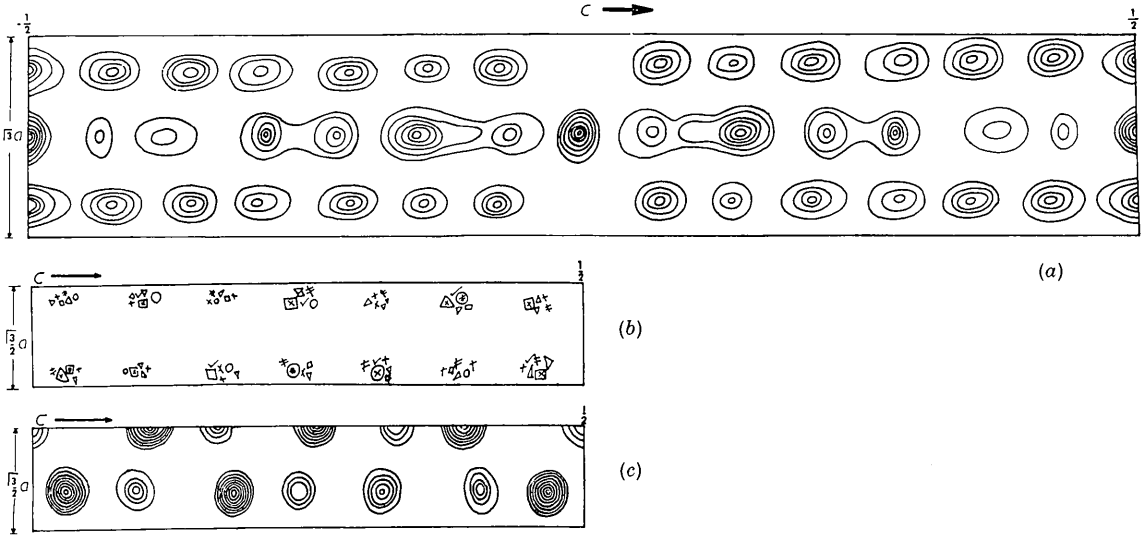


Fig. 4. Three-dimensional section syntheses at $x = 0$. (a) Patterson. (b) Vector convergence interpretation. (c) Fourier.

where $u = 0{\cdot}107,\ 0{\cdot}256,\ 0{\cdot}393,\ 0,\ \frac{1}{3},\ w;\ 0,\ \frac{2}{3},\ \frac{1}{2}+w;\ \frac{1}{2},\ \frac{5}{6},\ w;\ \frac{1}{2},\ \frac{1}{6},\ \frac{1}{2}+w$, where $w = 0{\cdot}031,\ 0{\cdot}182,\ 0{\cdot}318,\ 0{\cdot}469$. The carbon and nitrogen atoms were not distinguished at this stage and were placed between the aluminum atoms at reasonable interatomic distances consistent with the Patterson synthesis. This arrangement corresponded to the non-centrosymmetrical space group $Cmc2_1$ and its hexagonal equivalent, $P6_3mc$.

This initial model for the structure gave an agreement index of $R = 0{\cdot}29$. Successive Fourier refinement was carried out by structure factor calculations, Fourier syntheses and differential Fourier synthesis on the IBM 7070. The carbon and nitrogen atoms were clearly distinguished by the height of the electron density peaks, and successive refinement with isotropic temperatures factors reduced R to 0·147 excluding unobserved reflexions.

The final atomic parameters are given in Table 2

Table 3. *Interatomic distances and angles in* $Al_7C_3N_3$

The symmetry related atoms

I. x, y, z
II. $\frac{1}{2}+x, \frac{1}{2}+y, z$
III. $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
IV. $x, -y, \frac{1}{2}+z$

Interatomic distances with standard deviations (in parentheses)

Aluminum–aluminum distances	
Al$_1$(I)-Al$_2$(I)	3·10 Å (0·01)
Al$_1$(I)-Al$_1$(II)	3·23
Al$_1$(I)-Al$_7$(IV)	2·76
Al$_2$(I)-Al$_3$(I)	3·04
Al$_3$(I)-Al$_4$(I)	3·06
Al$_4$(I)-Al$_5$(I)	2·56
Al$_5$(I)-Al$_6$(I)	3·02
Al$_6$(I)-Al$_7$(I)	3·00

Aluminum–carbon distances	
C$_1$(I)-Al$_7$(IV)	2·17 Å (0·02)
C$_1$(I)-Al$_1$(I)	2·08
C$_1$(I)-Al$_2$(I)	3·40
Al$_3$(I)-C$_2$(I)	1·91
C$_2$(I)-Al$_4$(I)	1·94
C$_2$(I)-Al$_5$(I)	2·28
Al$_4$(I)-C$_3$(I)	2·06
Al$_5$(I)-C$_3$(I)	1·89
Al$_6$(I)-C$_3$(I)	2·06

Aluminum–nitrogen distances	
Al$_1$(I)-N$_1$(I)	2·03 Å (0·02)
N$_1$(I)-Al$_2$(I)	1·92
Al$_2$(I)-N$_2$(I)	1·91
N$_2$(I)-Al$_3$(I)	1·96
Al$_6$(I)-N$_3$(I)	1·93
N$_3$(I)-Al$_7$(I)	1·86
N$_1$(I)-Al$_3$(I)	2·86
N$_2$(I)-Al$_4$(I)	2·93
Al$_5$(I)-N$_3$(I)	2·86

Carbon–carbon distances Carbon–nitrogen distances Nitrogen–nitrogen distances	
C$_1$(I)-N$_1$(I)	3·49 Å (0·03)
N$_1$(I)-N$_2$(I)	3·01
N$_2$(I)-C$_2$(I)	3·04
C$_2$(I)-C$_3$(I)	3·18
C$_2$(I)-N$_3$(I)	3·16
N$_3$(I)-C$_1$(V)	3·53
C$_1$(I)-C$_1$(IX)	3·23

Bond angles

Central atom Al		
C$_1$(I)-Al$_1$(I)-N$_1$(I)	116°	(0·5)
C$_1$(I)-Al$_1$(I)-C$_1$(IV)	102	
N$_1$(I)-Al$_2$(I)-N$_2$(I)	104	
N$_1$(I)-Al$_2$(I)-N$_1$(IV)	114	
N$_2$(I)-Al$_3$(I)-C$_2$(I)	105	
N$_2$(I)-Al$_3$(I)-N$_2$(IV)	111	
C$_2$(I)-Al$_4$(I)-C$_3$(I)	106	
C$_2$(I)-Al$_4$(I)-C$_2$(IV)	113	
C$_2$(I)-Al$_5$(I)-C$_3$(I)	100	
C$_3$(I)-Al$_5$(I)-C$_3$(V)	117	
C$_3$(I)-Al$_6$(I)-N$_3$(I)	104	
N$_3$(I)-Al$_6$(I)-N$_3$(IX)	114°	(0·5)
N$_3$(I)-Al$_7$(I)-C$_1$(II)	121	
C$_1$(II)-Al$_7$(I)-C$_1$(III)	96	

Central atom N		
Al$_1$(I)-N$_1$(I)-Al$_2$(I)	103°	(0·5)
Al$_2$(I)-N$_1$(I)-Al$_2$(IV)	114	
Al$_2$(I)-N$_2$(I)-Al$_3$(I)	103	
Al$_3$(I)-N$_2$(I)-Al$_3$(IX)	111	
Al$_6$(I)-N$_3$(I)-Al$_7$(I)	104	
Al$_6$(I)-N$_3$(I)-Al$_6$(IX)	114	

Central atom C		
Al$_7$(II)-C$_1$(I)-Al$_7$(III)	96°	(0·5)
Al$_1$(I)-C$_1$(I)-Al$_1$(IV)	102	
Al$_3$(I)-C$_2$(I)-Al$_4$(I)	105	
Al$_4$(I)-C$_2$(I)-Al$_4$(IX)	113	
Al$_4$(I)-C$_2$(I)-Al$_5$(I)	75	
Al$_4$(I)-C$_3$(I)-Al$_5$(I)	80	
Al$_5$(I)-C$_3$(I)-Al$_5$(IV)	117	
Al$_5$(I)-C$_3$(I)-Al$_5$(IX)	100	

Table 4. *Table of observed and calculated structure factors*

(F_o for unobserved reflexions marked * were half the minimum observable value)

H=0

K	L	FCHS	FCAL	ACAL	HCAL
0	4	3	3	1	3
0	6	14	17	7	-16
0	8	25	25	14	21
0	10	50	72	70	-13
0	12	69	59	52	28
0	14	185	237	-237	-6
0	16	26	36	-5	36
0	18	8	21	-14	-14*
0	20	24	39	-14	37
0	22	22	19	16	-11
0	24	42	51	-50	11
0	26	35	33	28	-18
0	28	90	86	85	2
0	30	44	34	18	-28
0	32	28	21	21	2
0	34	34	36	33	-16
0	36	43	13	9	-9
0	38	48	43	42	4
0	40	41	30	-30	-1
2	0	59	57	57	0
2	1	90	100	100	-1
2	2	36	32	-32	-0
2	3	37	34	34	0
2	4	50	45	-43	10
2	5	42	39	38	-6
2	6	47	45	-42	-15
2	7	85	80	80	-2
2	8	94	97	93	25
2	9	13	11	-3	-10
2	10	38	35	24	-26
2	11	40	45	45	-2
2	12	35	38	32	19
2	13	108	90	90	-6
2	14	30	30	-18	-24
2	15	32	39	-39	1
2	16	30	29	21	20
2	17	9	16	16	-0*
2	18	96	111	105	-35
2	19	39	47	-46	11
2	20	43	46	36	29
2	21	57	64	-64	3
2	22	44	55	-46	-29
2	23	15	19	5	18
2	24	21	23	-7	22
2	25	38	38	-37	6
2	26	16	17	12	-13
2	27	45	38	-36	12
2	28	25	26	12	22
2	29	8	7	6	2*
2	30	19	21	19	-9
2	31	38	34	-34	1
2	32	88	78	-74	23
2	33	30	25	24	-7
2	34	11	8	-3	-8
2	35	24	28	28	-1
2	36	21	23	20	11
2	37	20	15	2	-14
2	38	21	13	13	-0
2	39	35	26	25	-3
4	0	44	34	34	0
4	1	70	62	-62	-0
4	2	28	22	-22	-1
4	3	23	18	-18	0
4	4	42	34	-33	7
4	5	28	27	-27	2

K	L	FOBS	FCAL	ACAL	HCAL
4	6	55	45	-43	-12
4	7	74	61	-60	1
4	8	76	69	67	15
4	9	13	8	-1	8
4	10	31	25	18	-17
4	11	33	33	-33	2
4	12	24	25	21	13
4	13	66	59	-59	3
4	14	21	23	-12	-19
4	15	22	28	28	0
4	16	25	20	14	14
4	17	11	14	-14	-0*
4	18	74	79	74	-25
4	19	30	35	34	-7
4	20	32	35	27	21
4	21	41	46	46	-1
4	22	29	38	-33	-20
4	23	15	15	-4	-14
4	24	15	17	-5	16
4	25	27	29	28	-5
4	26	12	13	8	-9
4	27	29	28	27	-8
4	28	23	20	9	18
4	29	8	5	-5	-2*
4	30	14	16	15	-7
4	31	31	27	27	-1
4	32	78	60	-57	19
4	33	25	20	-19	6
6	0	130	133	133	0
6	2	10	3	-3	-1
6	4	10	6	5	3
6	6	7	7	2	-6*
6	8	12	7	4	5
6	10	15	20	20	-4
6	12	16	16	10	12
6	14	82	90	-90	-3
6	16	8	14	-0	14
6	18	4	10	-8	-6*
6	20	13	15	-5	13
6	22	7	6	5	-2
H=1					
1	0	71	57	57	0
1	1	109	98	-98	0
1	2	38	32	-32	-0
1	3	39	33	-33	0
1	4	55	45	-44	9
1	5	43	40	-40	5
1	6	53	45	-42	-16
1	7	88	78	-78	1
1	8	104	96	93	25
1	9	14	12	3	12
1	10	39	36	24	-26
1	11	40	46	-46	2
1	12	31	38	33	19
1	13	89	89	-89	5
1	14	28	30	-18	-24
1	15	32	38	38	-0
1	16	33	29	21	20
1	17	9	17	-17	-0
1	18	111	111	105	-35
1	19	46	48	47	-10

K	L	FUBS	FCAL	ACAL	BCAL
1	20	50	47	36	29
1	21	66	64	64	-3
1	22	50	54	-46	-28
1	23	17	19	-6	-18
1	24	22	24	-7	22
1	25	45	38	37	-6
1	26	14	17	11	-12
1	27	43	37	35	-11
1	28	31	26	12	23
1	29	7	7	-6	-2*
1	30	17	21	19	-9
1	31	38	34	34	-1
1	32	95	78	-74	23
1	33	29	25	-24	7
1	34	6	8	-3	-8*
1	35	24	28	-28	0
1	36	22	23	20	11
1	37	19	14	-1	14
1	38	22	13	13	-1
1	39	32	26	-25	4
3	0	226	253	253	0
3	2	5	5	-4	-1*
3	4	5	5	4	3*
3	6	14	12	4	-11
3	8	21	15	7	13
3	10	35	42	41	-10
3	12	33	28	19	21
3	14	157	163	-163	-6
3	16	21	27	-1	26
3	18	8	16	-12	-11*
3	20	12	28	-11	25
3	22	14	12	10	-7
3	24	29	37	-37	7
3	26	29	25	21	-13
3	28	68	64	64	1
3	30	33	25	14	-21
3	32	20	17	17	1
3	34	28	28	26	-11
5	0	33	24	24	0
5	1	55	46	46	-1
5	2	20	15	-15	-1
5	3	20	13	13	0
5	4	30	25	-23	7
5	5	20	18	17	-3
5	6	43	32	-31	-8
5	7	57	47	47	-1
5	8	58	50	49	11
5	9	7	5	1	-4*
5	10	21	18	13	-11
5	11	24	24	24	-2
5	12	18	18	15	10
5	13	52	46	45	-3
5	14	16	17	-8	-14
5	15	15	22	-22	1
5	16	18	16	11	11
5	17	7	9	9	-0*
5	18	56	59	56	-19
5	19	23	25	-24	7
5	20	24	25	19	16
5	21	33	35	-35	1
5	22	27	29	-24	-15
5	23	11	10	1	10
5	24	9	12	-4	11
5	25	23	20	-20	2
5	26	9	10	6	-8
5	27	25	23	-22	8

K	L	FOBS	FCAL	ACAL	BCAL
H=2					
0	0	240	253	253	0
0	2	4	5	-5	-1
0	4	5	5	4	3
0	6	11	12	4	-11
0	8	19	15	7	13
0	10	33	42	41	-10
0	12	31	28	19	21
0	14	148	163	-163	-6
0	16	25	27	-1	26
0	18	8	17	-12	-11*
0	20	21	28	-11	25
0	22	19	12	10	-7
0	24	35	37	-37	7
0	26	33	25	21	-13
0	28	70	64	64	1
0	30	34	25	14	-21
0	32	20	17	16	1
0	34	32	28	26	-11
2	0	41	34	34	0
2	1	63	64	64	-0
2	2	26	22	-22	-1
2	3	23	19	19	0
2	4	39	33	-32	8
2	5	25	25	24	-4
2	6	52	44	-43	-11
2	7	67	63	63	-1
2	8	71	69	67	16
2	9	14	7	0	-7
2	10	31	24	18	-17
2	11	31	33	33	-2
2	12	23	25	21	13
2	13	61	61	61	-4
2	14	21	22	-12	-19
2	15	22	29	-29	1
2	16	25	20	14	14
2	17	8	12	12	0*
2	18	72	78	74	-25
2	19	30	34	-32	8
2	20	35	34	26	21
2	21	46	46	-46	2
2	22	36	39	-33	-20
2	23	15	14	3	13
2	24	17	17	-5	16
2	25	32	28	-28	4
2	26	14	13	8	-10
2	27	32	29	-27	10
2	28	24	20	9	17
2	29	7	5	5	1*
2	30	15	16	14	-7
2	31	32	26	-26	1
2	32	74	60	-57	19
2	33	25	20	19	-6
4	0	36	24	24	0
4	1	55	45	-45	0
4	2	18	15	-15	-1
4	3	20	12	-12	0
4	4	27	25	-24	6
4	5	20	20	-20	1
4	6	44	33	-32	-9
4	7	55	44	-44	0
4	8	54	50	49	10
4	9	11	7	-2	6
4	10	22	18	14	-12
4	11	23	24	-24	2

K	L	FUBS	FCAL	ACAL	HCAL
4	12	21	18	15	9
4	13	48	44	-44	2
4	14	17	17	-8	-14
4	15	14	21	21	-0
4	16	14	15	10	11
4	17	8	10	-10	-0*
4	18	52	59	56	-19
4	19	25	27	26	-6
4	20	27	26	19	16
4	21	34	35	35	-0
4	22	27	28	-24	-15
4	23	9	11	-2	-11
4	24	8	13	-3	12
4	25	25	21	21	-3
4	26	10	10	6	-7
4	27	24	22	21	-7
6	0	83	103	103	0
6	2	5	3	-3	-0*
6	4	5	5	4	2*
6	6	4	5	1	-5*
6	8	9	5	4	3
6	10	11	15	15	-2
H=3					
1	0	26	24	24	0
1	1	35	45	-45	0
1	2	15	15	-15	-1
1	3	16	12	-12	-0
1	4	19	25	-24	6
1	5	14	19	-19	2
1	6	30	33	-32	-8
1	7	31	45	-45	0
1	8	35	50	49	11
1	9	8	6	-2	6
1	10	17	18	14	-12
1	11	22	24	-24	2
1	12	15	18	15	10
1	13	37	44	-44	3
1	14	16	17	-8	-14
1	15	19	22	22	-0
1	16	19	15	11	11
1	17	9	10	-10	0*
1	18	47	59	56	-19
1	19	26	26	26	-6
1	20	27	25	19	16
1	21	34	35	35	-0
1	22	28	28	-24	-15
1	23	11	11	-2	-11
1	24	11	12	-3	12
1	25	19	21	20	-3
1	26	11	10	6	-7
3	0	103	133	133	0
3	2	9	3	-3	-0*
3	4	8	6	5	3*
3	6	8	7	2	-6*
3	8	11	7	4	5
3	10	16	20	20	-4
3	12	16	16	10	12
3	14	63	90	-90	-3
3	16	8	14	-0	14
3	18	8	10	-8	-6
3	20	7	15	-6	14
3	22	6	6	5	-2

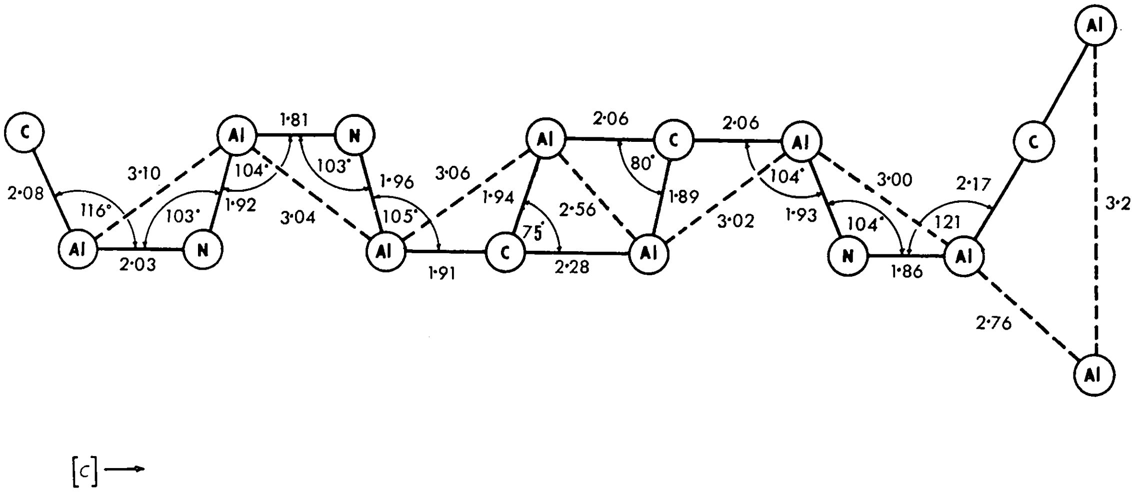


Fig. 5. Bond lengths, angles and intermetallic distances in $Al_7C_3N_3$.

and the observed and calculated structure amplitudes in Table 4. The interatomic distances and angles are given in Table 3.

Discussion of the structure

The structure analysis of the $Al_7C_3N_3$ compound confirmed the systematic description of the structural relationships deduced from the crystal data and from von Stackelberg's original analysis of the Al_4C_3 and Al_5C_3N. The bond lengths and angles associated with the three structural components, $-[Al_2C_2]_n-$, $-[AlN]_n-$, $-[Al_2C]_n-$ are shown in Figs. 1 and 5. It is convenient to discuss the geometry of these blocks separately.

(i) As pointed out in a previous paper (Amma & Jeffrey, 1961) the lozenge configuration obtained in the $[Al_2C_2]$ segment can be derived from the interpenetrating h.c.p. lattices of a wurtzite type structure by inverting the sequence of columns of atoms in the *c* axis direction. Compared with the wurtzite structure of AlN, for example, if the carbon atoms occupy approximately the same lattice sites as the nitrogens, the aluminum atoms occupy pairs of adjacent tetrahedral sites one set of which is inverted with respect to that in the wurtzite type structure. This gives rise to the five-coordination of the nonmetallic site, an inter-bond angle of about 75° and a short metal atom distance previously remarked upon.

In this aluminum carbonitride, the Al–Al distance across the short diagonal of the lozenge configuration is 2·56 Å, this is 0·34 Å shorter than the metallic diameter and almost exactly twice the tetrahedral covalent radius. The two carbon atoms are significantly different in environment. One of them has four C–Al bonds at 1·94 Å with approximately tetrahedral valence angles of 105° and the fifth 'bond' much longer at 2·28 Å. The other carbon approaches rather more closely to an ideal trigonal bipyramid configuration with the three 'equatorial' bonds of 1·89 Å and two 'polar' bonds of 2·06 Å; *cf.* the trigonal bipyramidal configuration in the hexagonal β-Be_3N_2, with Be–N 1·70 Å (polar) 1·64 Å (equatorial); (Eckerlin & Rabenau, 1960). The acute valence angles at the carbon atoms are also different, being respectively 75°, and 80°.

(ii) In the AlN blocks of the structure, the Al–N distances vary from 1·86 Å to 2·03 Å, compared with 1·89 and 1·92 Å in AlN itself. The departures from tetrahedral angles are about 5° and such as to bring the nitrogen atoms closer to the layers of metal atoms. This distortion is considerably larger, although in the same direction as that which corresponds to the departure from the ideal *c*/*a* ratio in AlN (Jeffrey, Parry & Mozzi, 1956).

(iii) The Al_2C layer resembles an interstitial structure with the carbon atoms in the octahedral voids between two hexagonal packed layers of aluminum atoms. The Al–Al distance between layers is 2·76 Å, as compared with 2·86 Å for the sum of the metallic radii. The Al–C distance are 2·08 and 2·17 Å.

The structure is thus a composite with both the features of a homopolar solid and of an alloy. The Al–N bonding is very similar to that in AlN, while the Al–C interatomic distances range from 1·91 Å to 2·28 Å depending upon the coordination of the surrounding metal atoms. This is also indicated by the wide range of Al–Al first neighbour distances. In the basal layers, the metal atoms lie in a hexagonal array at a distance of 3·23 Å. Between the layers which are separated by carbon or nitrogen atoms in the tetrahedral interstices the Al–Al distances range from 3·00 to 3·10 Å. Between layers separated by carbon atoms in octahedral sites the Al–Al distance is 2·76 Å. Finally, there are the two metallic layers with no intervening non-metallic atoms, where the inter-metallic distance is 2·56 Å. These crystal structural studies are being continued on the even members of the series, *i.e.* Al_6C_3N and $Al_8C_3N_4$, where the arrangement of the blocks is more symmetrical.

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The Crystal and Molecular Structure of Sodium α-Ketobutyrate*

BY S. S. TAVALE, L. M. PANT AND A. B. BISWAS

National Chemical Laboratory, Poona, India

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Sodium α-ketobutyrate, $CH_3CH_2COCOONa$, crystallized from aqueous solution, is orthorhombic, space group *Pbcn*, with eight molecules per unit cell of dimensions

$$a = 29{\cdot}28,\ b = 6{\cdot}045,\ c = 5{\cdot}90\ \text{Å}\ .$$

The detailed structure has been determined by two-dimensional Fourier, difference Fourier and least-squares methods.

The observed bond lengths and angles show that sodium α-ketobutyrate is enolized to a great extent in the crystalline state.

The crystal structures of sodium α-ketobutyrate and sodium pyruvate are similar. In both, the Na–O bonds tie the molecules into infinite double layers; any double layer is linked with the neighbouring double layers by van der Waals bonds.

Introduction

In a recent paper, the structure analysis of sodium pyruvate was reported (Tavale, Pant & Biswas, 1961). It was felt that a comparison of its crystal and molecular structure with those of its higher homologues should be of interest. Consequently, we started X-ray studies of the crystal structures of sodium α-ketobutyrate, $CH_3CH_2COCOONa$ and sodium α-ketocaprylate, $CH_3(CH_2)_5COCOONa$. The investigation of the structure of sodium α-ketocaprylate is still in progress. In the present paper, we report the structure analysis of sodium α-ketobutyrate.

Experimental details

Crystals were obtained from aqueous solution. They are orthorhombic and grow as very thin plates parallel to the (100) face. There is strong cleavage parallel to the plates. The unit cell has

$$a = 29{\cdot}28,\ b = 6{\cdot}045,\ c = 5{\cdot}90\ \text{Å}\ ,$$

these values being obtained from zero-layer Weissenberg photographs.

The observed density at 24 °C, measured by the flotation method, is 1·562 g.cm^{-3} and the calculated density for eight molecules of $CH_3CH_2COCOONa$ per unit cell is 1·578 g.cm^{-3}.

The systematic absences are: $0kl$ for k odd, $h0l$ for l odd and $hk0$ for $h+k$ odd, so that the space group is uniquely determined as *Pbcn*. The linear absorption coefficient μ for Cu $K\alpha$ radiation is 19·6 cm^{-1}. Reflexions of the type $hk0$ and $h0l$ were obtained from zero-layer Weissenberg photographs, using Cu $K\alpha$ radiation and the multiple-film technique. Of the 127 possible $hk0$ reflexions and 112 possible $h0l$ reflexions, 92 and 76 respectively were observed. The specimens used were flakes of roughly (0·5 × 0·7) mm^2 area,

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