

## References

- BENNETT, M. J., COTTON, F. A., EISSL, R. & ELDER, R. C. (1967). *Nature, Lond.* **213**, 174.
- BUCKINGHAM, D. A., GORGES, R. C. & HENRY, J. T. (1967). *Aust. J. Chem.* **17**, 281.
- BULLEN, G. J., MASON, R. & PAULING, P. (1965). *Inorg. Chem.* **4**, 456.
- COTTON, F. A. & EISSL, R. (1968). *J. Amer. Chem. Soc.* **90**, 38.
- COTTON, F. A. & ELDER, R. C. (1965). *Inorg. Chem.* **4**, 1145.
- COTTON, F. A. & ELDER, R. C. (1966). *Inorg. Chem.* **5**, 423.
- COTTON, F. A. & FACKLER, J. P. JR. (1961). *J. Amer. Chem. Soc.* **83**, 2818.
- COTTON, F. A. & SODERBERG, R. H. (1964). *Inorg. Chem.* **3**, 1.
- COTTON, F. A. & WISE, J. J. (1966). *Inorg. Chem.* **5**, 1200.
- COTTON, F. A. & WOOD, J. S. (1964). *Inorg. Chem.* **3**, 245.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
- CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 154.
- CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*. Edited by J.S.ROLLETT. New York: Pergamon Press.
- DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 204.
- DWYER, F. P. & SARGESON, A. M. (1956). *J. Proc. Roy. Soc. N. S. Wales*, **90**, 29.
- FACKLER, J. P., JR & COTTON, F. A. (1961). *J. Amer. Chem. Soc.* **83**, 3775.
- GILLESPIE, R. J. (1963). *J. Chem. Soc.* pp. 4672, 4679.
- GRADDON, D. P. (1962). *Nature, Lond.* **195**, 891.
- GRADDON, D. P. & MOCKLER, G. M. (1964). *Aust. J. Chem.* **17**, 1119.
- GRADDON, D. P. & WEEDON, D. G. (1963). *Aust. J. Chem.* **16**, 980.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- IBERS, J. A. (1962). In *International Tables for X-ray Crystallography*, Vol. III. Birmingham: Kynoch Press.
- LINGAFELTER, E. C. & BRAUN, R. L. (1966). *J. Amer. Chem. Soc.* **88**, 2951.
- LIPPERT, E. L. & TRUTER, M. R. (1960). *J. Chem. Soc.* p. 4996.
- MONTGOMERY, H. & LINGAFELTER, E. C. (1963). *Acta Cryst.* **16**, 748.
- ORIOLE, P. L., DI VAIRA, M. & SACCONI, L. (1966). *Inorg. Chem.* **5**, 400.
- PREWITT, C. T. (1962). *A Full-Matrix Crystallographic Least Squares Program for the IBM 709/7090*. SFLSQ3.
- PREWITT, C. T. (1966). *A Full-Matrix Crystallographic Least Squares Program for the IBM 360*. SFLS5. The function minimized during refinement was  $\sum \omega ||F_c| - |F_o||^2$ .
- RUDOLPH, G. & HENRY, M. C. (1964). *Inorg. Chem.* **3**, 1317.
- RUDOLPH, G. & HENRY, M. C. (1965). *Inorg. Chem.* **4**, 1076.
- SHOEMAKER, D. P. (1962). *MIXG-2, M.I.T. X-Ray Goniometer Package*.
- SHOEMAKER, D. P. & SRIVASTAVA, R. C. (1963). *VIBELL; Anisotropic Temperature Factor Interpreting Program*.
- SLY, W. G., SHOEMAKER, D. P. & VAN DEN HENDE, J. H. (1962). *A Two- and Three-Dimensional Fourier Program for the IBM 709/7090*, ERFR-2.

*Acta Cryst.* (1968). **B24**, 913

## The Structure of $\text{Li}_9\text{Al}_4$ \*

BY D. A. HANSEN† AND J. F. SMITH

*Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames, Iowa 50010, U.S.A.*

(Received 16 May 1967)

$\text{Li}_9\text{Al}_4$  has been found to crystallize in the monoclinic system, and a crystal structure with  $B2/m$  space group symmetry is compatible with observed intensities of X-ray reflections. Precision lattice parameters have been measured as  $a_0 = 19.1551 \pm 0.0005$ ,  $b_0 = 5.4288 \pm 0.0001$ ,  $c_0 = 4.4988 \pm 0.0001$  Å, and  $\gamma_0 = 107.671 \pm 0.002^\circ$  at  $23 \pm 2^\circ\text{C}$ . The unit cell contains two formulae of  $\text{Li}_9\text{Al}_4$ . A discrepancy index of 0.099 was obtained from three-dimensional intensity data with a total of 547 independent reflections. A difference density map at this discrepancy level contained no significant extrema or gradients. Thus, in the specific crystal from which the intensity data were taken there is no indication of a lithium deficiency which would alter the stoichiometry to 'Li<sub>2</sub>Al' as reported in the currently accepted temperature-composition diagram.

### Introduction

The structure of the phase  $\text{Na}_2\text{Tl}$  has recently been determined (Hansen & Smith, 1967) and found to be a new structure type. In a search for isoelectronic

phases which might be isostructural with  $\text{Na}_2\text{Tl}$ , available data (Hansen & Anderko, 1958; Elliott, 1965) on the binary phase relationships between alkali metals and Group III metals were examined. In the lithium-aluminum system one such phase 'Li<sub>2</sub>Al' was reported to form by peritectic reaction between LiAl and liquid (69 at.% Li) at  $522^\circ\text{C}$ ; the published phase diagram is reproduced in Fig. 1. The structure of 'Li<sub>2</sub>Al' has now been investigated and the results are herein reported.

\* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2089.

† Present address: Department of Mechanical Engineering University of North Dakota, Grand Forks, North Dakota 58201, U.S.A.

### Procedure and results

An alloy containing 72 at. % lithium was prepared from powdered aluminum, U.S.P. grade, supplied by Matheson Coleman and Bell Co. and from lithium supplied by the Lithium Corporation of America. The supplier's analysis of the lithium indicated a nominal purity of >99.8% with sodium as the major impurity at a concentration of <0.05%. All handling operations were conducted under an inert atmosphere. The alloy was sealed in a stainless steel crucible, then homogenized at 500°C for four days, and subsequently annealed at 200°C for two days. After removal from the crucible, the alloy was fragmented by a single blow in a diamond mortar. Suitable single-crystalline fragments were transferred to Lindemann glass capillaries and the capillaries were sealed by fusing the capillary ends with a hot wire. Crystalline fragments which were tested by deliberate exposure to air were observed to decompose rapidly.

Three different crystals were examined by X-ray diffraction and were found to have the same symmetry with only one symmetry axis being present. Weissenberg patterns taken about this unique axis showed diffraction symmetry, characteristic extinctions, and lattice parameters indicative of a *B*-centered monoclinic cell with  $2/m$  point symmetry. Hence, the probable space group was indicated to be  $B2/m$ ,  $Bm$ , or  $B2$ . Precision lattice constants were determined with  $\text{Cu } K\alpha$

radiation and a General Electric Spectrogoniometer equipped with a Single Crystal Orienter and a scintillation counter. The wavelength of the  $K\alpha_1$  line was taken to be 1.54051 Å. Twenty-two data points from the angular range  $140^\circ < 2\theta < 160^\circ$  were taken at ambient temperature ( $23^\circ \pm 2^\circ\text{C}$ ) and were used with a linear least-squares fit (Williams, 1964) to the Nelson & Riley (1945) function to obtain:

$$a_0 = 19.1551 \pm 0.0005 \text{ \AA}$$

$$b_0 = 5.4288 \pm 0.0001$$

$$c_0 = 4.4988 \pm 0.0001$$

and

$$\gamma_0 = 107.671 \pm 0.002^\circ.$$

The Single Crystal Orienter was used to accumulate three-dimensional intensity data from a crystal which approximated a rectangular prism with dimensions,  $0.24 \times 0.081 \times 0.14$  mm.  $\text{Cu } K\alpha$  radiation was again employed with the diffracted beam being passed through a Ni filter. Intensities were measured by the  $2\theta$  scan technique with 100 second scans at a scan rate of  $2^\circ (2\theta)$  per minute. It was found that to a good approximation background counts,  $C_B$ , could be represented as a linear function of the total counts,  $C_T$ , in a scan:  $C_B = (0.0301)C_T + 12$ . Since the absorption coefficient of the phase for  $\text{Cu } K\alpha$  radiation is small ( $\mu = 40 \text{ cm}^{-1}$ ) and the crystal was small, absorption corrections were neglected and the integrated intensities were taken to be  $I = C_T - C_B$ . The integrated intensities were corrected for Lorentz and polarization

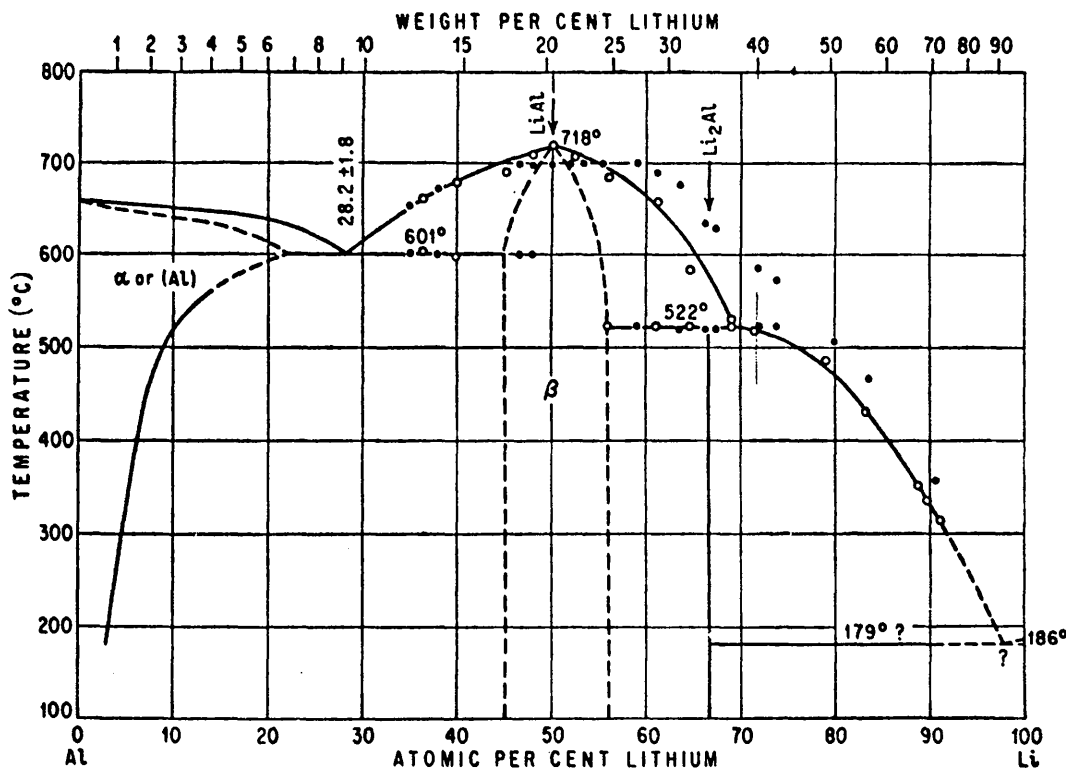


Fig. 1. Lithium-aluminum phase diagram (after Hansen & Anderko, 1958).

effects. A total of 495 independent reflections were measured in the angular range  $0^\circ < 2\theta < 160^\circ$ , and an additional 52 reflections were too weak to be observed with significant intensity.

A three-dimensional Patterson map  $P(x, y, z)$  was calculated from the intensity data. From this map it was inferred that there were no variable  $z$  parameters in the structure; this is compatible with atomic size considerations within the constraints of the magnitude of  $c_0$  and symmetry limitations of the probable space groups. An initial estimation of the unit cell content as 8 Al atoms and 16 Li atoms was made by comparing the volume per atom in the elemental structures with the available volume in the monoclinic unit cell, and further interpretation of the Patterson map was approached on this basis. The  $x$  and  $y$  coordinates of 8 Al atoms were readily identified from the  $P(x, y, 0)$  section and were found to be consistent with the centrosymmetric requirement of space group  $B2/m$ ; these Al positions correspond to occupancy of two fourfold sets. Since the Al atoms dominate the X-ray scattering from

the unit cell, the method of least squares could be used to obtain an initial refinement of the Al positional parameters. The least-squares program of Busing, Martin & Levy (1962) was employed. The partially refined positional parameters were then used to determine the phases of the structure factors of the observed reflections, and a three-dimensional electron density map was synthesized. The Li positions were quite evident in this map and were consistent with the occupancy of one twofold set and four fourfold sets in  $B2/m$ . The unit cell is thus indicated to contain two formula weights of  $\text{Li}_9\text{Al}_4$ , and the stoichiometry is somewhat more lithium-rich than the 'Li<sub>2</sub>Al' reported in the phase diagram.

A least-squares refinement of the values of the Al and Li coordinates with isotropic temperature factors resulted in a residual of 0.131 when the reflections were weighted with the finite difference formula of Williams & Rundle (1964). The form factors for Li and Al were taken from the work of Cromer & Waber (1965). Unobserved reflections were arbitrarily given a weight of  $10^{-4}$  in order to insure that their contribution to the refinement would be negligible. A difference density map was then synthesized, and this map indicated anisotropic thermal behavior in the Al positions. Further least-squares refinement of the positional parameters, isotropic Li temperature factors, and anisotropic Al temperature factors yielded a residual of 0.099 for all reflections and the same value for observed reflections only. The refined parameters are shown in Table 1; in the Table the anisotropic temperature coefficients,  $\beta_{ij}$ , combine to form the exponential temperature term in the following way:

$$- [h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12}].$$

A difference density map based on these values contained no significant extrema or gradients. Because of the large difference in scattering power between aluminum and lithium, the featureless nature of the difference density map indicates an ideal stoichiometry of  $\text{Li}_9\text{Al}_4$  and not a defect or substitutional solution with a stoichiometry of 'Li<sub>2</sub>Al'. Absence of a defect

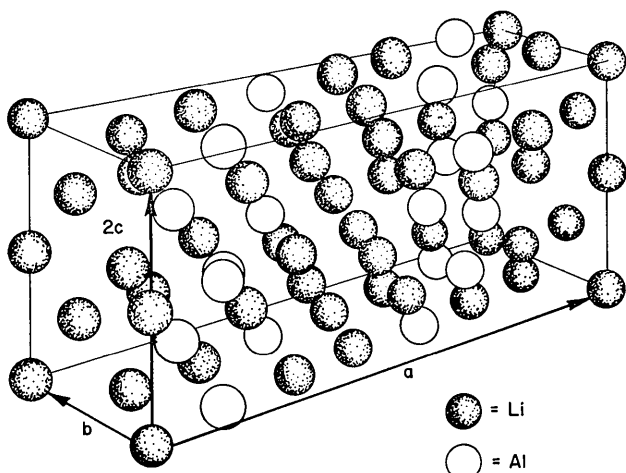


Fig. 2. Atomic array in  $\text{Li}_9\text{Al}_4$  shown by the content of two unit cells and illustrating the zigzag aluminum chains which parallel the  $c$  axis.

Table 1. Positional and thermal parameters in  $\text{Li}_9\text{Al}_4$ \*

	Set	$x$	$y$	$z$	Thermal parameters
Al(1)	4( <i>i</i> )	$0.1505 \pm 0.0001$	$0.0870 \pm 0.0004$	0	$\beta_{11} = 0.00171 \pm 0.00007 \text{ \AA}^2$ $\beta_{22} = 0.0149 \pm 0.0009$ $\beta_{33} = 0.011 \pm 0.001$ $\beta_{12} = 0.0026 \pm 0.0002$
Al(2)	4( <i>i</i> )	$0.3853 \pm 0.0001$	$0.7064 \pm 0.0004$	0	$\beta_{11} = 0.00187 \pm 0.00008$ $\beta_{22} = 0.0155 \pm 0.0009$ $\beta_{33} = 0.013 \pm 0.001$ $\beta_{12} = 0.0028 \pm 0.0002$
Li(1)	2( <i>a</i> )	0	0	0	$B = 3.0 \pm 0.8$
Li(2)	4( <i>i</i> )	$0.0863 \pm 0.0008$	$0.531 \pm 0.003$	0	$B = 2.6 \pm 0.5$
Li(3)	4( <i>i</i> )	$0.2326 \pm 0.0007$	$0.622 \pm 0.003$	0	$B = 2.6 \pm 0.5$
Li(4)	4( <i>i</i> )	$0.3080 \pm 0.0007$	$0.144 \pm 0.002$	0	$B = 2.2 \pm 0.5$
Li(5)	4( <i>i</i> )	$0.4564 \pm 0.0008$	$0.239 \pm 0.003$	0	$B = 2.8 \pm 0.5$

\* Symmetry requires  $\beta_{13} = \beta_{23} = 0$ .



structure or disorder is further substantiated by the comparatively normal character of the temperature factors. A comparison of observed and calculated structure factors is shown in Table 2 wherein the unobserved structure factors are identified by asterisks. Coordination and bond distances are shown in Table 3.

### Discussion

The atomic arrangement in the structure is illustrated in Fig. 2 where the contents of two unit cells are shown.

The Al atoms occur in the structure in an arrangement which forms planar zigzag chains with the zigzag pattern occurring in (610) planes and with the mean direction of all chains being parallel to the  $c$  axis. The Al-Al bond distances in the chains are 6% shorter than those in elemental aluminum. In spite of the aluminum-aluminum interaction indicated by the chain configuration, the compound does not conform to the general  $(8-N)$  valence rule (Kjekshus, 1964; Pearson, 1964) and can on this basis be presumed to be a normal metallic conductor.

Table 3. *Interatomic distances in  $\text{Li}_9\text{Al}_4^*$*

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Al(1)		Li(1)		Li(3)		Li(5)	
2Al(2)	2.693 Å	2Al(1)	2.776 Å	1Al(1)	2.851 Å	2Al(1)	3.191 Å
1Li(1)	2.776	4Al(2)	3.210	1Al(1)	3.357	1Al(2)	3.224
1Li(2)	3.021	2Li(2)	2.856	2Al(1)	3.230	1Al(2)	2.798
1Li(2)	2.892	2Li(2)	3.430	1Al(2)	2.820	1Al(2)	2.957
1Li(3)	2.851	4Li(5)	2.846	2Al(2)	3.299	2Li(1)	2.85
1Li(3)	3.357			1Li(2)	2.69	2Li(2)	2.81
2Li(3)	3.230			2Li(3)	2.79	2Li(2)	3.37
1Li(4)	2.938			1Li(4)	3.30	1Li(4)	2.73
2Li(4)	2.806			1Li(4)	2.77	1Li(5)	2.82
2Li(4)	3.191			2Li(4)	2.81	1Li(5)	3.49
Al(2)		Li(2)		Li(4)			
2Al(1)	2.693	1Al(1)	3.021	1Al(1)	2.938		
2Li(1)	3.210	1Al(1)	2.892	2Al(1)	2.806		
2Li(2)	2.729	2Al(2)	2.729	1Al(2)	2.960		
1Li(3)	2.820	1Li(1)	2.86	1Al(2)	3.158		
2Li(3)	3.299	1Li(1)	3.43	2Li(2)	3.18		
1Li(4)	2.960	1Li(2)	3.22	1Li(3)	3.33		
1Li(4)	3.158	1Li(3)	2.69	1Li(3)	2.77		
1Li(5)	3.244	2Li(4)	3.18	2Li(3)	2.81		
1Li(5)	2.798	2Li(5)	2.81	2Li(4)	3.21		
1Li(5)	2.957	2Li(5)	3.37	1Li(5)	2.73		

\* Distance                      Standard deviation

Al-Al	$\pm 0.002$ Å
Al-Li	$\pm 0.009$
Li-Li	$\pm 0.01$

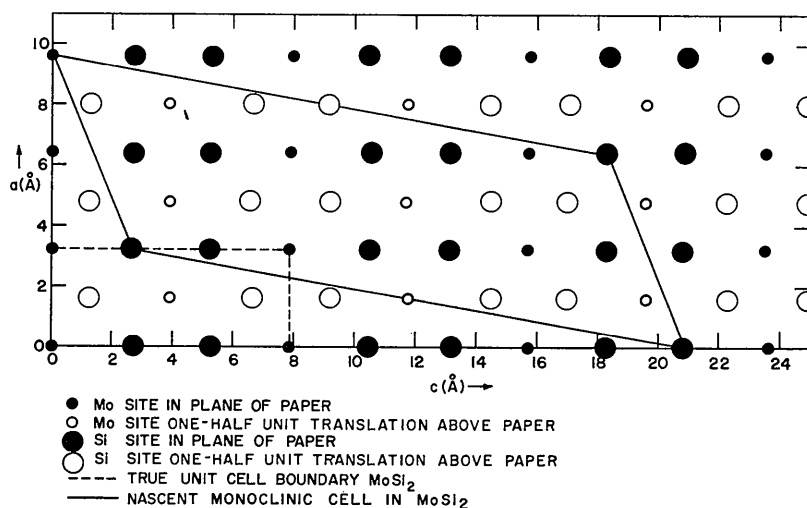


Fig. 4. Projection of the  $\text{MoSi}_2$  structure normal to the  $b$  axis and showing the conventional tetragonal cell and the nascent monoclinic cell.

From Table 3 it can be noted that each atom in the structure has a coordination atmosphere of 14 near neighbors with the coordinated atoms forming nearly regular rhombic dodecahedra with one of the major axes pointing in the  $[\bar{1}60]$  direction. The volume contraction associated with phase formation from the solid elemental components has been computed as 3%. The structure shows pronounced layering of the atoms in the (001), (610), ( $\bar{8}30$ ), ( $7\bar{1}2$ ), ( $\bar{1}21$ ), and (614) planes. This layering may well be associated with low activation energies for dislocation glide since it was observed qualitatively that  $\text{Li}_9\text{Al}_4$ , in contrast to  $\text{Na}_2\text{Tl}$ , could suffer appreciable plastic strain without fracture.

There is a formal relationship between the structure of  $\text{Li}_9\text{Al}_4$  and the tetragonal  $\text{MoSi}_2$ -type structure in the sense that, if one considers only atomic loci and not species, atomic arrays in the two structures are closely comparable. Both structures are formed by alternating atomic layers normal to the  $c$  axis in the case of  $\text{Li}_9\text{Al}_4$  and normal to the  $a$  or  $b$  axes in the case of  $\text{MoSi}_2$ . The relationship can be observed by

comparing Figs. 3 and 4. This relationship between the two structures may simply reflect the fact that geometric constraints govern the efficient filling of space, and both  $\text{Li}_9\text{Al}_4$  and  $\text{MoSi}_2$  are efficiently packed structures.

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Rept. No. ORNL-TM-305.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.  
 ELLIOTT, R. P. (1965). *Constitution of Binary Alloys, First Supplement*. New York: McGraw-Hill.  
 HANSEN, D. A. & SMITH, J. F. (1967). *Acta Cryst.* **22**, 836.  
 HANSEN, M. & ANDERKO, K. (1958). *Constitution of Binary Alloys*. 2nd ed. New York: McGraw-Hill.  
 KJEKSHUS, A. (1964). *Acta Chem. Scand.* **18**, 2379.  
 NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. Lond.* **57**, 160.  
 PEARSON, W. B. (1964). *Acta Cryst.* **17**, 1.  
 WILLIAMS, D. E. (1964). USAEC Rept. No. IS-1052.  
 WILLIAMS, D. E. & RUNDLE, R. E. (1964). *J. Amer. Chem. Soc.* **86**, 1660.

*Acta Cryst.* (1968). B24, 918

## The Crystal Structure of Tetracyanocyclobutane

BY B. GREENBERG\* AND B. POST

*Polytechnic Institute of Brooklyn, Brooklyn, N.Y. 11201, U.S.A.*

(Received 4 April 1967)

*cis,trans,cis*-1,2,3,4-Tetracyanocyclobutane,  $\text{C}_8\text{H}_4\text{N}_4$ , crystallizes in the monoclinic system; the space group is  $P2_1/n$ , with  $a=8.610$ ,  $b=6.193$ ,  $c=6.983$  Å (all  $\pm 0.005$  Å),  $\beta=98.4 \pm 0.1^\circ$ . There are two molecules per unit cell. The crystal structure has been determined from counter data with use of the symbolic addition phase determining procedure. The cyclobutane ring is planar and rectangular with C-C edges of  $1.561 \pm 0.003$  and  $1.547 \pm 0.003$  Å. Bond lengths in the C-C $\equiv$ N 'legs', corrected for the effects of thermal motion, are C-C,  $1.452 \pm 0.005$  Å and C $\equiv$ N,  $1.158 \pm 0.008$  Å.

### Introduction

The configuration of the highly strained cyclobutane ring in organic compounds has long been of considerable interest, but until recently only a few serious efforts had been made to investigate it by the methods of X-ray diffraction. These are summarized in Table 1. It appears that the cyclobutane ring is puckered in some compounds and planar in others. Additional studies are clearly needed to establish the conditions favoring one configuration over the other, as well as to determine bond lengths with maximum precision.

Tetracyanocyclobutane (TCCB) was synthesized by Griffin, Basinsky & Peterson (1962) by the solid state

photodimerization of fumaronitrile. Chemical and physical tests indicated that the product of the reaction was probably the *cis,trans,cis* isomer (Fig. 1).

Both TCCB and fumaronitrile crystallize in the monoclinic system, space group  $P2_1/n$ , with two mol-

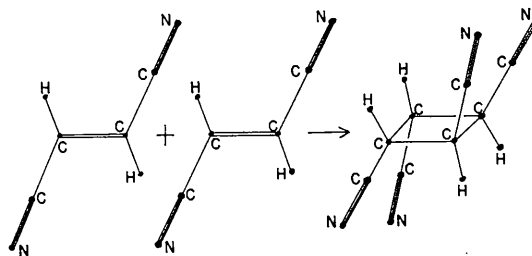


Fig. 1. Dimerization of fumaronitrile to form tetracyanocyclobutane.

\* Taken from a thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science.