

## The Crystal Structure of Dicyanoacetylene

BY R. B. HANNAN\* AND R. L. COLLIN†

University of Pittsburgh and Department of Research in Chemical Physics, Mellon Institute, Pittsburgh, Pa., U.S.A.

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Near 5° C., dicyanoacetylene forms monoclinic crystals belonging to the space group  $C_{2h}^5-P2_1a$ . Unit cell dimensions are  $a_0 = 8.93$ ,  $b_0 = 6.04$ ,  $c_0 = 3.86$  Å,  $\beta = 99^\circ 20'$ . The two molecules per unit cell are linear and have a center of symmetry. Bond lengths within the molecule are: C≡N 1.14, C-C 1.37, C=C 1.19 Å.

### Introduction

The synthesis of dicyanoacetylene,  $N\equiv C-C\equiv C-C\equiv N$ , was first reported by Moureu & Bongrand (1909). Following their discovery, the authors published several papers on the physical and chemical properties of the substance, and summarized their findings in a review (Moureu & Bongrand, 1920). No later references have been found which are pertinent to the structure of this unusual molecule.

Dicyanoacetylene is of particular interest because of its linear chain of six atoms and because of its system of three conjugated triple bonds. Fortunately, the physical properties of the compound are such that its molecular structure can be investigated by means of both X-ray and spectroscopic methods. An analysis of the vibrational spectra has appeared elsewhere (Miller & Hannan, 1953). This paper deals with the results obtained from X-ray diffraction studies.

### Experimental

The dicyanoacetylene used in this work was prepared by a method similar to that of Moureu & Bongrand (1920). The final product was a colorless liquid which solidified at 20° C. and boiled at 76° C. A mass spectrographic analysis indicated a purity of about 98.2% by weight.

A liquid sample of dicyanoacetylene was sealed inside a thin-walled glass tube and maintained at a temperature of about 5° C. by a stream of cold dry nitrogen prepared by passage through a copper coil immersed in ice water. Single crystals were then grown by the technique of Abrahams *et al.* (1950) and were used for the preparation of single-crystal photographs.

Precession photographs of the type described by Buerger (1944) were taken with Mo  $K\alpha$  radiation. The systematic extinctions and symmetry exhibited by the [100], [001] and [101] photographs indicated that the crystal belonged to the monoclinic space group

$C_{2h}^5-P2_1a$ .† From measurements of the photographs, the observed unit-cell dimensions were calculated as:

$$a_0 = 8.93, b_0 = 6.04, c_0 = 3.86 \text{ Å}; \beta = 99^\circ 20'.$$

The space group requires that there be either two or four molecules per unit cell, which two values lead to calculated densities of 1.2 and 2.4 g.cm.<sup>-3</sup>, respectively, for the solid at about 5° C. Moureu & Bongrand observed the density of the liquid to be 0.907 g.cm.<sup>-3</sup> at 25° C. Since there was no unusually large change in volume as the sample solidified, it was concluded that the solid density of 1.2 g.cm.<sup>-3</sup> is correct and that there are two molecules per unit cell.

The presence of only two molecules in the unit cell of space group  $C_{2h}^5-P2_1a$  requires that these molecules have centers of symmetry. It is further required that these centers be located at twofold special positions within the unit cell. The set of special positions chosen was (0, 0, 0), ( $\frac{1}{2}$ ,  $\frac{1}{2}$ , 0), as indicated in Fig. 1.

The intensities of the diffraction spots were estimated by visual comparison with a calibrated scale which

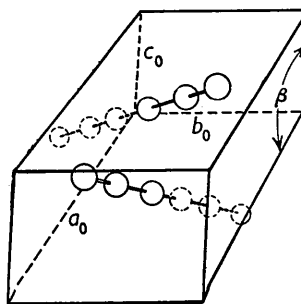


Fig. 1. Unit cell of dicyanoacetylene.

consisted of a series of spots on a strip of photographic film. These spots represented the blackening caused by a series of diffracted X-ray beams of known relative

† One of the precession photographs was repeated at a temperature near that of liquid nitrogen. The similarity between this photograph and the corresponding one taken at 5° C. appeared to be good evidence that there was no phase transition occurring between these two temperatures.

\* Present address: Standard Oil Company (Indiana), Whiting, Indiana, U.S.A.

† Present address: Cancer Research Institute, Boston, Massachusetts, U.S.A.

Table 1. *Calculated and observed structure factors*

<i>hk0</i>	$F_c$	$F_o$	<i>hk0</i>	$F_c$	$F_o$	<i>0kl</i>	$F_c$	$F_o$
020	0.86	0.62	460	0.05	< 0.17	001	3.54	3.56
040	-0.08	< 0.18	510	-0.18	0.21	002	-1.93	1.30
060	-0.63	0.43	520	-1.54	1.48	003	0.23	< 0.24
110	0.98	0.83	530	0.17	< 0.19	004	0.13	< 0.24
120	2.62	1.92	540	-0.61	0.64	011	5.14	5.01
130	0.36	0.35	550	0.14	< 0.19	012	0.93	0.96
140	0.47	0.37	560	-0.04	< 0.15	013	-0.17	< 0.24
150	-0.38	0.28	600	0.84	0.68	014	-0.01	< 0.24
160	0.13	< 0.19	610	0.15	< 0.18	020	0.85	0.81
170	0.01	< 0.14	620	0.99	1.00	021	-0.20	< 0.18
200	1.83	1.76	630	-0.87	0.98	022	0.41	0.98
210	-5.68	5.86	640	-0.34	0.32	023	0.70	0.80
220	-0.40	< 0.16	650	-0.001	< 0.18	024	0.06	< 0.22
230	0.86	0.61	710	-0.11	< 0.19	031	1.00	0.91
240	0.03	< 0.19	720	-0.07	0.28	032	-0.45	0.50
250	-0.65	0.64	730	-0.12	< 0.20	033	0.12	0.66
260	-0.05	< 0.18	740	0.12	< 0.19	034	0.30	0.47
270	0.09	< 0.14	750	0.02	< 0.15	040	-0.08	< 0.23
310	4.83	4.96	800	-0.09	< 0.20	041	0.02	< 0.24
320	-0.61	0.61	810	-0.03	< 0.20	042	-0.25	0.48
330	0.005	< 0.18	820	-0.29	0.31	043	-0.26	0.16
340	-0.65	0.46	830	-0.53	0.66	051	0.65	0.81
350	-0.47	0.42	840	0.13	< 0.17	052	0.14	< 0.24
360	0.10	< 0.18	910	0.12	< 0.19	053	0.04	< 0.19
400	-1.44	1.43	920	-0.19	0.32	060	-0.62	0.82
410	-0.34	0.60	930	0.05	< 0.17	061	-0.19	< 0.23
420	1.24	1.31	1000	0.03	< 0.17	062	0.08	< 0.23
430	0.71	0.51	1010	-0.03	< 0.16	071	-0.08	< 0.16
440	-0.47	0.60	1020	-0.14	0.22			
450	-0.03	< 0.19						

intensities. The observed intensities were corrected for the Lorentz and polarization factors in the manner described by Waser (1951), and then transformed into the structure factors,  $F_o$ , of Table 1.

A reasonable model was proposed for the molecule by assuming that it was linear and contained bond lengths similar to those found in such related molecules as cyanoacetylene, cyanogen and diacetylene. A set of expected structure factors,  $F_c$ , was calculated for each of several orientations of this model within the unit cell. Eventually, an orientation was found which gave fair agreement between the calculated and observed structure factors for the (*hk0*) zone. The data from this zone were then refined through the use of two-dimensional Fourier projections. Fig. 2 shows the final projection.

An additional projection was constructed, using the magnitudes of the calculated structure factors. The resulting shifts in the atomic positions were then used

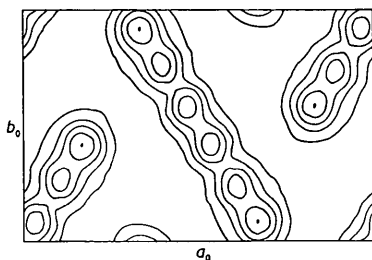


Fig. 2. Fourier projection on (001). Contours at intervals of  $1 \text{ e.}\text{\AA}^{-2}$ , running from 1 to  $5 \text{ e.}\text{\AA}^{-2}$  at the terminal peaks.

to correct the parameters for the effects of non-convergence of the Fourier series and overlap of the electron densities of adjacent atoms (Booth, 1946). The corrected *x* and *y* parameters are listed in Table 2.

A temperature factor of the form  $\exp[-B \sin^2 \theta/\lambda^2]$  was introduced into the calculated structure factors. The value  $B = 8.2 \text{ \AA}^2$  was determined by a least-squares minimization of  $\sum_{hk0} (|F_o| - |F_c|)^2$ , and a reliability index,  $\sum (|F_o| - |F_c|) / \sum |F_o|$ , of 0.13 was thereby obtained for the *hk0* zone.

A Fourier projection onto the (100) plane showed the molecules to be overlapped, so the *z* parameters of the approximate structure were refined by a least-squares minimization of  $\sum_{0kl} (|F_o| - |F_c|)^2$ . The *y* parameters were carried over from the refinement of the (*hk0*) data, leaving three *z* parameters to be determined from the fourteen observed (0*kl*) reflections. It was found, however, that the error function could not be minimized until the refinement was reduced to a one-parameter problem by assuming the molecule to be linear. The final *z* parameters are presented in Table 2.

The best value of the constant *B* in the temperature

Table 2. *Atomic coordinates expressed as fractions of the corresponding unit cell dimension*

	$C_1$	$C_2$	N
<i>x</i>	0.032	0.106	0.171
<i>y</i>	0.082	0.270	0.422
<i>z</i>	0.056	0.186	0.291

Table 3. Bond lengths in Ångströms

	C≡N	C-C	C≡C	Reference
Dicyanoacetylene	1.14	1.37	1.19	This paper
Cyanoacetylene	1.16	1.38	1.20	Westenberg & Wilson, 1950
Cyanogen	1.15	1.38	—	Langseth & Møller, 1950
Diacetylene	—	1.36	1.19	Pauling & coworkers, 1939

factor was found by a least-squares refinement to be  $9.0 \text{ \AA}^2$ . A value of 0.17 was obtained for the reliability index of the (0kl) zone.

### Discussion

The bond lengths obtained for dicyanoacetylene are shown in Table 3, along with the analogous bond lengths in some related molecules. Of particular interest is the fact that the single-bond length in dicyanoacetylene is about the same as that found in the three related molecules, suggesting that the addition of the third triple bond to a conjugated system has only a minor effect on the structure.

The smallest non-bonded approach in the crystal is  $3.30 \text{ \AA}$ , between one of the innermost carbon atoms and the nitrogen on an adjacent molecule. Assuming the van der Waals radius of carbon to be one-half the layer separation in graphite ( $1.7 \text{ \AA}$ ), and using Pauling's (1945) value for the nitrogen radius ( $1.5 \text{ \AA}$ ), the expected carbon-nitrogen separation would be equal to or greater than  $3.2 \text{ \AA}$ . The minimum carbon-

carbon separation is  $3.70 \text{ \AA}$ , while the minimum nitrogen-nitrogen separation is  $3.60 \text{ \AA}$ .

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## Spectre d'Émission K de l'Aluminium dans la Région de la Bande de Conductibilité

PAR Y. CAUCHOIS

*Laboratoire de Chimie Physique, Faculté des Sciences, 11 rue Pierre Curie, Paris 5<sup>e</sup>, France*

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The K emission spectrum of pure metallic aluminium has been studied with the help of the focusing spectrograph and experimental technique previously described and used for observing the absorption spectrum. The window of the tube was of beryllium or lithium, instead of aluminium as usual. The breadth of the  $K\beta$  band was found to be smaller than reported in the literature; the maximum of intensity close to the edge reported by Farineau could not be observed. The shape of the  $K\beta$  band is compared with that of the L band and discussed on the new hypothesis of bound levels due to the X ionization in connexion with the distribution of states in the first two Brillouin zones.

Le spectre d'émission K de l'aluminium métallique a fait l'objet de nombreuses publications.\*

La bande appelée  $K\beta$  correspond aux électrons de conductibilité. Le travail le plus complet sur la

variation d'intensité dans cette bande et son interprétation reste celui de Farineau (1938). La courbe de Farineau (Fig. 1) est généralement acceptée; la décomposition indiquée par Farineau lui a été suggérée par la considération des deux premières zones de Brillouin. Il existe entre la distribution d'intensité rapportée par Farineau pour la région de grande

\* On en trouvera les références dans Cauchois (1948). Voir aussi Das Gupta (1950).