Tabelle 3. *Atomabstände und Koordinationswinkel im* MF$_6$-*Koordinationspolyeder*

Atomabstand bzw. Koordinationswinkel	Anzahl der Abstände bzw. Winkel	MnF$_2$	FeF$_2$	CoF$_2$	NiF$_2$	ZnF$_2$
$(M\text{–F})_1$ (Å)	4	$2{,}13_2 \pm 9$	$2{,}12_2 \pm 9$	$2{,}04_6 \pm 9$	$2{,}01_8 \pm 9$	$2{,}04_3 \pm 9$
$(M\text{–F})_2$ (Å)	2	$2{,}10_2 \pm 13$	$1{,}99_3 \pm 13$	$2{,}03_2 \pm 13$	$1{,}98_6 \pm 13$	$2{,}01_5 \pm 13$
$(\text{F–F})_1$ (Å)	8	$2{,}99_4 \pm 5$	$2{,}91_1 \pm 5$	$2{,}88_4 \pm 5$	$2{,}83_2 \pm 5$	$2{,}87_0 \pm 5$
$(\text{F–F})_2$ (Å)	2	$2{,}68_8 \pm 26$	$2{,}65_7 \pm 26$	$2{,}57_6 \pm 26$	$2{,}60_4 \pm 26$	$2{,}62_1 \pm 26$
$(\text{F–F})_3 = c$ (Å)	2	$3{,}309_9 \pm 5$	$3{,}309_1 \pm 1$	$3{,}179_6 \pm 3$	$3{,}083_6 \pm 4$	$3{,}133_5 \pm 3$
$(\text{F–}M\text{–F})_1$ (°)	2	78,2	77,5	78,0	80,4	79,8
$(\text{F–}M\text{–F})_2$ (°)	2	101,8	102,5	102,0	99,6	100,2
$(\text{F–}M\text{–F})_3$ (°)	8	90,0	90,0	90,0	90,0	90,0

weichen zum Teil deutlich von den von Stout & Reed (1954) angegebenen ab. Doch sind die Parameterwerte dieser Autoren sicher weniger zuverlässig, da sie nur aus dem Intensitätsverhältnis von je zwei Debye–Scherrer-Linien bestimmt wurden.

Die mit den experimentell bestimmten Parametern berechneten Atomabstände und Koordinationswinkel im MF$_6$-Koordinationspolyeder sind in Tabelle 3 zusammengestellt. Es zeigt sich, dass bei allen diesen Fluoriden, wie auch schon beim MgF$_2$, die vier koplanaren Abstände $(M\text{–F})_1$ länger sind als die beiden anderen Abstände, $(M\text{–F})_2$. Beim CoF$_2$ ist diese Differenz nur gering und im Rahmen der Fehlergrenzen, beim FeF$_2$ beträgt sie über 6% und ist damit völlig gesichert, bei den übrigen Substanzen ist sie jedenfalls als wahrscheinlich reell anzusprechen. Auffällig ist, dass die Abweichung bei allen Fluoriden gleichsinnig ist und zwar umgekehrt wie bei den Oxygen TiO$_2$ und GeO$_2$. Bei diesen Oxyden sind die Abstände $(M\text{–O})_1$ kürzer als $(M\text{–O})_2$.

Ich danke Herrn Prof. Zemann für viele wertvolle Hinweise während dieser Arbeit. Frl. M. Binder danke ich für einen Teil der numerischen Berechnungen, Herrn Prof. Stout (University of Chicago) für die Überlassung des Untersuchungsmaterials und der Deutschen Forschungsgemeinschaft für die dem Institut zur Verfügung gestellten apparativen Hilfsmittel.

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The Crystal Structure of Cyanoacetylene

By F. V. Shallcross and G. B. Carpenter

Metcalf Chemical Laboratories, Brown University, Providence 12, *Rhode Island, U.S.A.*

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Crystalline cyanoacetylene at −25 °C. is monoclinic with $a = 6{\cdot}96$, $b = 6{\cdot}30$, $c = 3{\cdot}84$ Å, $\beta = 110{\cdot}5°$. The probable space group is $P2_1/m$, with two molecules per unit cell. Cyanoacetylene molecules are joined together by C–H · · · N hydrogen bonds into approximately linear infinite chains parallel to a, which are nearly close-packed. The bond lengths are C≡N = 1·14, C–C = 1·38, C≡C = 1·18, C–H = 0·9 and C–H · · · N = 3·27 Å. The molecules are linear within experimental error.

Introduction

Cyanoacetylene, H−C≡C−C≡N, exhibits a system of conjugated triple bonds similar to that found in diacetylene and cyanogen. The compound has been studied in the vapor from microwave absorption spectra (Westenberg & Wilson, 1950) and in the solid, liquid and vapor from infra-red absorption spectra (Turrell, Jones & Maki, 1957). Infra-red results indicate the presence of C–H · · · N hydrogen bonds in the condensed phases, similar to those in hydrogen cyanide. The microwave studies show that the free molecule is linear; they yield a central C–C single bond length of only 1·382 Å, implying resonance with ionic structures such as $\text{H}-{}^{+}\text{C}=\text{C}=\text{C}=\text{N}^{-}$. The X-ray investigation was undertaken to determine the nature of the hydrogen bonding and the relative importance of the possible resonance forms in the solid.

Experimental methods

Cyanoacetylene melts at 5 °C. and boils at 42 °C.; it polymerizes slowly at room temperature. A sample was obtained from Dr G. C. Turrell; it had been prepared from propiolic acid by the method described elsewhere (Turrell *et al.*, 1957). Specimens were vacuum-distilled into thin-walled Pyrex capillaries of about 0·2 mm. outside diameter. The capillaries were sealed and then stored at -10 °C. to prevent polymerization.

X-ray studies on single crystals were made at -25 ± 3 °C. with a Weissenberg camera adapted for use at low temperature. Samples in the camera were refrigerated by passing a stream of cold nitrogen gas over the capillaries. Single crystals were grown by melting part of the sample with a warm gas jet and slowly refreezing it in the cold gas stream. Two crystals were grown around the bends of L-shaped capillaries from seeds in the short end in order to obtain several orientations, because crystals tended to grow with the *a* axis parallel to the axis of straight capillaries.

Data were obtained from three crystals rotated about *a*, *b* and [110], respectively. Approximately 389 independent reflections lay in the limiting sphere for Cu $K\alpha$ radiation. There were 129 independent reflections of measurable intensity, 239 which were too weak to observe in the 10 hr. exposures used, and 21 at high values of θ which were not accessible in these experiments. Relative intensities were estimated visually by the multiple-film technique (Robertson, 1943). Relative observed structure factors were obtained in the usual manner. Data for different reciprocal-lattice layers and different crystal orientations were scaled empirically on a basis of common reflections. No absorption corrections were made because of the small sample size.

Powder patterns were obtained from samples at about -25, -40, -90 and -160 °C., but they gave no indication of polymorphism. Specimens were kept at -160 °C. for 55 min. without undergoing any detectable phase transition.

Cu $K\alpha$ radiation was used in all of the X-ray studies on cyanoacetylene.

Structure determination

Unit-cell dimensions

Lattice elements at -25 ± 3 °C. were determined by a least-squares treatment of 19 reflections with $\theta \geqq 28°$ appearing on the equatorial layers of rotation pictures calibrated with NaCl powder lines. The NaCl cell edge was taken as 5·631 Å at -25 °C. Cyanoacetylene is monoclinic with

$$a=6{\cdot}965\pm0{\cdot}009,\quad b=6{\cdot}300\pm0{\cdot}010,\quad c=3{\cdot}839\pm0{\cdot}004\ \text{Å},\quad \beta = 110{\cdot}5\pm0{\cdot}1°.$$

The uncertainties are the standard deviations from least-squares; they are probably somewhat optimistic in view of possible systematic errors. The X-ray density is $1{\cdot}075\pm0{\cdot}002$ g.cm.$^{-3}$ for two molecules in the unit cell. No experimental density determination was feasible, but the liquid density has been reported as 0·8159 g.cm.$^{-3}$ at 17 °C. (Moureu & Bongrand, 1920), and the density difference is consistent with the contraction observed during solidification.

Space group

The systematic absences were $0k0$ absent for k odd, implying that the space group is $P2_1/m$, $P2_1$ or Pm. (The absence would arise in Pm because the two molecules would lie in different mirror planes.) In $P2_1/m$ and Pm, the molecules would lie in mirror planes, while in $P2_1$ they would not. If the correct space group were Pm, there would be two non-equivalent molecules in the unit cell. The most probable space group is $P2_1/m$, and the structure was successfully refined, assuming this symmetry. The intensity data show that any deviations from $P2_1/m$ must be small; such deviations would affect the individual anisotropic temperature factors and are discussed later.

Trial structure

The $0kl$ reflections with $k+l$ odd were absent except for the very weak 001 and 021; $0kl$ with $k+l$ even showed normal decline of intensity with θ. Also, c^* was approximately $\sqrt{3}.b^*$. These facts showed that the structure projected along *a* could very nearly be referred to a plane hexagonal lattice with all scattering centers projected on the lattice points. The length of *a* was close to the sum of the bond lengths found for cyanoacetylene in the vapor and the expected C–H···N hydrogen-bond length. It was therefore evident that the structure was approximately close-packed linear chains parallel to *a*. The two molecules in the cell would have to be oriented in opposite directions in $P2_1$ or $P2_1/m$, but they could be oriented alike in Pm. As the refinement progressed, test structures in Pm with the two molecules parallel gave decidedly poorer agreement than the corresponding antiparallel arrangement. In $P2_1/m$ the coordinates of all independent atoms in the cell were then $x, \frac{1}{4}, z$, with z nearly $\frac{1}{4}$. It was possible to obtain initial scale factors and average temperature factors from the $0kl$ data by assuming $y = z = \frac{1}{4}$ for all atoms.

A trial set of x coordinates was obtained by assuming the bond lengths found in the vapor and determining the relative positions of two adjacent antiparallel molecules. The conventional discrepancy factor for $h00$ and $h10$ reflections was calculated as a function of the one undetermined x coordinate, chosen as x(N). This function is plotted in Fig. 1; it is sym-

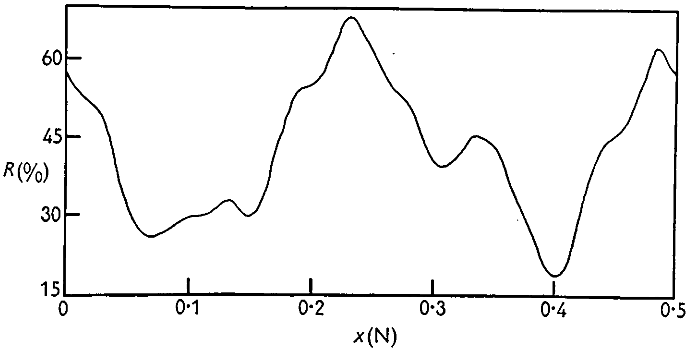

Fig. 1. Discrepancy factor R versus $x(\mathrm{N})$, for $h00$ and $h10$ reflections.

metrical about $x(\mathrm{N}) = 0$ and 0·5. The deepest and second deepest minima were investigated further. The second best structure differs from the first in interchange of N and terminal C atoms. With relatively good temperature factors, the discrepancy for all $hk0$ reflections was 0·06 for the first alternative and 0·14 for the second, indicating that the first, with $x(\mathrm{N})$ about 0·400, was correct.

Refinement

The structure was refined principally by Fourier methods. Beevers–Lipson strips (Beevers, 1952) were used in calculating the Fourier syntheses.

Two cycles of a two-dimensional Fourier refinement on $hk0$ data were followed by three-dimensional refinement, with direct and difference density sections calculated in the plane $y = \frac{1}{4}$. Initially, average anisotropic temperature factors were found by a least-squares procedure. Individual anisotropic temperature factors were obtained by the difference methods of Cochran (1951*a*, *b*) initially, and of Cruickshank (1956*a*) subsequently. It was necessary to introduce 'damping factors' (arbitrary factors less than unity) multiplying the indicated scale and temperature-factor changes to allow for neglected coupling effects. Coordinates were found by the usual difference refinement procedure (Lipson & Cochran, 1953). Temperature factors and coordinates were varied alternately; six coordinate cycles and five scale and temperature-factor cycles were computed. The difference refinement led to coordinate set 'A' given in Table 1. The atoms are designated so that the molecular formula is $\mathrm{N{\equiv}C_1{-}C_2{\equiv}C_3{-}H}$. Coordinates are given in fractions of a cell edge. For all atoms $y = \frac{1}{4}$. The discrepancy factor R, as listed in Table 1, is given by $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$; the sum is over independent observed reflections only. The difference refinement gave a low discrepancy factor, and both coordinates and temperature factors apparently converged. However, the bond lengths based on A differed from those in the vapor by as much as 0·05 Å, while the estimated standard deviation in coordinates (Cruickshank, 1949*a*, *b*, 1954; Cruickshank & Rollett, 1953) was only about 0·003 Å at this stage.

Table 1. *Atomic coordinates and discrepancy factors for cyanoacetylene*

Quantity	A	B	C	D
$x(\mathrm{N})$	0·4043	0·4019	0·4009	0·3990
$x(\mathrm{C_1})$	0·5617	0·5652	0·5641	0·5635
$x(\mathrm{C_2})$	0·7654	0·7621	0·7630	0·7637
$x(\mathrm{C_3})$	0·9311	0·9316	0·9320	0·9338
$x(\mathrm{H})$	0·129	0·085	0·067	0·070
$z(\mathrm{N})$	0·2438	0·2388	0·2397	0·2396
$z(\mathrm{C_1})$	0·2410	0·2400	0·2399	0·2399
$z(\mathrm{C_2})$	0·2577	0·2540	0·2531	0·2532
$z(\mathrm{C_3})$	0·2614	0·2598	0·2581	0·2581
$z(\mathrm{H})$	0·300	0·264	0·258	0·258
R	0·058	0·055	0·049	—

In order to investigate the significance of these results, a second structure was postulated having the bond lengths observed in the vapor, the molecular center of mass and orientation found by Fourier refinement, and 'calculated' temperature factors which were available from an analysis of rigid-body vibrations on structure A. The postulated structure gave an R of 0·062, which was reduced to 0·054 when temperature factors were varied again by the difference method (Cruickshank, 1956*a*). As a check, a further ϱ_o Fourier synthesis was calculated in the plane $y = \frac{1}{4}$, using structure-factor signs based on A. A difference cycle on the results of this Fourier gave a set of coordinates apparently significantly different from A; when temperature factors were varied, this refined to an R of 0·055. These studies implied that the estimates of error were inadequate and that the data were not very sensitive to changes in coordinates. This effect can probably be attributed to the large number of accidental absences, including nearly all reflections with $|h| = 3$, 4 or 7. The structure was apparently not greatly over-determined. The large number of absences probably caused appreciable coupling between thermal and positional parameters which could not be adequately considered in the difference methods used; this omitted coupling would affect the estimates of coordinate error.

Final coordinates were therefore obtained from a direct Fourier with the usual 'back-shift' correction (Booth, 1946) to allow for series termination. One weak reflection, $\bar{3}11$, was omitted. The final ϱ_o section at $y = \frac{1}{4}$ is shown in Fig. 2. Fourier centers were located assuming Gaussian peaks, using the interpolation method of Carpenter & Donohue (1950). Final scale and temperature factors were taken from the best values obtained by difference refinement; they were determined with the assumed microwave bond lengths but were very similar to those found with coordinates from an earlier Fourier. The atomic centers in the final Fourier section are listed in Table 1 as coordinate set '*B*'; the coordinates after the back-shift correction are listed as set '*C*'. The Fourier peak heights, $\varrho_{\max.}$, and the final temperature factor parameters are given in Table 2. Temperature factors were of the form $\exp\,[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{13}hl)]$. Although the N peak was higher than the C_3 peak, N and C_3 were lower than C_1 and C_2 because of rigid-body libration.

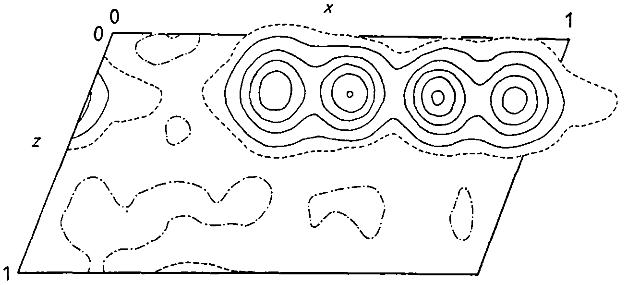

Fig. 2. Electron-density section $\varrho_0(x, \frac{1}{4}, z)$. Solid contours are drawn at 1·0, 2·0, 3·0, 4·0 and 5·0 e.Å^{-3}. Broken contour is drawn at 0·5 e.Å^{-3}. Zero contour is a chain line.

Table 2. *Electron-density maxima and temperature-factor parameters for cyanoacetylene*

Quantity	N	C_1	C_2	C_3
$\varrho_{\max.}$ (e.Å^{-3})	5·0	5·1	5·2	4·6
b_{11}	0·0342	0·0338	0·0332	0·0353
b_{22}	0·0607	0·0499	0·0505	0·0595
b_{33}	0·1944	0·1448	0·1429	0·1774
b_{13}	0·0731	0·0539	0·0526	0·0652

The hydrogen atom appeared as a distinct shoulder on C_3 in the direct Fourier syntheses and as a small Gaussian peak in difference maps when hydrogen contributions were omitted from F_c. The H coordinates given in set *C* were obtained from a difference section at $y = \frac{1}{4}$, $\varrho_o - \varrho_c$(C, N), with F_c's which neglected scattering by hydrogen. The synthesis was

Table 3. *Observed and calculated structure factors for cyanoacetylene*

hkl	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c	*hkl*	$\lvert F_o \rvert$	F_c
001	0·82	0·49	201	5·25	5·26	640	1·36	−1·33	$\bar{3}21$	1·26	−1·28
002	12·52	−12·19	202	0·95	−1·04						
004	0·99	0·98	210	8·98	8·44	810	0·70	−0·60	$\bar{4}01$	1·01	−1·51
011	30·20	−29·54	211	2·69	−2·90				$\bar{4}11$	0·78	0·94
013	3·30	3·42	212	1·28	−1·60	$\bar{1}01$	9·56	−9·90	$\bar{4}21$	0·70	0·94
020	28·55	−29·70	220	3·75	−3·81	$\bar{1}02$	2·93	3·17			
021	0·57	−0·31	221	3·24	−3·47	$\bar{1}03$	2·01	2·03	$\bar{5}01$	5·06	−5·18
022	8·65	8·57	222	0·80	0·74	$\bar{1}11$	6·06	6·15	$\bar{5}02$	2·43	−2·50
024	0·82	−0·77	230	3·16	−3·45	$\bar{1}12$	4·73	4·51	$\bar{5}03$	1·99	2·03
031	13·00	12·36	231	1·17	1·31	$\bar{1}13$	0·92	−0·99	$\bar{5}11$	2·98	−3·05
033	1·99	−2·04	240	1·02	1·13	$\bar{1}21$	6·24	6·13	$\bar{5}12$	3·48	3·63
040	8·33	8·69	241	0·94	1·16	$\bar{1}22$	2·14	−2·26	$\bar{5}13$	1·27	1·17
042	3·27	−3·43	250	0·93	0·82	$\bar{1}23$	1·42	−1·56	$\bar{5}14$	0·91	−0·77
051	3·30	−3·46				$\bar{1}31$	2·56	−2·83	$\bar{5}21$	3·94	3·93
053	0·86	0·76	301	0·75	−0·91	$\bar{1}32$	2·44	−2·43	$\bar{5}22$	1·83	1·87
060	1·88	−2·03	310	1·85	−1·73	$\bar{1}41$	2·33	−2·26	$\bar{5}23$	1·59	−1·60
062	0·99	0·97				$\bar{1}42$	0·90	0·92	$\bar{5}31$	1·78	1·68
			500	2·67	2·66	$\bar{1}43$	0·92	0·78	$\bar{5}32$	2·26	−2·17
100	8·36	−7·93	501	2·66	2·72	$\bar{1}51$	0·90	0·83	$\bar{5}41$	1·96	−1·83
101	5·47	5·42	510	4·36	4·25	$\bar{1}52$	0·94	0·90	$\bar{5}42$	0·83	−0·83
102	1·47	1·65	511	1·13	−1·30				$\bar{5}43$	0·87	0·81
110	9·47	9·49	512	1·05	−1·13	$\bar{2}01$	8·40	−8·31	$\bar{5}52$	1·04	0·85
111	3·98	4·18	520	1·89	−1·98	$\bar{2}02$	2·50	−2·39			
112	2·03	−1·85	521	2·08	−2·13	$\bar{2}03$	0·95	0·87	$\bar{6}02$	4·03	4·26
120	4·88	5·20	530	2·84	−2·52	$\bar{2}11$	5·16	−4·96	$\bar{6}04$	1·12	−1·09
121	3·48	−3·64	531	0·83	0·77	$\bar{2}12$	3·13	3·19	$\bar{6}11$	4·52	4·51
122	1·02	−1·23	532	0·83	0·71	$\bar{2}21$	5·05	5·19	$\bar{6}13$	2·47	−2·39
130	3·65	−3·86	540	1·03	0·87	$\bar{2}22$	1·71	1·57	$\bar{6}22$	3·13	−3·27
131	1·80	−2·04	541	1·23	1·05	$\bar{2}31$	1·95	2·02	$\bar{6}24$	0·88	0·86
132	1·11	1·13	550	1·12	0·97	$\bar{2}32$	1·18	−1·45	$\bar{6}31$	2·64	−2·67
140	1·66	−1·74				$\bar{2}41$	1·27	−1·59	$\bar{6}33$	1·40	1·46
141	1·38	1·50	600	3·65	−3·62				$\bar{6}42$	1·55	1·53
150	1·20	1·25	611	1·65	1·76	$\bar{3}01$	2·36	2·03	$\bar{6}51$	0·99	0·98
151	0·81	0·64	620	2·69	2·78	$\bar{3}11$	0·49	−0·18			
			631	1·06	−1·08	$\bar{3}12$	0·85	−0·86	$\bar{8}12$	1·03	−0·87
200	6·45	6·34							$\bar{8}21$	0·86	−0·73

based on reflections with $\theta < 33°$, because hydrogen contributions were negligible at higher values of θ. This section is shown in Fig. 3. The hydrogen peak height was about 0·36 e.Å^{-3} in the difference section. Hydrogen coordinates *A* were found from earlier difference syntheses, and H coordinates *B* were taken as expected values based on vapor bond lengths. The temperature factor for hydrogen was an assumed isotropic factor $\exp(-10 \sin^2 \theta/\lambda^2)$. This value was chosen for convenience and corresponds to a somewhat greater amplitude of vibration than occurs in C_3.

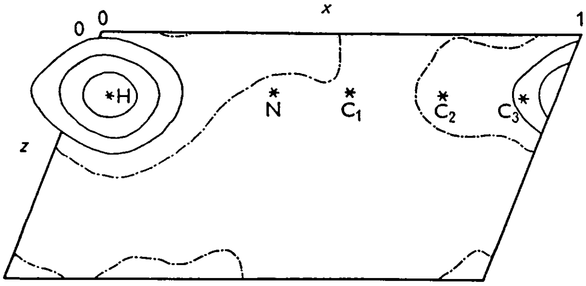

Fig. 3. Electron-density difference section $\varrho_o(x, \frac{1}{4}, z) - \varrho_c(x, \frac{1}{4}, z)$, with H contribution omitted from ϱ_c. Solid contours are drawn at 0·1, 0·2 and 0·3 e.Å^{-3}. Zero contour is a chain line.

Final observed and calculated structure factors for independent observed reflections are compared in Table 3. Calculated structure factors are based on coordinate set *C* and the final scale and temperature factors. Hydrogen contributions are included. Atomic scattering factors for carbon and nitrogen were obtained from Berghuis *et al.* (1955), and those for hydrogen were obtained from McWeeny (1951). Reflections that were too weak to be observed were assigned upper limiting $|F_o|$'s that depended on the background. Only six of the 239 independent reflections in this class had $|F_c|$'s which exceeded the upper limit on $|F_o|$. In no case did the $|F_c|$ exceed this observed upper limit by more than 25%. The agreement obtained for very intense reflections indicates that extinction effects were negligible.

Analysis of thermal motion

The final temperature factors were analyzed in terms of rigid-body motion with the procedure given by Cruickshank (1956*b*). The molecule was assumed to be linear for this treatment. The resultant root-mean-square amplitudes of translational vibration were: along the molecule, 0·265±0·003 Å; along *b*, 0·313 ±0·004 Å; perpendicular to the molecule, in the mirror plane, 0·300±0·004 Å. The root-mean-square amplitudes of libration were: about an axis parallel to *b*, 5·5±0·3°; about an axis perpendicular to the molecule, lying in the mirror plane, 4·7±0·4°. Uncertainties are standard deviations from least-squares.

Cruickshank (1956*c*) derives the amount of displacement of a Fourier peak due to rigid-body librations. The resultant increases in bond lengths were: $N{\equiv}C_1$, 0·007; C_1–C_2, 0·011; $C_2{\equiv}C_3$, 0·007; C_3–H, 0·005 Å. Coordinates which include the correction for rigid-body libration are listed as set 'D' in Table 1.

Tests of the space group

The agreement obtained with the structure in $P2_1/m$ indicates that any deviation from that space group would be small. The electron-density projection along *c* was calculated, and the map resembled Fig. 2 closely. There was no indication of peak doubling which would occur if the assumed centers of symmetry were spurious and atoms deviated from $y = \frac{1}{4}$ by more than about 0·3 Å. Smaller deviations from centrosymmetry would affect the temperature factors. Displacement of an atom from $y = \frac{1}{4}$ would be interpreted as an increase in its b_{22}. The most likely deviation from $P2_1/m$ would be a tilt of the whole molecule out of the assumed mirror plane. A deviation of an atom from $y = \frac{1}{4}$ by 0·15 Å should produce a significant asymmetry in the apparent thermal vibration about the molecular axis for a structure refined in $P2_1/m$. In particular, the observed amplitude of libration in the mirror plane should be less than the amplitude in a plane perpendicular to the mirror plane if the molecule as a whole were tilted out of $y = \frac{1}{4}$. Actually, the libration was found to be slightly greater in the mirror plane than out of it. The packing of molecules in adjacent mirror planes also does not seem to favor deviations from $y = \frac{1}{4}$, because ends of molecules in one plane are opposite centers of molecules in the next plane.

A final difference section at $y = \frac{1}{4}$ gave no evidence which would favor the two non-equivalent molecules required in *Pm*. There were no large peaks or depressions at the atomic centers in this map which would indicate an error involving reversed or disordered orientation of the molecules.

Estimation of errors

Standard deviations in coordinates were estimated, using appropriate formulas for atoms in special positions in the mirror planes, with *z* nearly equal to $\frac{1}{4}$ (Cruickshank, 1949*a*, *b*, 1954; Cruickshank & Rollett, 1953). These methods gave standard deviations between 0·002 and 0·003 Å for all N and C coordinates, and between 0·05 and 0·1 Å for H coordinates. Application of the formulas of Booth (1946) and of Booth & Britten (1948) gave a coordinate standard deviation of about 0·004 Å for N and C, using the earlier coordinate set *A*.

Comparison of parameter sets *A*, *C* and a theoretical structure based on microwave bond lengths, all of which gave nearly the same discrepancy factor, indicated that the calculated standard deviations in N and C coordinates were unreasonably small; the true standard deviations are probably about 0·015 Å. The large difference between the theoretical and empirical values of the error is probably the result of coupling between thermal and positional parameters, which is neglected in the estimation of the standard deviations. Neglect of absorption may also contribute to the effect. Standard deviations in bond lengths are probably about 0·02 Å (except bonds to H).

A final difference section, $\varrho_o - \varrho_c$, at $y = \frac{1}{4}$, was calculated including hydrogen contributions to ϱ_c. The maximum difference density magnitude was slightly less than 0·1 e.Å^{-3}. The principal significant features indicated some uncorrected anisotropy of thermal vibration (or distortion of the electronic distribution) in the hydrogen atom, but implied that the average scattering factor for hydrogen was approximately correct. The estimated standard deviation in electron-density (Cruickshank, 1949*a*, *b*; Cruickshank & Rollett, 1953) was about 0·05 e.Å^{-3} near atomic centers.

Approximate values of standard deviations in temperature factors were available both from the analysis of thermal vibration (Cruickshank, 1956*b*) and from the estimated standard deviation in F (Cruickshank, 1956*a*). These methods were reasonably consistent; they indicated standard deviations in b_{11}, b_{22} and b_{33} between 3 and 5%, and in b_{13}, about 10%. The agreement between the two methods for determining $\sigma(b)$ indicates that they were probably not underestimated, as were the errors in coordinates. Changes in the b's on the order of $\sigma(b)$ made appreciably larger changes in R than did changes in coordinates on the order of $\sigma(x)$, where the standard deviations were both found by Cruickshank's procedures.

Discussion of the structure

A projection of the structure along b is shown in Fig. 4. Atoms are drawn with approximate van der Waals radii of 1·7 Å for C, 1·6 Å for N and 1·2 Å for H. The most prominent features of the structure are the approximately linear chains of cyanoacetylene, which are very nearly close-packed, and the hydrogen bonding between molecules in the chains. All molecules in a given chain are oriented alike; each chain is surrounded by two parallel and four antiparallel nearest-neighbor chains.

Individual molecules have a slight mean tilt (1·2°) to the a axis, which is probably significant. The atoms in each molecule also appear to be displaced slightly from linearity, although the deviations are of questionable significance. The atoms in a molecule fit a least-squares straight line within 0·015 Å. The bond angles along the molecule are all within 2° of 180°, which is the estimated standard deviation in these angles if $\sigma(x)$ is assumed to be 0·015 Å. Bond lengths along the molecule are given in Table 4, which also lists bond lengths for other comparable systems. If the correct space group were $P2_1$, the bond lengths would probably be increased somewhat, but it is very unlikely that the increase would be greater than 0·02 Å.

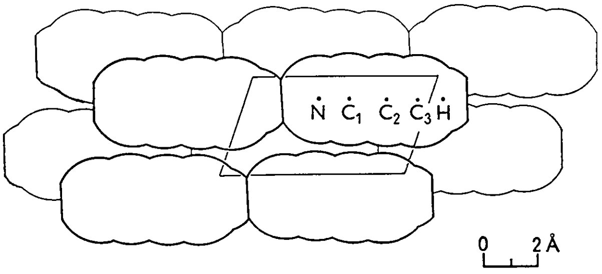

Fig. 4. Projection of the structure along b.

All nearest-neighbor interatomic distances between adjacent chains are within 0·1 Å of 3·7 Å, which is somewhat greater than the sum of the van der Waals radii. There is no obvious explanation for the relative positions of molecules in adjacent chains. The fact that C≡N and C–H groups tend to lie adjacent in anti-parallel molecules suggests an effect of dipole–dipole interaction.

The principal intermolecular interaction is that along the chains, caused by hydrogen bonding. Although the C–H · · · N distance is relatively long, the hydrogen location and shifts in C–H stretching and C≡C–H bending frequencies during the transition from vapor to liquid to solid (Turrell *et al.*, 1957) confirm the presence of hydrogen bonding. The C–H · · · N distance in crystalline cyanoacetylene is 3·27±0·02 Å. The only analogous hydrogen-bonding

Table 4. *Comparison of bond lengths for cyanoacetylene and related molecules*

Molecule	H–C (Å)	C≡N (Å)	C≡C (Å)	C–C (Å)	Method*	Ref.†
HCCCN	0·95 ±0·10	1·14 ±0·02	1·18 ±0·02	1·38 ±0·02	XRD	1
	1·057±0·001	1·157±0·001	1·203±0·001	1·382±0·001	MW	2
NCCCCN	—	1·14	1·19	1·37	XRD	3
HCCCCH	—	—	1·19 ±0·03	1·36 ±0·03	ED	4
NCCN	—	1·16 ±0·02	—	1·37 ±0·02	ED	4
HCN	—	1·19 ±0·15	—	—	XRD	5
	1·061±0·002	1·157±0·0005	—	—	MW	6
HCCH	1·05 ±0·05	—	1·20 ±0·02	—	XRD	7
	1·059	—	1·205	—	IR	8

* XRD = X-ray diffraction; MW = microwave spectra; ED = electron diffraction; IR = infra-red spectra.

† References: 1. This work. 2. Westenberg & Wilson, 1950. 3. Hannan & Collin, 1953. 4. Pauling, Springall & Palmer, 1939. 5. Dulmage & Lipscomb, 1951. 6. Simmons, Anderson & Gordy, 1950. 7. Sugawara & Kanda, 1952. 8. Overend & Thompson, 1956.

system which has been studied in detail is that of hydrogen cyanide; the hydrogen-bond length there has been reported for the crystal (Dulmage & Lipscomb, 1951) as 3·18 Å, probably ±0·02 Å.

The bond lengths found for cyanoacetylene in the crystal are in reasonably good agreement with the results obtained on the vapor from microwave studies (Westenberg & Wilson, 1950). The agreement with similar systems such as dicyanoacetylene, cyanogen, diacetylene, hydrogen cyanide and acetylene is also good, as indicated in Table 4. In this table estimated errors are given where available, although many of these are of uncertain significance. The errors for cyanoacetylene are estimated standard deviations, as previously discussed. Electron-diffraction, micro-wave and infra-red studies were on vapors, and X-ray-diffraction studies were on crystals.

The X-ray results confirm the importance of resonance forms for cyanoacetylene having central C=C double bonds. As indicated in Table 4, unusually short C–C bonds are observed in all comparable systems having conjugated triple bonds.

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