

Neutron Powder Diffraction Study of the Low-Temperature Phase of Solid Acetylene-d₂

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Acetylene-d₂ (C₂D₂) has two solid phases. The crystal structure of the low-temperature phase has been determined at 4.2 K by neutron powder diffraction. The structure is orthorhombic, with $a = 6.193$ (3), $b = 6.005$ (3), $c = 5.551$ (3) Å, space group *Acam*, $Z = 4$. The linear molecules lie in layers parallel to (001) in slightly off-diagonal directions. The final agreement index $R_2 = 0.071$. Bond lengths are $C \equiv C = 1.18$ (1), $C-D = 1.06$ (2) Å. The apparent shortening of the C-C bond compared with the value calculated from high-resolution Raman spectra in the gas phase is attributed to the effect of molecular libration.

Introduction

Acetylene is the simplest compound with a carbon-carbon triple bond. Its molecular structure in the gas phase has been widely investigated and the molecule is known to be linear. Less information is available about properties in the solid and liquid phases, probably because of the explosion hazard.

In his polarizing microscope studies of the solid phase of C₂H₂ Wahl (1913) established that acetylene undergoes at 88 K a phase transition from an optically isotropic high-temperature to an anisotropic low-temperature phase. Mooy (1932) and Washer (1935) suggested that the lattice symmetry of acetylene was lower than cubic, hexagonal or tetragonal on the basis of their X-ray powder diffraction work. The information content of the powder patterns was probably too low to draw a more definite conclusion. Moreover, these two investigations were not completely consistent. Washer recorded some extra lines in the low 2θ range not seen by Mooy, which could arise from impurities in the sample. Single-crystal X-ray diffraction was used by Sugawara & Kanda (1952) to determine the crystal structure of the high-temperature phase at 156 K. The cubic structure with a lattice parameter $a = 6.14$ Å and most probable space group *Pa3* has a molecular arrangement similar to that of solid carbon dioxide. The transparent single crystal undergoes a phase transition at 133 K, turning to opaque powder. Comparison of the X-ray powder patterns of the high and low-temperature phases suggested that the latter was orthorhombic. No definite conclusion about the space group was made.

Spectroscopic studies of crystalline acetylene and acetylene-d₂ support the space group *Cmca* (D_{2h}^{18}) as most probable. On analysing the crystal-field splitting in the fundamental infrared band of polycrystalline C₂H₂ and C₂D₂ films, Bottger & Eggers (1964) concluded that the low-temperature phase of both sub-

stances (i) was orthorhombic with point group D_{2h} and (ii) had, in the primitive unit cell, two molecules occupying sites of C_{2h} symmetry. By correcting an error in their correlation table the results of Bottger & Eggers (1966) are consistent with the observations made by Anderson & Smith (1966)(A & S) in the far-infrared spectra of polycrystalline acetylenes. In the high-resolution study of the ν_3 stretching mode A & S observed a doublet with a narrow splitting which substantiates the Cl₂ structure (Collin, 1952). Ito, Yokohama & Suzuki (1970) interpreted the results of the polycrystalline low-temperature phase acetylene, concluding that the D_{2h}^{18} structure was the most probable one. On analysing the observed splitting and intensity ratio of the Raman-active ν_2 intramolecular C-H stretching vibration they proposed (i) that the two orthorhombic crystal axes parallel to molecular layer planes are nearly equal in length and (ii) that the molecules are along face diagonals formed by these two axes.

The present investigation was carried out in order to resolve the crystal structure and to compare it with the proposed model of the low-temperature phase of acetylene. The high incoherent scattering cross section of the hydrogen nucleus for thermal neutrons restricted the diffraction studies to acetylene-d₂. The results, however, are expected to apply to C₂H₂ as well, in view of the isomorphism observed in the spectroscopic studies cited.

Experimental

Acetylene-d₂ (C₂D₂) was prepared by the reaction of deuterium oxide with calcium carbide which was previously baked at about 500°C for several hours under vacuum. The generating apparatus was basically similar to that of Lind, Jugners & Schiflett (1935). The C₂D₂ was purified several times by fractional sublimation.

The powder specimen, about 10 cm³, for the diffrac-

tion study, was condensed in a cylindrical thin-walled boron-free silica sample holder immersed in liquid nitrogen. A liquid helium cryostat with a thin-walled vanadium tail was used with the sample holder with C_2D_2 immersed in liquid He. The powder specimen was tested for random orientation by rotating the cryostat/sample combination with respect to the thermal neutron beam and recording the variation of the most intense diffraction maximum. The powder pattern was recorded with the multicounter neutron powder diffractometer PANDA (UKAERE, Didcot, Berks, England). The thermal neutron beam was monochromated by the germanium (331) plane, $\lambda = 1.848$ (1) Å at a take-off angle of about 91° . Three counter blocks each containing 3 counters were separated by 5° in 2θ . The individual counters in the blocks were placed to record patterns in planes above, at, and below the equatorial diffractometer plane. At the time of measurement the middle counter block was not used. The wavelength was calibrated against a nickel standard. In order to collect a pattern with reasonable statistics and to gain from the instrumental resolution, the 2θ scanning was performed in steps of 0.02° with a monitor counter value M.C. of $2^6 \times 10^3$. For the experiment quoted a peak-to-background ratio 15:1 for the highest peak was obtained. The non-linear background containing contributions from scattering by liquid helium, the silica sample holder, the cryostat and the incoherent interaction of thermal neutrons with C and D atoms was about 400–500 counts per step. The overlapping intensity data collected from the two equatorial counters $\Delta 2\theta = 10^\circ$ apart (with the background subtracted) were corrected for the Lorentz factor. The information obtained above the instrumental take-off angle could only partly be used in the analysis owing to the uncertain background level and strongly increasing broadening of the diffracted peaks far from the focusing angle. The recorded powder pattern consisted of 28 intensity maxima in the useful range ($2\theta < 104^\circ$). From these, 22 were found to be peaks from single reflexions and one a resolvable doublet; the remainder could not be resolved into singlets in the limits of the resolution. All the observed maxima could be unambiguously indexed on the basis of the lattice parameters of an orthorhombic cell listed in Table 1. The observed systematic absences are: hkl for $k+l$ odd, $h0l$ for h odd, $0kl$ for either k or l odd. Two orthorhombic space groups are compatible with the rules found, the centrosymmetric *Acam* (No. 64) and the polar *Aba2* (No. 41). The intensity distribution among $\{200\}$ reflexions with 002 very strong and both 200 and 020 exceedingly weak suggests that the molecules probably lie in planes parallel to (001) in layers $c/2$ apart. In this model the z coordinates of the atoms can be chosen as $z=0$ and $z=\frac{1}{2}$ and the *Aba2* 8(*b*) general setting coincides with the *Acam* 8(*f*) special point position for a linear C_2D_2 molecule. On the basis of these considerations the polar *Aba2* model was excluded from the refinement. The eight equivalent positions for both types of atoms are:

$$\begin{array}{l} \textit{Acam} \left\{ \begin{array}{ll} xy0 & \frac{1}{2} + x, \frac{1}{2} - y, 0 \\ \bar{x}\bar{y}0 & \frac{1}{2} - x, \frac{1}{2} + y, 0 \end{array} \right. & \begin{array}{ll} x, \frac{1}{2} + y, \frac{1}{2} & \frac{1}{2} - x, y, \frac{1}{2} \\ \bar{x}, \frac{1}{2} - y, \frac{1}{2} & \frac{1}{2} + x, \bar{y}, \frac{1}{2} \end{array} \end{array}$$

All the positional parameters of the C and D atoms can be thus obtained from four values to be refined: x_C , y_C , x_D and y_D . The initial values of the parameters were chosen on the assumptions that the face diagonal orientation of the molecules is expected (Ito *et al.*, 1970) and that the bond lengths are the same as in the gas phase. The equilibrium values from high-resolution Raman spectra by Fast & Welsh (1972) were chosen: $r_e(C \equiv C) = 1.2033$ (2) and $r_e(C-D) = 1.0605$ (3) Å. The information content of the pattern was such that the value for the overall isotropic thermal parameter derived from a Wilson plot could be limited to $1.0 \text{ \AA}^2 < \bar{B} < 2.1 \text{ \AA}^2$. The initial thermal parameters for C and D were set at $\bar{B} = 1.5 \text{ \AA}^2$ with $B_C/B_D = \frac{1}{2}$.

Table 1. *Crystal data for C₂D₂*

Orthorhombic, space group *Acam* (No.64). Method: thermal neutron powder diffraction.

$a = 6.193$ (3) Å	$\lambda = 1.848$ (1) Å
$b = 6.005$ (3)	$T = 4.2$ K
$c = 5.551$ (3)	$D_c = 0.902$ g cm ⁻³
$V = 206.4$ (3) Å ³	$Z = 4$

Structure refinement

The least-squares isotropic refinement of the *Acam* model was carried out by the *ORXFLS3* program (Busing *et al.*, 1971). The function minimized was $\sum w(F_o^2 - F_c^2)$. The residuals are $R_1 = \sum \Delta F / \sum F_o$, $R_2 = \sum (F_o^2 - F_c^2) / \sum F_o^2$ and $R_w = \sqrt{\{ \sum [w(F_o^2 - F_c^2)]^2 / \sum (wF_o^2)^2 \}}$. The integrated intensities were weighted by the reciprocal squares of the estimated statistical error or by the standard deviation of the observation, whichever was smaller. The weighting scheme applied to the F^2 refinement was tested for bias (Cruickshank & Robertson, 1953) and appropriate adjustments were made where necessary. The coherent scattering amplitudes for C and D by Bacon (1972) were used. The positional and isotropic temperature parameters are in Table 2. Details of the refinement with the values given for unobserved reflexions are in Table 3. The intensities for the unobserved peaks were estimated on the basis of the local statistical error for the background by assuming that the maximum height of the reflexion = $\sqrt{I_b/2}$. The error for this value was set at one half. For computational reasons crystallographically equivalent positions were treated as occupied by 4×1 atoms. In scaling, the observed integrated intensities corrected

Table 2. *Fractional positional parameters ($\times 10^3$) and isotropic temperature parameters ($\times 10$)*

Final R values after 4 cycles of isotropic refinement: $R_1 = 5.6\%$, $R_2 = 7.1\%$, $R_w = 4.2\%$.

	x	y	z	$B(\text{\AA}^2)$
C	60.5 (4)	75.7 (4)	0	10 (2)
D	169.8 (6)	212.5 (6)	0	24 (1)

Table 3. *Observed and calculated diffraction maxima data for a wavelength $\lambda = 1.848$ (1) Å*

The columns from left to right are: Miller indices, observed and calculated positions in 2θ , observed and calculated ($\times 16$) values for $|F|^2$ and intensities. The figures in parentheses are estimated standard deviations tested for bias and in units of the last significant digit.

Parameters used for the structure-factor calculations: C: $x = 0.0605$, $y = 0.0757$, $B = 1.01$ Å²; D: $x = 0.1698$, $y = 0.2125$, $B = 2.40$ Å².

<i>hkl</i>	POSOBS	POSCAL	F ² OBS	F ² CAL	IOBS	ICAL
111	31.50	31.50	382 (5)	374	3055 (34)	2994
200	34.78	34.73	16 (2)	18	32 (4)	36
020	35.86	35.85	25 (2)	34	50 (4)	69
002	38.90	38.90	1796 (37)	1615	3592 (73)	3229
120	40.00	40.00	216 (2)	195	854 (8)	781
211	44.03	44.03	479 (9)	497	3829 (72)	3977
220	50.77	50.78	270 (10)	301	1081 (41)	1202
202	53.11	53.12	37 (10)	21	148 (38)	82
022	53.91	53.93	18 (4)	24	72 (16)	97
122	57.03	57.03	201 (7)	174	1610 (54)	1391
311	60.23	60.24	9 (1)	10	75 (2)	77
131	61.67	61.73	9 (1)	9	69 (1)	70
†222		65.77		269		
†320	65.82	65.82		192	5855 (78)	5492
†113		65.86		322		
231	70.15	70.12	4 (1)	5	36 (3)	38
400	73.27	73.30	38 (1)	38	77 (3)	77
213	74.01	74.01	430 (11)	384	3437 (89)	3072
040	—	76.00		12	31‡	24
140	78.62	78.61	24 (1)	23	95 (2)	95
†322		79.18		180		
†411	79.18	79.37		30	1480 (16)	1685
331	83.26	83.26	124 (1)	123	990 (9)	1006
004	83.51	83.51	1163 (6)	1167	2326 (11)	2333
420	84.40	84.38	41 (4)	43	164 (5)	169
†402		86.25		32		
†240	86.32	86.34		84	501 (10)	464
313	86.97	86.97	15 (1)	11	118 (28)	84
133	—	88.28		5	34†	43
042	—	88.85		3	35‡	37
142	91.43	91.39	20 (3)	18	160 (22)	140
204	93.72	93.74	52 (7)	28	207 (15)	110
024	—	94.41		7	51‡	28
233	95.92	95.94	17 (8)	9	139 (65)	67
†124		96.97		124		
†422	97.00	97.13		37	1414 (35)	1283
†242		99.09		75		
†340	99.13	99.15		255	1950 (75)	1618
431	101.21	101.21	751 (7)	736	6007 (56)	5884

† Reflexions not included in the lattice-parameter and structure-factor refinement.

‡ Estimated values for reflexions not observed based on the background fluctuation.

for the geometrical factor were divided by $10 \times (0.9094)^2$. In Table 4 the derived bond lengths and some distances between atoms in neighbouring molecules are given.

Table 4. *Interatomic distances* (Å)

C≡C	1.18 (1)
C—D	1.06 (2)
DC≡CD	3.31 (1)
D···D	2.95 (2) (nearest)
C···C	3.64 (2) (nearest)
D···D	3.13 (2) (in-plane)
C···D	2.73 (2) (in-plane)
C···D	3.34 (2) (out-of-plane)

Discussion

The results of this work agree well with the D_{2h}^{18} model proposed by several authors on the basis of the spectro-

scopic investigations. The final atomic arrangement (Fig. 1) differs slightly from the initial model as (i) the molecules lie in slightly off-diagonal directions with an angle of 39.5 (2)° between the molecular axis and the crystal b axis and (ii) the C—C bond length shows an apparent shortening. This effect can be assigned to molecular angular vibrations (Cruickshank, 1956). To calculate the corrected bond lengths of the vibrating molecule the anisotropic temperature parameters should be known. Several attempts were made to refine the structure anisotropically but no consistent set of thermal parameters could be obtained; this was assumed to arise from the limited information content of the powder pattern.

The nearest distances between atoms of the same kind in neighbouring molecules are in Table 4. The in-plane non-bonded distances are of the order proposed by Ito *et al.* whereas the values calculated for

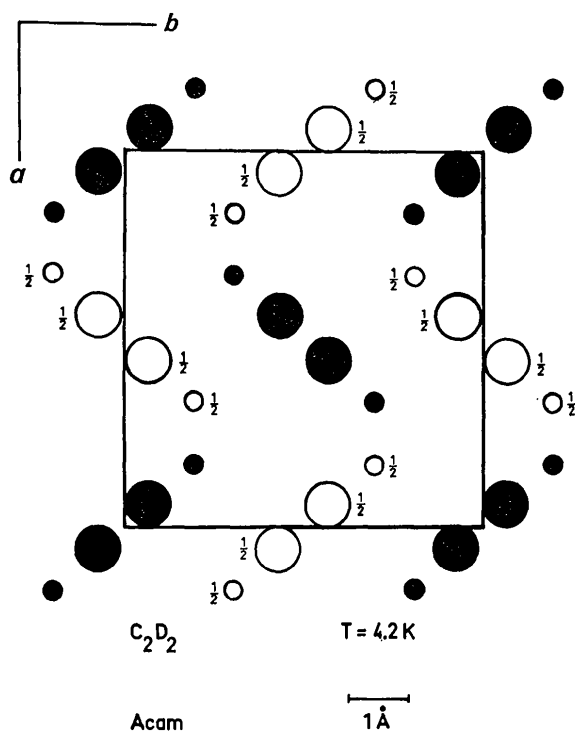


Fig. 1. The unit cell of the orthorhombic low-temperature phase with the most probable *Acam* 8(*f*) space-group arrangement. The large circles represent the carbon atom positions, the small circles are those of the deuterium atoms. The full (●) circles are in the plane of the page; the open (○) ones are the equilibrium positions of atoms at $z = c/2$.

two neighbouring molecules in different layers can only be derived after the structure in detail is known. Owing to the relatively short *c* axis the small value for the D...D distance for two molecules in different planes is expected. This should have a strong influence on the repulsion energy (Hashimoto, Hashimoto & Isobe, 1971).

The observed volume of the unit cell, $206.4(3) \text{ \AA}^3$, is of the order of that in the cubic phase, $V_{\text{calc}} = 231 \text{ \AA}^3$ (156 K). The density of solid C_2D_2 was not measured at liquid helium temperature. The value for C_2H_2 at 77 K, $D_m = 0.81 \text{ g cm}^{-3}$ (*Gmelins Handbuch der anorganischen Chemie*, 1970; *Beilsteins Handbuch der organischen Chemie*, 1958) was used as a basic value. Taking

into account the isotopic replacement of H by D and allowing for lattice shrinkage, an estimated value $D_e = 0.9 \text{ g cm}^{-3}$ was found. This agrees with the experimental density.

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