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The Crystal Structure of Dimethyl Acetylene at −50° C*

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The crystal structure of dimethyl acetylene (m.p. −32° C.) has been determined. The unit cell is tetragonal, with $a = 5{\cdot}42$, $c = 6{\cdot}89$ Å, and with two molecules per unit cell. The space group is $P4_2/mnm$. The bond lengths are C–C $1{\cdot}45_7$ Å and C≡C $1{\cdot}21_1$ Å.

Introduction

Dimethyl acetylene is one of the simplest organic molecules containing a conjugated system of single and triple carbon-to-carbon bonds. Its molecular structure was investigated by Pauling, Springall & Palmer (1939) by the method of electron diffraction; they reported single and triple bond lengths of 1·47 and 1·20 Å. The present study was undertaken to obtain an independent check of those results and to furnish a more direct basis for comparison with bond lengths determined in recent X-ray diffraction studies of two closely related compounds: dimethyl diacetylene (Himes & Harris, 1953), and dimethyl triacetylene (Jeffrey & Rollett, 1952).

Experimental

Dimethyl acetylene melts at −32° C. and boils at 27° C. A small amount of the liquid was sealed into a thin-walled glass capillary tube (inside diameter 0·5 mm.) and mounted on the goniometer arcs of a precession camera. The liquid was frozen and single crystals were grown and oriented, using standard low-temperature techniques. X-ray diagrams were obtained at −50±5° C.; filtered Mo radiation was used. Complete data were recorded in three dimensions, out to $\sin\theta/\lambda = 0{\cdot}71$.

Dimethyl acetylene crystallizes in the tetragonal system; unit cell dimensions are

$$a = 5{\cdot}42,\quad c = 6{\cdot}89 \pm 0{\cdot}02 \text{ Å}\,.$$

The volume of the unit cell is 202 Å^3; there are two molecules per unit cell and the calculated density is 1·13 g.cm.$^{-3}$. The Laue symmetry is $4/mmm$. Systematic absences are: $(h0l)$ with $h+l$ odd, and $(0kl)$ with $k+l$ odd; the possible space groups are $P4_2nm$, $P\bar{4}n2$ and $P4_2/mnm$.

Of the 125 independent reflections within the range of the precession camera (using Mo $K\alpha$ radiation and a 30° precession angle) 65 were sufficiently intense to be measured and used in the structure determination. Intensities were estimated by visual comparison with calibrated intensity strips and the usual Lorentz and polarization corrections were applied. Since μr was about 0·02, no absorption corrections were needed.

Structure determination

The intensities of reflections with the same h and k indices and with l even decreased monotonically with increasing l; the same effect was observed for corresponding reflections with odd l indices. The molecules could therefore be assumed to lie in layers perpendicular to the c axis, separated by $\frac{1}{2}c$. The overall length of the molecule is approximately $\sqrt{2}$ times the length of the a axis, indicating that the molecules are oriented parallel to the [110] direction.

A survey of the available equivalent positions in the three possible space groups showed that the asymmetric unit of structure is half of one molecule (two carbon and three hydrogen atoms). The sterically permissible fourfold positions in these space groups are all equivalent to positions $4(f)$ of $P4_2/mnm$:

$$x, x, 0;\quad \bar{x}, \bar{x}, 0;\quad \tfrac{1}{2}+x, \tfrac{1}{2}-x, \tfrac{1}{2};\quad \tfrac{1}{2}-x, \tfrac{1}{2}+x, \tfrac{1}{2}\,.$$

Dimethyl acetylene undergoes a structural transformation at −119° C. This has been interpreted (Yost, Osborne & Garner, 1941) as due to the onset of free rotation of the methyl groups. This would raise the point symmetry of the molecule to mmm, which is the molecular symmetry needed for $P4_2/mnm$. The three possible space groups differ, so far as this structure is concerned, only with respect to the permitted hydrogen atom positions. However, the resulting differences in hydrogen-atom contributions to the X-ray scattering are very small and are probably in all cases much less than the experimental error of intensity measurement. In the calculations of structure factors it was assumed that the hydrogen atoms were freely rotating about the C–C axis.

So far as the positions of the carbon atoms are concerned, the determination of the structure was a two-parameter problem. Actually, since the molecule clearly lay along the [110] direction, and since its

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configuration and approximate bond lengths were known from previous work, the determination was effectively a 'no-parameter' problem, an almost unique occurrence among organic crystals.

A map (Fig. 1) of the electron density at $z = 0$ was computed. In no case did the inclusion of hydrogen-atom contributions in the calculation of structure factors change the signs of the Fourier coefficients.

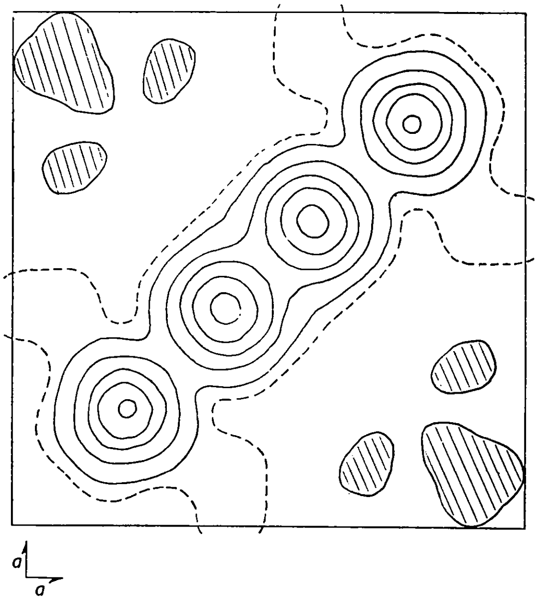


Fig. 1. Electron density at $z = 0$. Solid contour lines are drawn at intervals of 1 e.Å^{-3}. The broken line corresponds to an electron density of $\frac{1}{2}$ e.Å^{-3}. Negative regions are shaded (maximum 'negative' electron density is less than $\frac{1}{3}$ e.Å^{-3}).

After correction for series-termination effects by the 'back shift' procedure, the parameters of the carbon atoms were found to be: $x(C_1) = 0{\cdot}2310$; $x(C_2) = 0{\cdot}4210$.

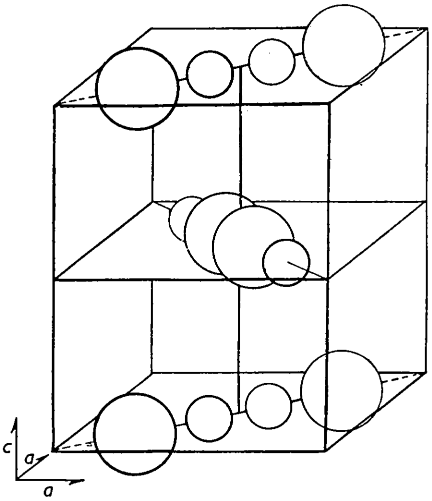


Fig. 2. Arrangement of dimethyl acetylene molecules in the unit cell. Small circles represent carbon atoms; large circles represent methyl groups.

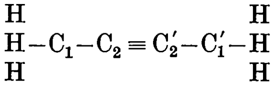
Discussion

The arrangement of molecules in the unit cell is shown in Fig. 2. The molecules lie in planes perpendicular to the c axis; the layers are separated by $\frac{1}{2}c$ ($3{\cdot}44_5$ Å), i.e. approximately the separation of layers of carbon atoms in graphite.

The distance between carbon atoms in adjacent, collinear methyl groups is only 3·54 Å, indicating an effective methyl group radius of 1·77 Å. It therefore appears likely that the rotations of methyl groups in adjacent molecules are synchronized; independent rotations of methyl groups would lead to larger effective radii.

Bond lengths in dimethyl acetylene and two similar molecules with conjugated single and triple carbon to carbon bonds are

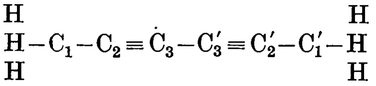
Dimethyl acetylene



$$\begin{array}{c}\mathrm{H}\qquad\qquad\qquad\qquad\mathrm{H}\\ \mathrm{H-C_1-C_2\equiv C_2'-C_1'-H}\\ \mathrm{H}\qquad\qquad\qquad\qquad\mathrm{H}\end{array}$$

$$C_1-C_2 = 1{\cdot}457\ \text{Å};\quad C_2-C_2' = 1{\cdot}211\ \text{Å}\,.$$

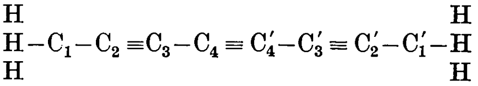
Dimethyl diacetylene



$$\begin{array}{c}\mathrm{H}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{H}\\ \mathrm{H-C_1-C_2\equiv C_3-C_3'\equiv C_2'-C_1'-H}\\ \mathrm{H}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{H}\end{array}$$

$$C_1-C_2=1{\cdot}466\ \text{Å};\quad C_2-C_3=1{\cdot}199\ \text{Å};\quad C_3-C_3'=1{\cdot}375\ \text{Å}\,.$$

Dimethyl triacetylene



$$\begin{array}{c}\mathrm{H}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{H}\\ \mathrm{H-C_1-C_2\equiv C_3-C_4\equiv C_4'-C_3'\equiv C_2'-C_1'-H}\\ \mathrm{H}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{H}\end{array}$$

$$C_1-C_2 = 1{\cdot}47\ \text{Å};\quad C_2-C_3 = 1{\cdot}20\ \text{Å};\quad C_3-C_4 = 1{\cdot}38\ \text{Å};\quad C_4-C_4' = 1{\cdot}20\ \text{Å}\,.$$

The magnitude of the discrepancy coefficient, R, $[= \Sigma||F_o|-|F_c||\div\Sigma|F_o|]$ was 10·1% for all observed reflections. The value of R increased to 13·4% if hydrogen-atom contributions were omitted from the calculation of structure factors. The difference between the calculated and 'observed' values of $F_{(002)}$ is large and is probably due to extinction; if this reflection is disregarded in the calculation of R, the latter drops to 8·5%. Calculated and 'observed' structure factors are listed in Table 1. Values of F_c were computed using an anisotropic temperature factor according to the following equation:

$$F_c = F \exp\left[-\{\alpha(h^2+k^2)a^{*2}+\gamma l^2c^{*2}\}\right],$$

with $\alpha = 0{\cdot}045$ Å^2 and $\gamma = 0{\cdot}03$ Å^2.

The electron-density curvatures of the carbon atoms are: $C_1 = -41{\cdot}2$ e.Å^{-5}; $C_2 = -36{\cdot}6$ e.Å^{-5}. Calculations based on Cruickshank's method (1949) indicate that the standard deviations of atomic positions and bond lengths are:

Table 1. *Calculated and 'observed' structure factors*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
002	27·4	+35·1	512	1·7	− 1·0	125	2·2	− 1·7
004	12·4	+12·5				141	1·8	+ 1·5
006	5·5	+ 5·2	212	1·2	+ 1·5	143	1·6	+ 1·1
008	2·1	+ 2·1	214	1·5	+ 0·9	321	1·4	+ 1·4
			410	2·6	+ 3·0	323	1·6	+ 0·9
200	6·0	− 6·8	412	2·3	+ 2·4			
202	2·8	− 3·6	414	1·8	+ 1·6	111	23·2	−23·6
400	1·6	+ 1·8	230	5·7	+ 5·1	113	9·0	− 9·3
402	1·5	+ 1·9	232	4·3	+ 3·9	115	3·2	− 4·3
600	1·9	− 1·9	234	2·3	+ 2·4	117	2·0	− 1·8
602	1·8	− 1·6	236	1·8	+ 1·3	311	2·0	+ 2·7
						313	1·4	+ 1·7
220	9·7	+10·7	101	12·5	−11·1	511	1·8	− 1·9
222	7·1	+ 7·2	103	7·3	− 7·5	513	1·8	− 1·5
224	3·0	+ 3·9	105	3·3	− 2·9			
226	1·9	+ 2·0	107	1·8	− 1·3	331	5·3	− 5·7
420	2·6	− 2·9				333	4·8	− 4·2
422	2·3	− 2·5	301	2·5	− 2·6	335	2·5	− 2·4
424	2·0	− 1·7	303	1·6	− 1·6			
			501	2·6	+ 2·6	221	4·3	− 6·1
110	12·3	+14·8	503	2·0	+ 2·0	223	3·0	− 3·3
112	9·3	+ 9·6	505	1·7	+ 1·2	225	2·0	− 1·8
114	4·4	+ 4·0				227	1·8	− 0·8
116	2·2	+ 1·8	121	7·2	− 6·6	421	2·0	− 1·7
510	1·6	− 1·2	123	3·6	− 3·4	423	1·9	− 1·3

$$C_1,\ 0{\cdot}007\ \text{Å};\ C_2,\ 0{\cdot}0085\ \text{Å};\ C_1{-}C_2,\ 0{\cdot}010\ \text{Å};\ \text{and}\ C_2{\equiv}C_3,\ 0{\cdot}017\ \text{Å}.$$

The 'true' standard deviations may be somewhat greater than shown above; in those calculations it is assumed that the atoms are in general positions, and Cruickshank & Rollett (1953) have recently shown that the estimated error of atomic coordinates should be significantly increased when atoms are in special positions. In any event, the differences between the bond lengths determined in this investigation and those reported for corresponding bonds by Himes & Harris (1953) and by Jeffrey & Rollett (1952) are less than the standard deviations of the bond lengths and are therefore of no statistical significance.

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