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The Structure Parameters of Dimethyldiacetylene

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Electron diffraction studies have been carried out on the structure of dimethyldiacetylene. The following structure parameters have been obtained, C-H = 1.09 Å, C≡C = 1.208 Å, C_2-C_4 = 1.377 Å, C_1-C_2 = 1.450 Å and HCC = 111.6°

Accurate determinations of bond distances in conjugated systems seem to be of considerable interest. A new electron diffraction apparatus now in operation in Oslo has made it possible to determine internuclear distances with a rather high accuracy. A series of compounds containing conjugated systems is now being studied with the new technique. The investigations include dimethyldiacetylene, vinylacetylene, butadiene and *cyclo*octatetraene. In the present note the results for dimethyldiacetylene will be described.

As the new electron diffraction apparatus and the calculation technique have been described elsewhere [1,2] only a few comments concerning the procedure will be given. The intensity values obtained in this case range from about $s = 1$ up to $s = 60$ Å^{-1}. From the intensity data radial distribution curves have been calculated. Various damping factors have been used. The radial distribution curve presented in Fig. 1. is calculated by applying a damping factor of $e^{-0.0015\,s^2}$. The inner complex of peaks ranging from about 1 Å until 1.6 Å contains the bond distances. The peaks beyond this point contain internuclear distances between atoms which are not directly linked together. In the curve of Fig. 1 the inner complex of peaks is not very well resolved. A better resolution is obtained by applying a smaller damping factor or simply by omitting the damping factor altogether. Detailed studies of this inner complex in the various radial distribution curves, including the use of normal curves, lead to the four first entries in the first column of Table 1. A study of the outer part of the radial distribution curve gives the other internuclear distances listed in the table.

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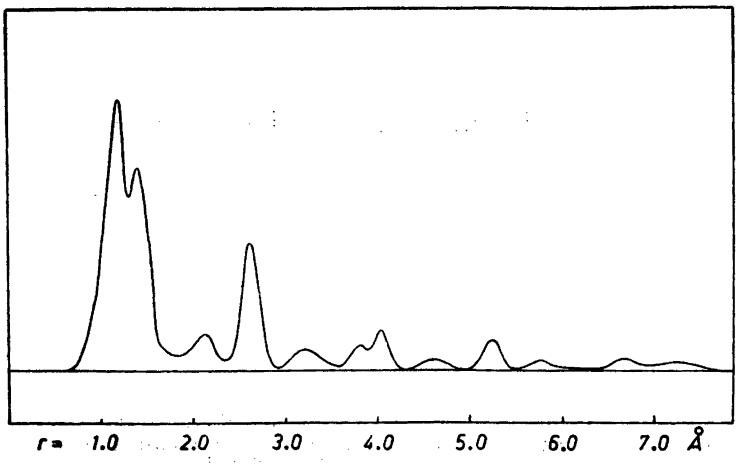

Fig. 1. Radial distribution curve of dimethyldiacetylene.

The geometry of the carbon skeleton is determined by three parameters if a linear arrangement is assumed. These three parameters were obtained from the nine experimental C—C distances by a least-square procedure. The two parameters necessary for the location of the hydrogen atoms were calculated in a similar way. The best structural parameters thus obtained from our experiment are the following: C—H = 1.09 Å, $C_2 \equiv C_3$ = 1.208 Å, C_3—C_4 = 1.377 Å, C_1—C_2 = 1.450 Å and ∠ HCC = 111.6°. These values are in good agreement with those obtained by Jeffrey and Rollett for dimethyltriacetylene [3]. On the basis of the five parameters obtained all the internuclear C—C and C—H distances were calculated. These values are listed in the second column of the table. The correspondence between the values read off from the radial distribution curves and those calculated from the best parameters is in general remarkably good. For the carbon skeleton the average deviation between the two sets of distances is between 0.2 and 0.3 %. This indicates a rather high accuracy in the distance determination, though it does not give any indication concerning the absolute values. Estimations of the various sources of errors, and comparison between results obtained by our electron diffraction procedure and microwave studies seem to indicate that our scale error is about of the same order of magnitude as the deviation observed within a single radial distribution curve [4].

The positions of the hydrogen atoms are not determined with the same degree of accuracy as the carbon atoms. The C—H bond distance does not lead to a resolved peak in the radial distribution curve, and the longer C—H distances are not well suited for accurate determinations of the C—H bond and the HCC angle.

By studying the half widths of the peaks of the radial distribution curves experimental values for the root mean squares of the deviations from the equilibrium distances have been calculated. These values for the C—H bond and

Table 1. Experimental and calculated distances and average displacements from equilibrium, all in Ångstrom units.

	r_{exptl}	r_{calc}	$(\overline{l^2})^{1/2}_{exptl}$	$(\overline{l^2})^{1/2}_{calc}$
C –H	1.08	1.09	0.077	0.075
$C_2 \equiv C_3$	1.210	1.208	0.040	0.036
$C_3 - C_4$	1.379	1.377	0.061	0.044
$C_1 - C_2$	1.452	1.450	0.061	0.045
$C_2 - C_4$	2.590	2.585	0.050	0.049
$C_1 - C_3$	2.661	2.658	0.066	0.049
$C_2 - C_5$	3.778	3.793	0.049	0.053
$C_1 - C_4$	4.026	4.035	0.060	0.057
$C_1 - C_5$	5.228	5.243	0.072	0.059
$C_1 - C_6$	6.661	6.693	0.080	0.065
$H - C_2$	2.110	2.110		
$H - C_3$	3.220	3.222		
$H - C_4$	4.571	4.550		
$H - C_5$		5.734		
$H - C_6$	7.201	7.166		

all the C—C distances are listed in the third column of the table. In the last column of the table are listed the corresponding theoretical values calculated applying the stretching vibrations known from spectroscopical data [5] assuming a temperature of 310°K. As one sees, the correspondence between these sets of values obtained in two entirely different ways is fairly good.

A comparison between the experimental and calculated distances in Table 1 seems to indicate a systematic deviation between the two sets of values for the largest C—C distances. For the four largest C—C distances the experimental values are smaller than the calculated ones, while the opposite is the case for the shorter distances. This fact might be explained by taking into consideration the bending vibrations of the molecule. These vibrations should lead to a decrease in the long distances. If this argument is correct, the longest C—C distances should perhaps have been omitted in the least-square procedure. A correction for this effect, however, would lead only to very small changes in the structure parameters.

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Added in proof: Since this article was submitted for publication an article concerning the structure of dimethylacetylene has been published [6]. In this article a report from Ohio State University has been quoted dealing with the structure of dimethyldiacetylene [7]. Unfortunately the latter was unknown by the present authors. Both compounds were studied by X-ray methods, and the agreement with the present work is very good.

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