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An Electron Diffraction Investigation of the Molecular Structure of Monobromodiacetylene (Br—C≡C—C≡C—H) in the Vapour Phase

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The electron diffraction intensities are consistent with a linear arrangement of atoms. The following values were obtained for bond lengths: r_a(Br–C)=1.790(5) Å, r_a(C–C)=1.385(8) Å, r_a(C–H)=1.10(5) Å, and an average C≡C triple-bond r_a(C≡C)= 1.223(4) Å. The values in parentheses are estimated standard deviations.

Most of the important shrinkage parameters and mean amplitudes of vibration are determined and compared with parameters calculated from spectroscopic data.

Both diagonal and non-diagonal weight matrices have been used in the least-squares refinements, and the results thus obtained have been compared.

Several investigations of the molecule Br–C≡C–C≡C–H exist.** Infrared spectra have been published, including force constants, mean amplitudes of vibration and shrinkage parameters.[1] Far infrared spectra have also been reported.[2] An attempt to observe the microwave spectrum of the molecule was unsuccessful.[3] The spectra can be interpreted in terms of a linear structure.[1,2]

The present investigation was started to obtain the bond distances of the molecule, and to compare the vibrational parameters obtained by electron diffraction with those calculated from spectroscopic data.

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EXPERIMENT AND TREATMENT OF DATA

The compound was synthesized and purified as described elsewhere.[4]

Diffraction photographs were obtained in the usual way with the Oslo apparatus.[5] The nozzle temperature was approximately −5°C. The electron wavelength was determined from a gold foil diffraction pattern and corrected according to an experiment with CO_2. Plates from two different nozzle-to-plate distances of about 48 cm (48.295) and 19 cm (20.133) were obtained. The corresponding electron wavelengths were 0.064968 Å and 0.064826 Å, determined with a standard deviation of *ca.* 0.14 %.

Four plates from each camera distance were photometered, and the intensity data treated in the usual way.[6]

A statistical analysis of each set of data was carried out on the modified molecular intensity curves.[7,8] The general trend in the curves for standard deviations of the average intensities is the same as earlier obtained in this laboratory.[7,8]

Individual curves for both sets of data show satisfactory mutual agreement. The two average curves were used in the refinements. The 48 cm data cover the s range 1.75−19.375 Å^{-1} with $\Delta s = 0.125$ Å^{-1}, and the 19 cm data cover the s range 6.25−42.75 Å^{-1} with $\Delta s = 0.25$ Å. Intensities in the s range 31.25−42.75 Å^{-1} were not included in the final refinements because of noise.

Average intensity curves, modified [6] by

$$s/|f_C'|\,|f_{Br}'|$$

are presented in Fig. 1. The curves show satisfactory mutual agreement in the overlap region.

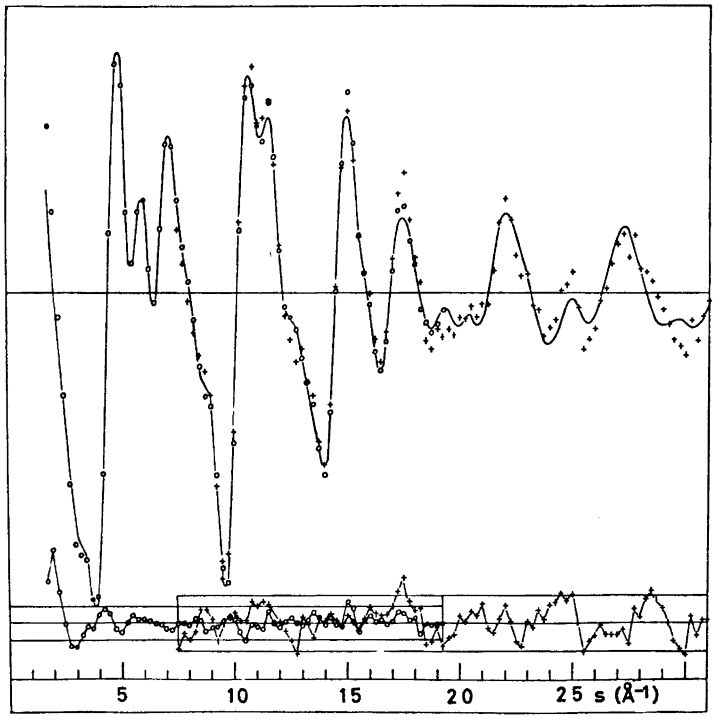

Fig. 1. 48 cm (O) and 19 cm (+) experimental average intensity curves, and the average theoretical intensity curve. Residuals corresponding to parameters in Table 1, column b_2, are plotted below together with the experimental error limits. On the 48 cm curve, only every second point is plotted.

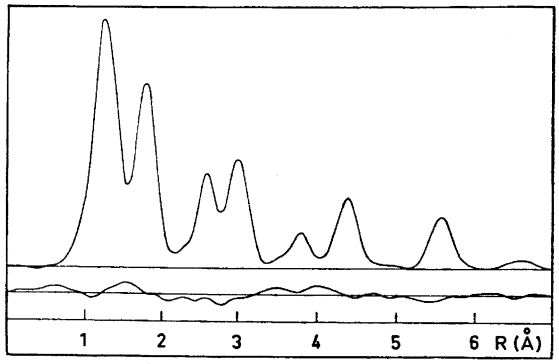

Fig. 2. Experimental radial distribution function (RD curve), and residuals corresponding to parameters in Table 1, column b_2. An artificial damping constant equal to 0.0036 Å^2 has been applied.

The experimental radial distribution (RD) function [6] is presented in Fig. 2. Approximate values for the bond lengths were obtained from the RD curve. The bond distances (Br—C_1≡C_2—C_3≡C_4—H) C—H (1.10 Å), C≡C (1.22 Å) and C—C (1.39 Å) contribute to the peak between 0.5 Å and 1.6 Å, while the peak between 1.6 Å and 2.1 Å corresponds to the bond distance Br—C (1.79 Å). The contributions from non-bonded distances are found in the range 2.1—7.0 Å. The dominating peaks in this range correspond to $C_1 \cdots C_3$ (2.60 Å), $Br \cdots C_2$ (3.00 Å), $C_1 \cdots C_4$ (3.80 Å), $Br \cdots C_3$ (4.38 Å), $Br \cdots C_4$ (5.58 Å), and Br···H (6.65 Å). The contributions from $C_3 \cdots H$ (2.30 Å), $C_2 \cdots H$ (3.67 Å), and $C_1 \cdots H$ (4.88 Å) are too small to be identified.

LEAST-SQUARES REFINEMENTS

The refinements [6] were carried out using the two average intensity curves simultaneously. Preliminary results from the 48 cm data alone have been reported elsewhere.[7] An individual scale factor was refined for each curve.

For each set of data an individual weight matrix was applied. A diagonal weight function was chosen taking into consideration the variation in the standard deviation for the intensities.[6,7] The relative weight between the two curves was chosen equal to 0.4. A reasonable change in the relative weight resulted in negligible changes in the parameters refined, while the standard deviations for parameters were influenced more by such changes, as might be expected.[7,8]

Two types of refinements were carried out:

I. A linear model was used to introduce relations between the internuclear distances due to geometry. The bond distances were chosen as independent parameters.[6] Shrinkage parameters calculated by Cyvin *et al.*[1,9] were included in the refinements with small modifications. The shrinkage parameters given by Cyvin *et al.* refer to the mean distance (r_g), while the distance r_a is the one which is obtained from the refinements.[6] Results using two different weight matrices are presented in columns a_1 (diagonal) and b_1 (non-diagonal) in Table 1.

Table 1. Least-squares results for $Br-C_1\equiv C_2-C_3\equiv C_4-H$.

	a_1	a_2	b_1	b_2	c_1	c_2	d_1	d_2
$r(C-H)$	1.1246 (168)	1.1028	1.1071 (334)	1.1028	2.0		0.5	
$r(C\equiv C)$	1.2252 (9)	1.2305 (11)	1.2242 (21)	1.2289 (35)	2.3	3.2	0.5	0.5
$r(C-C)$	1.3859 (15)	1.4011 (24)	1.3821 (36)	1.3945 (77)	2.4	3.2	1.1	0.9
$r(Br-C)$	1.7906 (11)	1.7918 (11)	1.7936 (28)	1.7960 (37)	2.5	3.4	1.1	1.1
$r(C_3\cdots H)$	2.3083 (167)		2.2905 (336)		2.0		0.5	
$r(C_1\cdots C_3)$	2.6016 (15)	2.5959 (19)	2.5969 (31)	2.5942 (46)	2.1	2.4	1.5	0.4
$r(Br\cdots C_2)$	3.0098 (12)	3.0100 (20)	3.0115 (29)	3.0082 (52)	2.4	2.6	0.6	0.3
$r(C_2\cdots H)$	3.6853 (170)		3.6637 (336)		2.0		0.6	
$r(C_1\cdots C_4)$	3.8102 (19)	3.8262 (79)	3.8046 (41)	3.8287 (163)	2.2	2.1	1.4	0.2
$r(Br\cdots C_3)$	4.3818 (16)	4.3729 (31)	4.3798 (30)	4.3753 (51)	1.9	1.6	0.7	0.5
$r(C_1\cdots H)$	4.8939 (169)		4.8714 (339)		2.0		0.7	
$r(Br\cdots C_4)$	5.5834 (19)	5.5853 (41)	5.5804 (35)	5.5811 (60)	1.8	1.5	0.9	0.7
$r(Br\cdots H)$	6.6638 (169)	6.6369 (414)	6.6440 (335)	6.6450 (497)	2.0	1.2	0.6	0.2
$u(C=C)$	.0534 (18)	.0510 (15)	.0467 (37)	.0484 (37)	2.1	2.5	1.8	0.7
$u(Br-C)$	.0617 (22)	.0635 (18)	.0574 (63)	.0598 (61)	2.9	3.4	0.7	0.6
$u(C_1\cdots C_3)$	.0449 (33)	.0480 (27)	.0471 (60)	.0482 (58)	1.8	2.1	0.4	0.0
$u(Br\cdots C_2)$	.0675 (31)	.0699 (26)	.0661 (69)	.0680 (67)	2.2	2.6	0.1	0.3
$u(Br\cdots C_3)$	.0742 (42)	.0761 (36)	.0630 (71)	.0657 (69)	1.7	1.9	1.6	1.5
$u(Br\cdots C_4)$	.0770 (52)	.0800 (46)	.0820 (68)	.0851 (67)	1.3	1.5	0.7	0.7
$\delta(C_1\cdots C_3)$	(.0095)	.0357 (36)	(.0095)	.0291 (109)		3.0		0.6
$\delta(Br\cdots C_2)$	(.0060)	.0123 (25)	(.0060)	.0165 (72)		2.9		0.6
$\delta(C_1\cdots C_4)$	(.0260)	.0359 (88)	(.0260)	.0235 (205)		2.3		0.6
$\delta(Br\cdots C_3)$	(.0198)	.0504 (45)	(.0198)	.0440 (114)		2.5		0.6
$\delta(Br\cdots C_4)$	(.0434)	.0686 (57)	(.0434)	.0672 (143)		2.5		0.1
$\delta(Br\cdots H)$	(.0876)	.1198 (416)	(.0876)	.1062 (515)		1.2		0.3
k (48 cm)	14.96 (16)	15.37 (14)	14.72 (49)	15.03 (49)	3.1	3.5		
k (19 cm)	14.39 (39)	14.84 (35)	13.73 (67)	14.19 (69)	1.7	2.0		
R_1	14.3	13.0	15.0	13.7				
R_2	10.4	9.2	11.1	9.9				
R_3	10.4	9.2	28.6	28.2				
$\mathbf{V'PV}\times 10^{-5}$	5.855	4.623	1.134	1.105				

Distances (r), mean amplitudes of vibration (u), and shrinkage parameters (δ) are in Å (standard deviations in parentheses).

The k-values are scale factors for the two camera distances, and the quantities R_1, R_2, R_3 (agreement factors, or R-factors) and **V P V** (the weighted sum of squared residuals) are defined in a previous paper.[7]

For all refinements the diagonal weight w for the *48 cm data* was given by $w=\exp(-0.60(s-3.5)^2)$ for $s<3.5$, $w=1.0$ for $3.5\leq s\leq 18.0$, $w=\exp(-0.1(s-18.0)^2)$ for $s>18.0$. The corresponding weight w for the *19 cm data* was given by $w=w_0\exp(-0.7(s-8.5)^2)$ for $s<8.5$, $w=w_0$ for $8.5\leq s\leq 20.0$, $w=w_0\exp(-0.0025(s-20.0)^2)$ for $s>20.0$, where $w_0=0.4$.

The off-diagonal elements of ϱ^{-1} are $p_2=-0.64$ and $p_3=0.144$ for the 48 cm data, while $p_2=-0.60$ and $p_3=0.125$ for the 19 cm data. These values are quite close to the average values found for several sets of data from our laboratory.[7]

Results for diagonal weight matrices are in columns marked by a, off-diagonal elements have been included in columns marked b, and the ratios in columns c are σ_b/σ_a (F-values), where σ is the standard deviation given in parentheses. The difference between values in columns b and a

II. All distances were treated as independent parameters. Some of them did not refine and were given the values of columns a_1 or b_1. The bond distance C–H could not be refined, and after some trial and error that parameter was fixed on the value 1.1028 Å, which is close to the value obtained in column b_1. Most of the non-bonded distances were determined and the corresponding shrinkage parameters. Results using two different weight matrices are presented in columns a_2 (diagonal) and b_2 (non-diagonal) in Table 1.

In both types of refinements some mean amplitudes of vibration (u-values) could not be refined, and values calculated by Cyvin *et al.*[1] were used for those distances.

The two bond distances $r(C_1 \equiv C_2)$ and $r(C_3 \equiv C_4)$ are expected to be different, but the difference is probably small. An attempt to determine this difference in bond length was not successful.

Small differences in the parameters obtained from the two weight matrices might be expected.[7,8,10] The difference between values in columns b and a has been divided by the standard deviation (σ_b) in column b, and the absolute value of this ratio is found in columns marked d. The d-values for independent parameters are found in the range from 0.0 to 1.5, the average value being 0.6. For the u-values the situation is very much the same as for the geometrical parameters. The d-values are in most cases acceptable, however, some rather large values are found for $u(C \equiv C)$ and $u(Br \cdots C_3)$.

In columns marked c are given the ratios $F = \sigma_b/\sigma_a$ where σ_b is the standard deviation obtained with a non-diagonal weight matrix, while σ_a was obtained with a diagonal matrix. The results in c_2 illustrate that the F-values depend on the interatomic distance both for r and for the u-values.[7,8]

The decrease in the F-value with increasing distance may also be predicted from the formula given in Ref. 7 on p. 621. In Fig. 3 are presented the F-values from columns c_1 and c_2 together with the curve corresponding to the

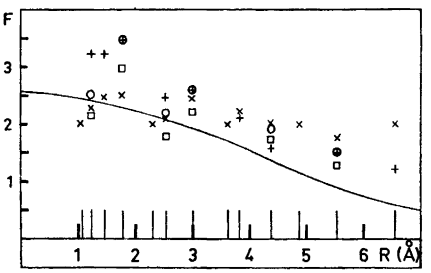

Fig. 3. F-values for distances (+) and u-values (○), corresponding to results in Table 1, column c_2; and F-values for distances (×) and u-values (□), corresponding to results in Table 1, column c_1. The curve was calculated according to the formula for F, given in Ref. 7.

has been divided by the standard deviation in column b, and the *absolute* value of this ratio is found in columns d.

In a_1, b_1, c_1, and d_1 the non-bonded distances were regarded as *dependent* parameters, and the geometrical restrictions correspond to a linear molecule. Shrinkage parameters calculated by Cyvin *et al.* were included in the least-squares refinements, with small modifications to obtain the shrinkage parameters consistent with the r_a distances.

In a_2, b_2, c_2, and d_2 all distances were independent parameters. The distances $C_3 \cdots H$, $C_2 \cdots H$, and $C_1 \cdots H$ could not be refined together with the other parameters, and values from columns a_1 and b_1 were used for these parameters. Nor could the distance C–H be refined together with the other parameters.

formula mentioned above. The curve is clearly predicting the general trend in the F-values, however, most of the F-values are a little larger than those calculated according to the formula. The formula predicts the same F-value for a distance r and the corresponding u-value. The results in Fig. 3 indicate that this is approximately the case.

The formula in Ref. 7 was derived assuming all distances and u-values to be independent parameters in the least-squares refinement. In accordance with this, the F-values from column c_2 (independent parameters) are seen to have the same trend as the curve, while the F-values from column c_1 (dependent parameters) have a more horizontal trend.

The correlation matrix [6,11] for the parameters in Table 1, column b_2, is presented in Table 2. The correlation coefficients for the parameters in column a_2 are very much the same as those in Table 2. Coefficients obtained with a diagonal weight matrix (column a_2) are usually smaller in absolute value compared with those obtained with a non-diagonal matrix. Correlation between refined parameters have been included in the calculation of standard deviation for dependent parameters.

The average experimental modified molecular intensity curves for the two camera distances are presented in Fig. 1. Theoretical intensities [6] were calculated according to the parameters in Table 1, column b_2. The residuals between theoretical intensities and experimental ones are plotted together with the experimental error limits for the average intensities. Twice the average standard deviation for the intensities was chosen as an experimental error limit. Practically all the residuals fall within the experimental error limits. A background adjustment in the inner part of the 48 cm curve could remove the rather large discrepancy in this region. However, we do not feel justified in doing so, and finally it should be remembered that the weight of the intensities in this region is small.

Table 2. Correlation coefficients (×100) for refined parameters corresponding to column b_2 in Table 1.

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	r(Br—C)	100																
2	r(C≡C)	3	100															
3	r(C—C)	−11	48	100														
4	r(Br···C_2)	2	−1	−6	100													
5	r(Br···C_3)	0	1	−1	−4	100												
6	r(Br···C_4)	0	−1	−2	1	1	100											
7	r(Br···H)	0	0	−1	0	−2	6	100										
8	r(C_1···C_3)	5	−5	2	−3	4	−1	0	100									
9	r(C_1···C_4)	2	−1	2	0	−2	0	1	−2	100								
10	u(Br—C)	−6	9	23	−6	1	−3	−1	−7	3	100							
11	u(C≡C)	1	12	32	−6	4	−2	−1	−9	1	32	100						
12	u(Br···C_2)	−12	12	20	−9	−1	−2	−1	4	1	34	33	100					
13	u(Br···C_3)	−5	7	20	−7	−2	−1	−1	1	4	30	25	24	100				
14	u(Br···C_4)	−7	8	18	−6	−3	−4	1	3	6	29	27	21	24	100			
15	u(C_1···C_3)	1	−4	4	−2	−2	−1	−1	−2	4	21	21	8	18	15	100		
16	k (48)	−7	10	33	−7	−2	−3	−2	−1	3	47	39	38	38	35	23	100	
17	k (19)	−11	15	36	−13	0	−4	−1	1	7	57	49	46	47	42	33	48	100

Table 3. Final structural parameters for $Br-C_1\equiv C_2-C_3\equiv C_4-H$.

	Distance (r_a) Å	Shrinkage (δ) Å		Mean amplitudes of vibration (u) Å	
C–H	1.10(5)				.074 [b]
C≡C	1.223(4)			.048(4)	.036
C–C	1.385(8)				.043
Br–C	1.790(5)			.059(6)	.040
$C_1\cdots C_3$		.029(15)	.010 [a]	.048(6)	.047
$Br\cdots C_2$		.017(13)	.006	.068(7)	.045
$C_1\cdots C_4$		.024(27)	.026		.051
$Br\cdots C_3$		.044(20)	.020	.064(7)	.051
$Br\cdots C_4$		.067(25)	.043	.084(7)	.054
$Br\cdots H$		.106(95)	.088		.088

[a] Shrinkage parameters calculated by Cyvin *et al.*,[1] and modified to be consistent with the r_a distances used in the refinements.

[b] u-Values calculated by Cyvin *et al.*[1] Standard deviations for the parameters given in parentheses. The r_a and u-values are computed from the average of parameters in columns b_1 and b_2 in Table 1.

The R-factors obtained for the two types of refinements (see Table 1) strongly suggest that the deviations from a linear model is not significant. However, the noise in the intensities is rather large, specially for the 19 cm data.

The experimental RD-curve together with the curve of residuals corresponding to parameters in Table 1, column b_2, is presented in Fig. 2.

FINAL PARAMETERS AND STANDARD DEVIATIONS

The final results are based on those parameters obtained with non-diagonal weight matrices. For bond lengths and u-values the average of parameters in Table 1, columns b_1 and b_2, are used. Final structural parameters from this work are presented in Table 3 together with parameters obtained by spectroscopic means.[1]

An experiment with CO_2 gave a correction of -0.25 % in the s scale. The distances in Table 3 are thus 0.25 % shorter than those in Table 1. The uncertainty in the wavelength (0.14 %) is included in the standard deviations for distances and shrinkage parameters in Table 3. For the bond distance r(C–H), an uncertainty was estimated based on the standard deviation in column b_1 in Table 1, and this uncertainty is also included in the standard deviations for shrinkage parameters.

DISCUSSION

The bond length r_a(Br–C) = 1.790(5) Å may be compared with the values found in the following molecules: 1.790 ± 0.005 Å in bromochloroacetylene,[3] 1.793 Å in methylbromoacetylene,[12] and 1.790 Å in bromine cyanide.[13]

The value of the bond distance $r_a(C-C) = 1.385(8)$ Å may be compared with the value 1.377 Å, found in dimethyldiacetylene.[14] If the standard deviations for the two values are assumed to be equal, then the difference in bond length is not significant.

Since it was not possible to determine the difference between $r(C_1 \equiv C_2)$ and $r(C_3 \equiv C_4)$, only an average value $r_g(C \equiv C) = 1.224(4)$ Å ($r_a = 1.223$ Å) has been obtained. This average value may be compared to the values $r_g = 1.2176 \pm 0.0014$ Å, found in diacetylene,[15] and $r_a = 1.208$ Å, found in dimethyldiacetylene.[14] A discussion on the dependence of C≡C triple-bond lengths on environment is presented in Ref. 15.

The C–H bond length, $r_a(C-H) = 1.10(5)$, is very uncertain, and no comparison with relevant C–H bond lengths in other molecules is found useful. It is a fact that values in the range 1.036 – 1.076 Å were obtained when only the 48 cm intensities were used in the least-squares refinements.[7]

The shrinkage parameters determined in this work all have the proper sign, and the general increase in the shrinkage parameters with increasing intermolecular distance is very much the same as calculated from spectroscopic data (see Table 3). However, our vibrational parameters, shrinkage parameters, and mean amplitudes of vibration (u-values) are systematically larger than those calculated by Cyvin *et al.*[1] The electron diffraction experiment was carried out at a nozzle temperature of approximately −5°C, and the vibrational parameters have been computed by Cyvin *et al.*[1] for 25°C. A systematic discrepancy like the one mentioned above could therefore not be explained by the difference in temperature.

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