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Electron Diffraction Investigation of Gaseous Chlorocyano-, Chlorobromo-, and Bromoiodoacetylene

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Electron diffraction data for the three asymetrically substituted acetylenes confirm their expected linear structures. The following R_α distances, and standard deviations including contributions from systematic errors of 0.001 R_α, were obtained: $R(C\equiv C) = 1.205(3)$, 1.206(4), and 1.206(8) Å for chlorocyano-, chlorobromo-, and bromoiodo-acetylene, respectively. $R(C-Cl) = 1.624(2)$ and 1.636(3) Å in chlorocyano- and chlorobromoacetylene, and $R(C-Br) = 1.784(3)$ and 1.795(6) Å in chlorobromo- and bromoiodoacetylene, for the latter molecule $R(C-I) = 1.972(8)$ Å. For chlorocyanoacetylene, $R(C-C) = 1.364(3)$ and $R(C\equiv N) = 1.160(3)$ Å.

The three asymmetrically substituted acetylenes, chlorocyano-, [1] chlorobromo-,[2] and bromoiodoacetylene [3] were all synthesized by E. Kloster-Jensen. The IR and Raman spectra of the molecules are known.[4–8] The crystal structure of chlorocyanoacetylene has been given,[9] and recently a complete microwave substitution structure was published for this molecule.[10] The results of the microwave structure of chlorobromoacetylene [11] depend slightly on the assumed bond shrinkage values, only for the chlorine-bromine distance was the R_s value obtainable.

The present electron diffraction investigation was carried out to increase the available structural data of substituted acetylenes. In addition it is of interest to compare microwave and electron diffraction distances when the latter distances are corrected for harmonic vibrational effects. To experimentally study the accuracy of computed atomic scattering factors of heavier atoms, the electron diffraction investigation of the simple, linear bromine and iodine containing compounds seemed interesting, as contributions from interatomic multiple scattering to the molecular intensities are expected to be unimportant for linear molecules.[12]

EXPERIMENTAL AND CALCULATION PROCEDURES

Diffraction photographs of the samples [1–3] were obtained from the Oslo apparatus [13] for an electron wavelength of 0.06461(5) Å corresponding to an accelerating voltage of about 35 kV. Values for the long and short camera distances applied, the number of plates for each distance, and the nozzle temperatures are included in Table 1.

Atomic scattering factors were computed for 35 keV electrons by a program originally written by A. C. Yates.[14] For C, N, and Cl the calculations were for analytical expressions for the HF potentials of the atoms [15] while the scattering factors for Br and I were computed from tabulated values of relativistic HFS potentials.[16]

The plates were photometered and the data treated as usually.[17] The first backgrounds were drawn on leveled intensity curves from each plate and the molecular intensities were all modified by $s/|f_C'|^2$. The final background adjustments were achieved by comparing the experimental to the best calculated intensities and were carried out on the data for each plate. These intensities were scaled and averaged, and the average correlation coefficients and the standard deviations at each point were computed.[18] Using $\Delta s = 0.125$ and 0.25 Å^{-1} for the data of the long and short camera distances, the correlation was taken care of by values of the elements p_2 and p_3 of the matrix ϱ^{-1} for the weight matrix [17] of -0.640 and 0.146, and -0.600 and 0.125, for the long and short camera distances, respectively.

Constants for the diagonal part of the weight matrix were estimated from the standard

Table 1. Nozzle temperatures (t_n), camera distances (l), number of plates (n), applied data range, and constants for the diagonal part of the weight matrix (s_1, s_2, w_1, w_2).[17]

Molecule	t_n °C	l mm	n	s(min) Å^{-1}	s(max) Å^{-1}	s_1 Å^{-1}	s_2 Å^{-1}	w_1 Å^2	w_2 Å^2	w [a]
ClCCCN	−3	480.60	5	1.375	19.875	7.0	15.0	1.10	0.41	
		200.60	6	7.00	35.00	12.0	28.0	0.06	0.08	0.14
ClCCBr	−20	480.75	6	1.375	19.125	7.0	16.0	1.75	0.07	
		260.75	6	5.25	30.00	10.5	22.0	1.10	0.20	0.25
BrCCI	12	480.60	6	1.500	19.375	7.0	14.5	1.75	0.29	
		200.60	5	7.00	25.00	9.5	18.0	1.38	0.19	0.24

[a] w is the overall weight factor for the data of the short camera distance relatively to the part of the long camera distance data of unit weight.

deviation of the intensities except for the inner part of the long camera distance data where the differences between experimental and calculated intensities were much larger than expected from the standard deviations of the experimental intensities. In this region the weights were estimated from the differences with the calculated intensities. Also the overall weight of the short camera distance data relative to overall unit weight on the long camera distance data was estimated from the standard deviations of the intensities. The constants applied in the least-squares refinement are included in Table 1, and the molecular intensities with standard deviations are illustrated in Fig. 1.

To the approximation of small vibrations and disregarding the centrifugal distortion term, the distance R_α is defined in terms of the electron diffraction parameter R_a by [19]

$$R_e + \langle \Delta z \rangle \approx R_a + D \equiv R_\alpha \qquad (1)$$

where $D = u^2/R - K$, u being the root mean-square amplitude of vibration, $u = (\langle \Delta z^2 \rangle)^{\frac{1}{2}}$, and K is the perpendicular amplitude correction term, $K = (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)/2R$. Values of u, K, and D were computed by a modified [20] computer program by W. D. Gwinn.[21]

To calculate the normal vibrations of chlorocyanoacetylene [6] with sufficient accuracy, stretch-stretch and bend-bend interaction force constants were included in the force field. For chlorobromo- and bromoidoacetylene the published force fields were applied.[8]

The numbering of the atoms is given in Fig. 2, the applied force field for chlorocyanoacetylene is tabulated in Table 2, calculated u- and D-values for this molecule are included in Table 3, and the same values for chlorobromo- and bromoiodoacetylene are given in Table 4.

The final least-squares refinements were carried out on the average molecular intensities keeping the data for each camera distance separated and applying a nondiagonal weight matrix with constants for the off diagonal elements given above. The constants for the diagonal part of the weight matrix are included in Table 1. The R_a distances were corrected to R_α ones by the computed D values given in Tables 3 and 4, and the linear geometry of the molecules was satisfied by the latter distances, keeping only the bond distances as independent geometrical parameters in the least-squares refinements.

For chlorocyanoacetylene all the u-values were refined along with the geometrical parameters and the two scale factors, however, to make the iteration converge, $u(2,3)$, $u(3,4)$, and $u(4,5)$ were given the same shifts in the refinement starting from the calculated values. In the same way $u(2,4)$ and $u(3,5)$ were refined in one group. u-Values refined in one group got the same standard deviations. The obtained root mean-square amplitudes and standard deviations thus obtained are included in Table 3. For chlorobromoacetylene, the u-values of the bonded distances were fixed on the calculated values, and of the u-values of the nonbonded distances, only $u(1,4)$ could be varied together with the other parameters.

For bromoiodoacetylene the u-values of the nonbonded distances were determined. The experimental u-values for these two molecules are given in Table 4.

Most of the elements of the moment matrix of the parameters were small. Correlation coefficients with absolute values larger than 0.5 were for chlorocyanoacetylene $\varrho[R(2,3), R(1,2)] = -0.62$, $\varrho[R(4,5), R(2,3)] = -0.58$, $\varrho[u(1,2), K(20)] = 0.62$, and $\varrho[K(48), K(20)] = 0.56$, where $K(48)$ and $K(20)$ are the scale factors for the data from the long and short camera distance data, respectively. In the same way for chlorobromoacetylene $\varrho[R(1,2), R(2,3)] = -0.72$, $\varrho[R(3,4), R(2,3)] = -0.72$, $\varrho[u(1,4), K(48)] = 0.59$, and $\varrho[u(1,4), K(20)] =$

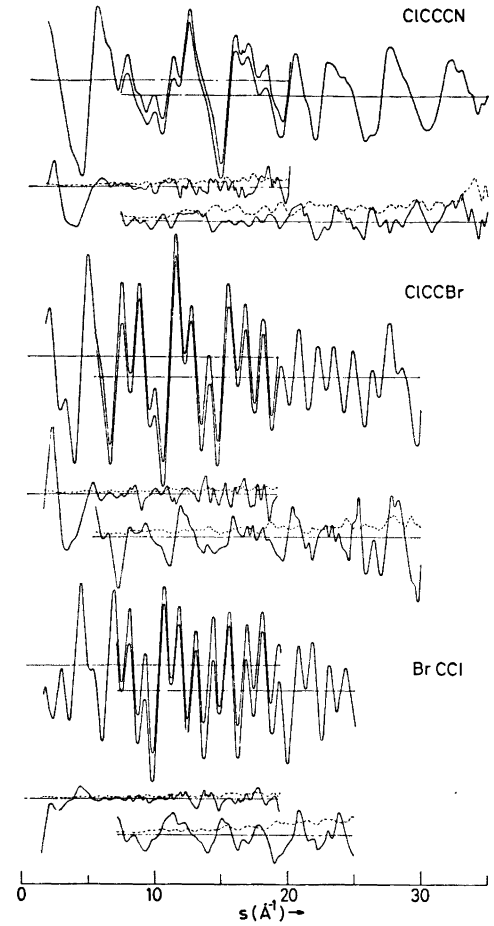

Fig. 1. $s/|f'_{Cl}|^2$-modified average experimental intensities for the long and short camera distance data (two upper curves for each molecule). The corresponding standard deviations of the average intensities (broken curves), and the differences between the experimental intensities and the intensities calculated from the parameters of Table 5 and Table 3 or Table 4 using experimental u-values when possible (solid curves) are given below the molecular intensities for the two camera distances.

0.74, and for bromoiodoacetylene $\varrho[R(3,4), R(2,3)] = -0.74$, $\varrho[R(1,2),R(2,3)] = -0.51$, $\varrho[u(1,4),K(48)] = 0.74$, $\varrho[u(1,4),K(20)] = 0,85$, and $\varrho[K(48), K(20)] = 0.64$. The final results are given in Table 5.

Applying the scale factors from the least-squares refinements, the intensity curves from the two camera distances were connected, calculated intensities were added to the inner part, and radial distribution functions were computed and compared to functions calculated for the parameters of Table 5 and Table 3 or 4, respectively. The radial distribution functions are illustrated in Fig. 3.

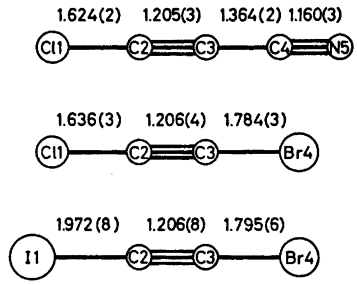

Fig. 2. Numbering of the atoms of the molecules. Final corrected R_α distances and standard deviations are included.

Table 2. Applied force field for chlorocyanoacetylene. Stretching force constants K and stretch-stretch interaction force constants F in mdyn/Å and force constants for bending, H and bending-bending interaction, G, in mdyn Å/rad.[2]

$K(1,2)$	3.7	$F(1,2/2,3)$	1.080
$K(2,3)$	18.0	$F(1,2/3,4)$	0.771
$K(3,4)$	10.0	$F(1,2/4,5)$	0.629
$K(4,5)$	16.1	$F(2,3/3,4)$	1.270
		$F(2,3/4,5)$	0.286
		$F(3,4/4,5)$	0.589
$H(1,2,3)$	0.340		
$H(2,3,4)$	0.286	$G(1,2,3/2,3,4)$	0.044
$H(3,4,5)$	0.255	$G(2,3,4/3,4,5)$	0.044

Table 3. Chlorocyanoacetylene, calculated root mean-square amplitudes of vibration, u, and correction terms between R_a and R_α, D of eqn. 1, at -3 °C. Experimental u-values with least-squares standard deviations are included.

Distance	D (Å)	u (Å) calc	u (Å) exp
1 – 2	−0.0101	0.046	0.033(4)
2 – 3	−0.0056	0.035	0.041(3)
3 – 4	−0.0087	0.039	0.046(3)
4 – 5	−0.0172	0.035	0.042(3)
1···3	−0.0072	0.047	0.051(4)
1···4	−0.0012	0.049	0.048(4)
1···5	−0.0002	0.051	0.067(4)
2···4	−0.0044	0.044	0.050(4)
2···5	−0.0078	0.047	0.059(8)
3···5	−0.0152	0.044	0.051(4)

Table 4. Chlorobromo- and bromoiodoacetylene, calculated root mean-square amplitudes of vibration, u, and correction terms between R_a and R_α, D of eqn. 1, at 15 and 25 °C, respectively. Experimental u-values with least-squares standard deviations are included.

Distance	ClCCBr D (Å)	ClCCBr u (Å) calc	ClCCBr u (Å) exp	ICCBr D (Å)	ICCBr u (Å) calc	ICCBr u (Å) exp
1–2	−0.0118	0.044		−0.0128	0.045	
2–3	−0.0096	0.036		−0.0112	0.037	
3–4	−0.0086	0.041		−0.0109	0.043	
1···3	−0.0067	0.049		−0.0062	0.050	0.040(31)
1···4	0.0004	0.050	0.048(2)	0.0006	0.055	0.055(3)
2···4	−0.0045	0.043		−0.0091	0.048	0.060(13)

DISCUSSION

For small vibrations, the R_α distance is according to eqn. 1 equal to the equilibrium distance plus an anharmonicity term. These distances should therefore approximately satisfy the molecular geometry and be close to the equilibrium distances. Also the microwave R_s distances should be close to the equilibrium distances and the two types of distances should be comparable.

The R_α distances fit linear structures of the three molecules satisfactorily, and the expected linear geometries are confirmed (Fig. 1). For chlorocyanoacetylene the largest discrepancies between the present result and the microwave R_s structure [10] are for the C3 – C4 and the C2≡C3 distances with differences of 0.005 and −0.004 Å, respectively. These differences are

Table 5. R_α distances with standard deviations, including contributions from systematic errors of 0.001 R_α, in Å.

	ClCCCN	ClCCBr	ICCBr
$R(1-2)$	1.624(2)	1.636(3)	1.972(8)
$R(2-3)$	1.205(3)	1.206(4)	1.206(8)
$R(3-4)$	1.364(2)	1.784(3)	1.795(6)
$R(4-5)$	1.160(3)		
$K(48)$ [a]	0.93(3)	0.95(2)	1.02(3)
$K(20)$ [a]	0.95(4)	0.96(3)	1.03(4)
$R(48)$ [b]	7.0	7.8	9.5
$R(20)$ [b]	13.1	16.2	28.4

[a] Scale factors for the data of the long and short camera distances. [b] Weighted R-factors for the data of the long and short camera distances, $R = 100\{\sum_i w_i[I(\text{exp}) - I(\text{calc})]^2 / \sum_i w_i I(\text{exp})^2\}^{\frac{1}{2}}$.

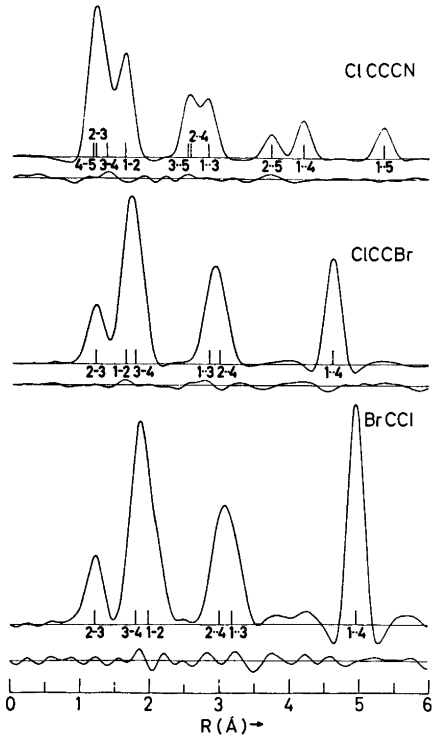

Fig. 3. Experimental radial distribution functions of the molecules obtained from connecting the average experimental intensities of Fig. 1 and adding theoretical intensities inside $s = 4.75$ Å^{-1}. The damping functions were $\exp(-0.005s^2)$ for chlorocyanoacetylene and $\exp(-0.007s^2)$ for chlorobromo- and bromoiodoacetylene. Differences between experimental and calculated functions from the parameters of Tables 5 and 3 or Table 4 multiplied by a factor of 2 are given below each radial distribution function.

not significant. For chlorobromoacetylene $R_\alpha(\mathrm{Cl1\cdots Br4}) = 4.626(5)$ Å is in good agreement with the R_s distance of 4.625 – 4.626 Å of Ref. 11, and also the other structure parameters from the two investigations agree satisfactorily.

The obtained values for the C≡C bonds are the same while the difference of 0.012(4) Å between the carbon-chlorine bonds of chlorobromo- and chlorocyanoacetylene may be significant.

The carbon-bromine distances of the present investigation agree with the R_s value of 1.785 Å for bromocyanoacetylene [10] and the carbon-iodine distance of 1.972(8) Å is not significantly different from the R_0 value of 1.985 Å of iodocyanoacetylene.[10]

As seen from the standard deviations of the intensities of Fig. 1 and the R-factors of Table 5 the data are not very accurate, and the accuracies and the maximum s-values for obtaining meaningful molecular intensities decrease with increasing atomic numbers of the heaviest atom. This is at least partly due to the combined effect of increasing background scattering from the heavier atoms and phase shifts in the atomic scattering. The computed atomic scattering factors are, however, expected to be more than sufficiently accurate to analyze the present data. This is confirmed by the experimental u-values for chlorobromo- and bromoiodoacetylene of Table 4, which are all within one standard deviation of the calculated ones. The scattering factors for bromine and iodine were also computed from an analytical potential which is known to be less accurate for heavier atoms.[22] While the scattering factor for Br agreed relatively well with the function obtained from the tabulated HFS potential, the scattering factor for iodine showed large discrepancies, and the obtained g-functions [17] for bromiodoacetylene differed considerably from the g-functions for the tabulated HFS potential. Applying the former g-functions in the least-squares refinement, about the same overall agreement with the experimental data was obtained. However, the C – Br distance increased by 0.021 and the C – I distance decreased by 0.019 Å with practically no changes in the C≡C and Br···I distances, and the u-value of the Br···I distance converged to 0.042(4) Å. These values for the distances are less reasonable, and the u-value is in poorer agreement with the calculated one, than the results obtained for g-functions based on the more accurate tabulated values for the HFS potential of iodine.

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REFERENCES

1. Kloster-Jensen, E. *Acta Chem. Scand. 18* (1964) 1629.
2. Kloster-Jensen, E. *J. Am. Chem. Soc. 91* (1969) 5673.
3. Kloster-Jensen, E. *Tetrahedron Lett. V* (1969) 5323.
4. Cyvin, S. J., Kloster-Jensen, E. and Klæboe, P. *Acta Chem. Scand. 19* (1965) 903.
5. Klæboe, P. and Kloster-Jensen, E. *Spectrochim. Acta A 23* (1967) 1981.
6. Christensen, D. H., Klæboe, P., Kloster-Jensen, E. and Johnsen, I. *Spectrochim. Acta A 25* (1969) 1569.
7. Christensen, D. H., Klæboe, P., Kloster-Jensen, E. and Johnsen, I. *Spectrochim. Acta A 26* (1970) 1567.
8. Christensen, D. H., Stroyer-Hansen, T., Klæboe, P., Kloster-Jensen, E. and Tucker, E. E. *Spectrochim. Acta A 28* (1972) 939.
9. Bjorvatten, T. *Acta Chem. Scand. 22* (1968) 410.
10. Bjorvatten, T. *J. Mol. Struct. 20* (1974) 75.
11. Bjørseth, A., Kloster-Jensen, E., Marstokk, K. M. and Møllendal, H. *J. Mol. Struct. 6* (1970) 181.
12. Bartell, L. S. *J. Chem. Phys. 63* (1975) 3750, and references therein.
13. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand. 9* (1955) 232.
14. Yates, A. C. *Comput. Phys. Commun. 2* (1971) 175.
15. Strand, T. G. and Bonham, R. A. *J. Chem. Phys. 40* (1964) 1686.
16. Liberman, D., Waber, J. T. and Cromer, D. *Phys. Rev. 137* (1965) 1727.
17. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand. 23* (1969) 3224.
18. Seip, H. M., Strand, T. G. and Stølevik, R. *Chem. Phys. Lett. 3* (1969) 617.
19. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys. 36* (1962) 1108.
20. Stølevik, R., Seip, H. M. and Cyvin, S. *Chem. Phys. Lett. 15* (1972) 263.
21. Gwinn, W. D. *J. Chem. Phys. 55* (1971) 477.
22. Cox, Jr., H. L. and Bonham, R. A. *J. Chem. Phys. 47* (1967) 2599.

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