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Molecular Structure of Cyclopropylacetylene as Studied by Gas Electron Diffraction

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The average CC bond distance of the three-membered ring was found to be the same as in cyclopropane, methylcyclopropane and *trans*-1,2-dimethylcyclopropane. No deviation from equilateral symmetry of the three-membered ring could be detected, though a small asymmetry cannot be excluded.

The CC bond between the triple bond and the cyclopropyl group is found to be shorter than that between the triple bond and the methyl groups in dimethylacetylene by about 0.027 Å. This is interpreted in terms of hybridization differences between cyclopropane carbon and carbon in saturated open chain molecules and of conjugation between the cyclopropane ring and the acetylene group.

The experimentally determined bond distances r_a are the following: $r(C-H, \text{ring})=1.089$ (6), $r(C-H, \text{ethinyl})=1.052$ (30), $r(C_1-C_2)=1.510$ (1), $r(C_1-C_4)=1.440$ (3) and $r(C_4-C_5)=1.208$ (2) Å. Numbers in parentheses are estimated standard deviations.

According to the generally accepted model of bonding in cyclopropane put forward by Walsh,[1] the carbon atoms of that molecule though tetravalent are hybridized in such a way as to give the exocyclic orbitals sp^2 character. The substituent carbon should therefore form a shorter bond to a cyclopropane carbon than to an sp^3-carbon. Moreover, if the three-membered ring is substituted by an unsaturated group, conjugative interaction might be anticipated, and the presence of conjugation would render the CC single bond to the cyclopropane moiety shorter than to, for example, a methyl group.

Conjugative interaction between the acetylene group and the cyclopropane ring is expected to show up in a deviation from equilateral symmetry of the ring. According to Hoffmann,[2] the ring CC distances adjacent to the substituent should have increased and that opposite the substituent should have shortened in comparison to cyclopropane. So far, this effect has been observed for cyclopropyl cyanide only.[3]

The geometry of cyclopropylacetylene has been investigated previously using microwave spectroscopy.[4] Only two isotopic species were studied, and among other assumptions, the ring bonds were fixed at 1.514 Å. The length of the bond attaching ethinyl to the ring was then found to be 1.47 Å, which is a little longer than the single CC bond in methylacetylene, for which a precise r_s value of 1.459 Å was determined.[5] This experimental result is not in accord with the above predictions.

In the hope of contributing to the elucidation of these problems, we decided to undertake an electron diffraction study of the geometry of cyclopropylacetylene in the gas phase.

EXPERIMENTAL

The preparation of the title compound was initially attempted using the procedure of Schoberth and Hanack.[6] This procedure yielded only a small amount of product and, therefore, another method was used. The first step was to prepare vinylcyclopropane by a well-established route,[7] the final step in the preparation followed the procedure of Slobodin and Egenburg.[8]

The product was distilled at 51 – 52 °C at 760 mm. Gas chromatography showed the sample to be approximately 97 % pure. The product was identified by NMR and IR spectroscopy. The sample of cyclopropylacetylene used in the present study was additionally purified by preparative gas chromatography.

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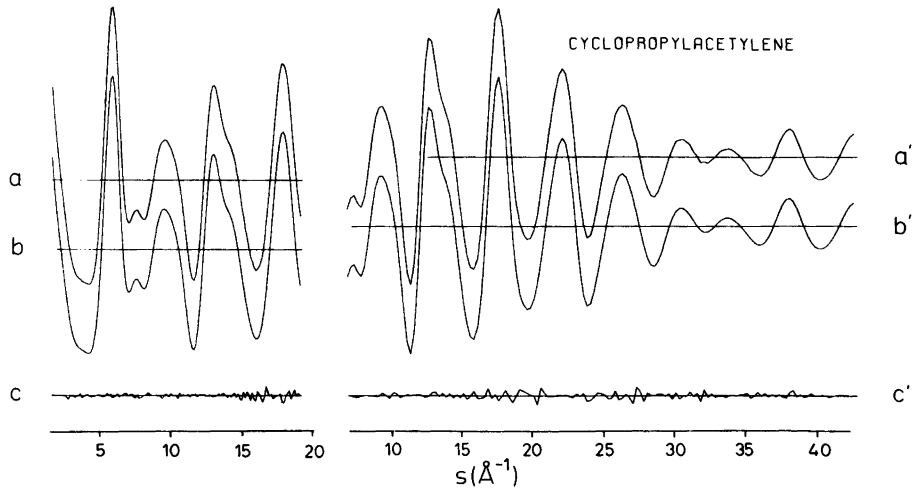

Fig. 1. (a) Experimental and (b) calculated molecular intensity curve for nozzle to photographic plate distance of 48 cm; (c) difference curve (a) − (b) multiplied by a factor of 2. (a'), (b') and (c') are the corresponding curves for the 20 cm distance.

Diffraction photographs were obtained in the usual way with the Oslo apparatus.[9] The experimental conditions, the data processing[10] and the calculation of the scattering functions were as described for the concurrent study of the methylcyclopropanes.[11]

Four apparently faultless plates from each of the two camera lengths were selected for analysis. The range of data for the 48 cm distance was $1.500 \leqslant s \leqslant 19.000$ Å^{-1} with data interval $\Delta s = 0.125$ Å^{-1} and $7.00 \leqslant s \leqslant 42.75$ Å^{-1} with $\Delta s = 0.25$ Å^{-1} for the 20 cm distance. The resulting $s/|f'_C(s)|^2$-modified molecular intensities are shown in Fig. 1.

Radial distribution functions were calculated by Fourier inversion of experimental and theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

STRUCTURE ANALYSIS AND FINAL RESULTS

A molecular model of cyclopropylacetylene is shown in Fig. 2 which also gives the numbering of the atoms. In order to reduce the number of parameters to be refined to a practical limit, the following assumptions about the molecular structure were made: (a) The molecule possesses C_s symmetry, (b) the acetylene group is linear, (c) the five carbon hydrogen bond lengths of the ring are equal, and (d) the CH_2-groups have local C_{2v} symmetry.

With these assumptions, the geometry of the molecular model could be completely defined by nine parameters. These were chosen as six bond lengths r(C−H, ring), r(C−H, ethinyl), $r(C_1-C_2)$, $r(C_2-C_3)$, $r(C_1-C_4)$, $r(C_4-C_5)$, and three bond angles $H_1C_2H_2$, $C_2C_1H_6$, $C_2C_1C_4$.

The imposed linearity of the acetylene group might slightly affect the results obtained from this model, for the shrinkage effects which might become important for nonbonded distances involving the atom C_5 have not been corrected for in the present investigation.

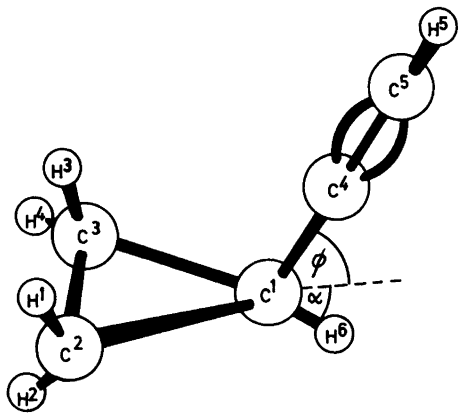

Fig. 2. Cyclopropylacetylene. Molecular model which shows the numbering of the atoms.

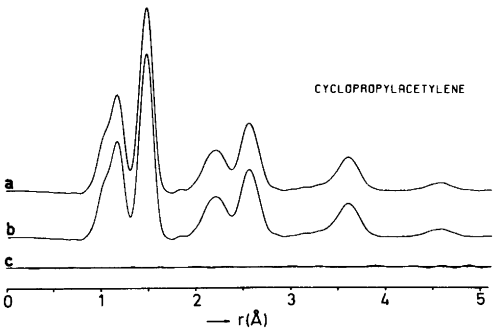

Fig. 3. (a) Experimental and (b) calculated radial distribution curve with an artificial damping factor $k=0.0015$ Å^2: (c) difference curve (a)−(b) multiplied by a factor of 2.

Preliminary values for the bond distances and bond angles were obtained from the radial distribution curve (Fig. 3). The range of this curve below about 2.7 Å has four more or less well-resolved peaks that might be attributed to the ≡C−H and −C−H, the C≡C, the C−C bond distances, and to the non-bonded carbon hydrogen and carbon carbon distances over one bond angle.

Preliminary u-values were assigned by using experimental data obtained for similar molecules.[12-17] The molecular structure was then refined by least squares calculations on the intensity data[18] using a non-diagonal weight-matrix with standard values[19,11] for the non-diagonal elements. The computations involved strongly damped iterations using 0.5 times the calculated shift of the current iteration cycle and 0.2 times the shift of the previous cycle.

It was possible to refine all geometrical parameters together with the u-values for the bond distances and those for the nonbonded C−C distances simultaneously. Least squares refinement of a model with unequal C_1C_2 and C_2C_3 bonds yielded an R-factor of 2.0 %. However, there was a high degree of coupling between the endocyclic carbon carbon bonds and the corresponding u-values shown by the large correlation coefficients and standard deviations. The two bond lengths and their correlation coefficient were: $r(C_1C_2)=1.509$ (10), $r(C_2C_3)=1.512$ (20) Å and $\rho=-0.96$, which demonstrate clearly that it was not possible to distinguish the endocyclic bond distances.

The lengths of the ring bonds were then treated as one single parameter yielding the same R-factor as before. The results are given in Table 1. The theoretical intensity and radial distribution functions calculated from these parameters are shown in Figs. 1 and 3 together with their experimental counterparts.

Table 1. Cyclopropylacetylene. Molecular parameters resulting from least squares refinements on the molecular intensities.[a]

	r_a	u
C_1-C_4	1.440(3)	0.048(5)
C_1-C_2	1.510(1)	0.048(2)
C_4-C_5	1.208(2)	0.037(2)
C_2-H_1	1.089(6)	0.076(8)
C_5-H_5	1.052(30)	0.064(22)
$\rho_{14,12}$	−0.54	
$\rho_{14,45}$	−0.35	
$\rho_{12,45}$	0.02	
Angles		
ϕ^b	55.6(0.2)	
α^b	59.6(2.8)	
∠HCH	116.7(1.4)	
∠CCH	117.1(1.1)	

[a] Bond distances (r_a) and root mean square amplitudes (u) are given in Å, angles are in degrees. The numbers in parentheses are standard deviations. [b] See text and Fig. 1 for the definition of ϕ and α.

DISCUSSION

In Table 2 the structural parameters obtained for cyclopropylacetylene are compared with those for some related molecules.

The length of the CC triple bond compares favourably with that of other acetylenic compounds. There seems to be no obvious trend in this type of bond distance, and the claimed conjugation does not seem to lead to any significant bond lengthening. Acetylenic bonds generally are considered to be rather insensitive to conjugative interaction.[24,25] Bond length changes of a few thousandths of an angstrom are the order of magnitude expected.[23,26]

The exocyclic CC bond between the cyclopropane moiety and the triple bond is found to be 1.441 Å. The comparisons in Table 2 show this to be definitely shorter than the single bonds in dimethylacetylene and methylacetylene, and drastically shorter compared to that in isopropylacetylene derived from a

Table 2. Comparison of the bond lengths (Å) of cyclopropylacetylene with related molecules.

Molecule		C–C	C≡C	CC(ring)	Ref.
Acetylene	r_g	–	1.212	–	20
Methylacetylene	r_s[a]	1.459	1.207	–	5
Dimethylacetylene	r_g	1.468	1.214	–	21
Isopropylacetylene	(r_s)[a]	1.495	1.205	–	22
Cyclopropylacetylene	r_g	1.441	1.209	1.511	this work
Vinylacetylene	r_g	1.434	1.215	–	15
Diacetylene	r_g	1.384	1.218	–	23
Bicyclopropyl	r_g	1.501	–	1.509	17
Vinylcyclopropane	r_g	1.477	–	1.524	14

[a] The r_s-values are usually shorter than the corresponding r_g-values by 0.005 to 0.010 Å.

partial substitution structure. The bond length contraction of 0.027 Å relative to dimethylacetylene is somewhat larger than that of methylcyclopropane[11] relative to ethane.[27] In the latter case, the effect of substituting a methyl carbon in ethane by a carbon of a cyclopropane moiety is a bond shortening of 0.015 Å. This reflects the effect of hybridization changes in going from methyl carbon to cyclopropane carbon the latter being half way between an sp^3 and an sp^2 state. Assuming additivity of covalent radii[28] there is an additional contraction of the length of the exocyclic CC bond in cyclopropylacetylene of 0.012 Å. This is very close to the situation in vinylcyclopropane[14] where the total bond shortening of about 0.030 Å compared to propene[29] exceeds the contraction brought about by hybridization effects by 0.01 Å. Using a similar reasoning for butadiene[30–32] one arrives at an extra bond shortening of about 0.01 Å due to electron delocalization.

The average CC ring bond length of 1.511 Å is close to that of cyclopropane[12] itself and of methylcyclopropane and *trans*-1,2-dimethylcyclopropane[11] the corresponding distance in all three molecules being 1.510 Å. According to Hoffmann,[2] conjugative interaction between the cyclopropane ring and an unsaturated substituent is accompanied by a lengthening of the adjacent ring CC bonds and a shortening of the bond opposite to the carbon atom bearing the substituent, thereby altering the equilateral symmetry of the ring. The average CC bond distance in the ring, however, might well be close to that of the parent hydrocarbon, although there is a considerable difference between the individual bond lengths because of conjugation with a substituent.

Some independent information on the ring CC bond distances derived from microwave data is suggestive of ring asymmetry and a C_2-C_3 bond length of 1.498 Å in cyclopropylacetylene was estimated from the planar moments of a series of cyclopropyl derivatives.[33]

Our data cannot rule out small bond length differences. It appears that the asymmetry is smaller than in the isoelectronic molecule cyclopropyl cyanide, where a ring bond difference of 0.028 Å and an average distance of 1.519 Å is observed.[3] There is other evidence to show that the amount of delocalization is greater in molecules containing lone pairs adjacent to multiple bonds,[24] so our finding is quite reasonable.

A study of the rotational spectra of additional ^{13}C species of cyclopropylacetylene aimed at obtaining a substitution structure of the carbon skeleton will lead to some more definite conclusion with regard to the substituent induced asymmetry of the cyclopropane ring. This might also solve the discrepancy between the results for the exocyclic CC single bond length obtained by the two methods. Vibrational spectroscopic studies of cyclopropylacetylene are in progress in our laboratory with the aim of further analysis of the electron diffraction data with calculated *u*-values and including the reported rotational constants.

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