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Structure of Vinylacetylene Determined by Electron Diffraction and Spectroscopy

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The average structure of vinylacetylene has been determined by making combined use of the electron-diffraction intensities obtained in the present study and the rotational constants supplied by microwave spectroscopy. The two sorts of data have been found consistent to the uncertainties given below. With the molecular symmetry assumed to be C_S, the following parameters have been obtained in regard to the zero-point average structure: $r(\text{C–C})=1.431_0\pm0.003_4$, $r(\text{C=C})=1.341_6\pm0.004_2$, $r(\text{C}\equiv\text{C})=1.208_6\pm0.002_8$, $r(\text{C–H})_{\text{vinyl}}=1.087\pm0.010$, $r(\text{C–H})_{\text{ethynyl}}=1.062\pm0.018$ Å, $\angle(\text{C=C–C})=123.1\pm0.5°$, $\angle(\text{C–C}\equiv\text{C})=177.9\pm1.2°$, $\angle(\text{H–C=C})=120.6\pm1.5°$, $\angle(\text{C}\equiv\text{C–H})=182.3\pm3.8°$. There seems to be a significant difference between the C–C length of vinylacetylene and that of propynal. The result has been discussed in terms of the bond-order bond-length correlation.

How does the length of a carbon-carbon bond vary with its environment? This is one of the problems which attract the interest of physical and organic chemists. On the basis of the extensive research by means of rotational spectroscopy, Stoicheff and Costain[1,2] deduced a comprehensive rule, which states that the length of a CC bond is primarily determined by a linear relation depending on the number of atoms adjacent to the carbon atoms at both ends. This rule was shown to hold for a wide range of molecules. For a critical examination of the validity and the limit of applicability of the rule, it is necessary to obtain precise structural parameters of molecules for which neither spectroscopy nor electron diffraction alone can give unique geometry. This requirement was shown to be met in our studies[3-5] by a complementary combination of the two sorts of data. The results of those studies have shown significant deviations from the Stoicheff rule when heteroatoms are present in the system, whereas the rule is valid for pure hydrocarbons.

For butadiene, acrolein, and glyoxal, the central C–C bond increases its length according as it is adjacent to the C=O bond.[3] A similar systematic lengthening has been observed for cyanogen[4] as compared with diacetylene.[6] The first three are conventionally classified as molecules with an sp^2-sp^2 C–C bond, while the latter two are those with an sp-sp C–C bond. It is natural, then, to expect an analogous heteroatom effect in a system containing an sp^2-sp C–C bond. In fact, a deviation from the Stoicheff rule was first observed for an sp^2-sp C–C system by Costain, Stoicheff, and Morton.[1,7] They pointed out that the $r_s(\text{C–C})$ distance of propynal was longer by 0.0025 Å than the value predicted by the linear rule, to which the $r_s(\text{C–C})$ distance of vinylcyanide fitted nicely.

There remains, however, another simple molecule which has a C–C bond of this type: vinylacetylene. No precise structure has been reported for this molecule, although an unpublished work of Bastiansen[8] was cited by Serre,[9] and an r_0 structure was calculated by Whiffen[10] from the rotational constants reported by Morgan and Goldstein.[11] A favorable situation for filling this gap has been brought about by a recent investigation of the microwave spectrum of this molecule by Hirose[12] and by the study of its intramolecular force field by Abe.[13] Taking advantage of these circum-

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[13] K. Abe, private communication.

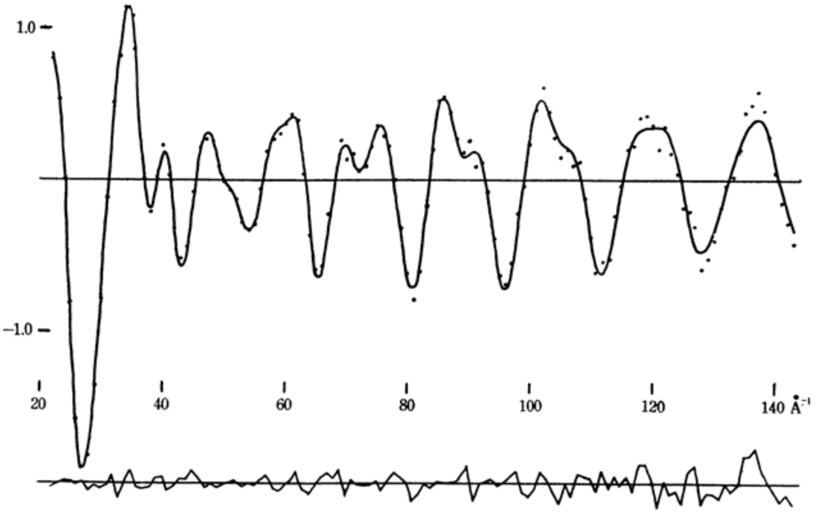

Fig. 1. Molecular scattering intensity. Observed values are shown in dots, and the solid curve represents the best-fit theoretical intensity. The residuals are shown below.

stances, an electron diffraction measurement has been carried out, and the average structure of vinylacetylene has been determined following the procedure applied to butadiene, acrolein, and glyoxal.

Experimental

The vinylacetylene sample supplied by the Tokyo Kagaku Seiki Co., Ltd. as a standard substance for gas chromatography was used without further purification. No impurity line was observed in the infrared spectrum of a freshly supplied sample.[13] Experimental conditions were similar to those described elsewhere.[3] The observed molecular intensity is shown in Fig. 1. Figure 2 illustrates the radial distribution curve.

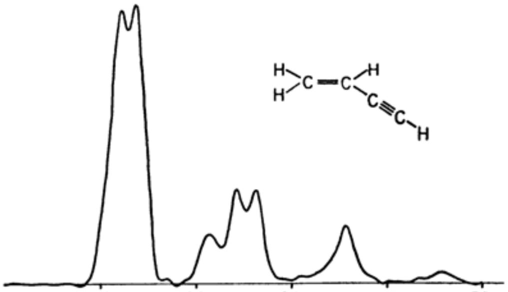

Fig. 2. Radial distribution curve for vinylacetylene.

Analysis

Since the details of the analytical procedure are the same as those described in Ref. 3, only an outline is given here. The calculations have been carried out by a HITAC 5020E Computer at the Computer Center, the University of Tokyo.

It was assumed that the molecule has C_S symmetry, namely that it is planar. With this assumption the number of independent parameters is thirteen for defining the molecular geometry, but in the analysis of the molecular scattering intensity the number of parameters was reduced by the following additional assumptions: Three C–H bond lengths and C=C–H angles in the vinyl group were assumed to be equal. The difference between the C–H bond length in the ethynyl group and those in the vinyl group was fixed at 0.027 Å according to the difference between the r_z(C–H) of acetylene[14] and that of ethylene.[15] Furthermore, the C≡C–H angle was assumed to be 180°. All the above assumptions were applied to the $r_\alpha{}^0$ structure, from which the effect of thermal vibrations was removed.

The correction terms for the conversion of r_a into $r_\alpha{}^0$ distances were calculated by the procedure given in Refs. 16 and 3. The force constants necessary for the calculation were offered for our use by Abe.

The most probable values of the parameters, $r_\alpha{}^0$, obtained by the least-squares analysis are shown in Table 1 with their uncertainties. Table 2 lists the most probable values and the uncertainties of the mean square amplitudes in comparison with the values calculated with the force constants determined by Abe. The agreement is satisfactory. The mean amplitudes for the other atom pairs were fixed at the calculated values throughout the analysis. The parameters of asymmetry κ were estimated as described in Ref. 3, and were fixed at 1.89×10^{-5} and 1.59×10^{-5} Å^{-3} for C–H$_{\text{vinyl}}$ and C–H$_{\text{ethynyl}}$, respectively.

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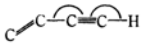
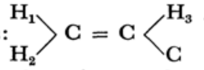
TABLE 1. STRUCTURE OF VINYLACETYLENE (in Å and degrees)

	$r_\alpha{}^0$	$\sigma^{d)}$	r_{av}	$\sigma^{d)}$	Bastiansen[e)]
r(C–C)	1.4314	0.0036	1.4310	0.0034	1.430
r(C=C)	1.3414	0.0042	1.3416	0.0042	1.335
r(C≡C)	1.2090	0.0030	1.2086	0.0028	1.206
r(C–H)$_v$[a)]	1.087	0.007	1.087	0.010	
r(C–H)$_e$[a)]	(1.060)	—	1.062	0.018	
∠(C=C–C)	123.0	0.5	123.1	0.5	123.4
∠(C–C≡C)[b)]	177.0	1.7	177.9	1.2	
∠(H_1–C=C)[c)]	120.8	1.5	118.7	4.2	
∠(H_2–C=C)			121.6	3.8	
∠(H_3–C=C)			121.7	4.0	
∠(C≡C–H)[b)]	(180)	—	182.3	3.8	
k[f)]	1.016	0.022	1.012	0.020	

a) Suffices v and e denote vinyl and ethynyl, respectively.

b) The angles are taken as 

c) Numbering of the hydrogen atoms: 

d) 2.5 times the random errors plus the estimates of systematic errors.

e) Ref. 8.

f) Index of resolution.

TABLE 2. MEAN SQUARE AMPLITUDES OF VINYLACETYLENE (in Å)

	$l_{obs.}$		$l_{calc.}$
C–C	0.048	±0.006	0.0473
C=C	0.043_9	±0.004	0.0439
C≡C	0.038	±0.005	0.0367
C–H_v[a)]	0.074	±0.006	0.0775
$C_1\cdots C_3$[b)]	0.059_4	±0.002	0.0635
$C_2\cdots C_4$	0.053_9	±0.003	0.0520
$C_1\cdots C_4$	0.084	±0.005	0.0867

a) All the vinyl C–H amplitudes were assumed to be equal. Mean amplitudes for C–H_e were varied with fixed difference from those for C–H_v (l(C–H)$_v$ − l(C–H)$_e$=0.0033 Å).

b) Numbering of carbon atoms: C_1=C_2–C_3≡C_4.

The rotational constants B_0 and C_0 for the normal and the deuterated species (deuterated on the ethynyl hydrogen) determined by microwave spectroscopy were communicated by Hirose. After being converted into B_z and C_z, namely into the rotational constants corresponding to the average structure r_z, they were used in the least-squares calculations, in which the rotational constants were combined with the molecular scattering intensity as joint observables. The method is based on the assumption that the $r_\alpha{}^0$ structure obtained from electron diffraction and the r_z structure from spectroscopy have essentially the same physical significance so that it is possible to use the two sorts of data to complement one another upon the conversion into those structures. The result is shown in Table 1 as r_{av}. Most of the assumptions with regard to the structure of the vinyl and the ethynyl groups were removed by this procedure. Namely, it became possible to treat the three C=C–H angles, r(C–H)$_{ethynyl}$ and the angle C≡C–H as independent parameters. Although it was not possible to set the C–H distances of the vinyl group free from the restraint that they were equal, this assumption turned out to have no significant effect upon the values of the other parameters: even if any two of the three C–H lengths were assumed to be different by ±0.005 Å, the rest of the parameters changed by not more than 0.001 Å. The isotopic difference r_{av}(C–H) − r_{av}(C–D) was assumed to be 0.0012±0.0020 Å, the value calculated by Eq. (5) of Ref. 5. The observed rotational constants B_0 and C_0, B_z and C_z derived from B_0 and C_0, and the best-fit B_z and C_z are shown in Table 3. The consistency of the electron-diffraction and spectroscopic data is seen by the comparison of the $r_\alpha{}^0$ structure with the r_{av} structure in Table 1. The uncertainties in the parameters were estimated in a way similar to that described in Ref. 3. They consist of 2.5 times the random errors plus the estimates of systematic errors.

TABLE 3. OBSERVED AND CALCULATED ROTATIONAL CONSTANTS (in MHz)

	CH_2=CHC≡CH		CH_2=CHC≡CD	
	B	C	B	C
B_0, C_0, obs	4744.95	4329.81	4403.97	4037.86
B_z, C_z, obs	4740.74	4329.93	4400.44	4038.15
B_z, C_z, calc	4740.65	4330.20	4400.50	4037.94

The r_g structure of vinylacetylene was derived from the r_{av} structure of Table 1 by using the

TABLE 4. COMPARISON OF STRUCTURES (in Å and degrees)

	r(C–C)	r(C=C)	r(C≡C)	r(C–H)$_{\text{vinyl}}$	r(C–H)$_{\text{ethynyl}}$
Vinylacetylene (r_g)	1.434 ± 0.003	1.344 ± 0.004	1.215 ± 0.003	1.106 ± 0.010	1.090 ± 0.018
Vinylcyanide (r_s)	1.426 ± 0.001	1.339 ± 0.001	—	1.086 ± 0.001	—
Propynal (r_s)	1.445 ± 0.001	—	1.209 ± 0.001	—	1.055 ± 0.001
Ethylene (r_g)	—	1.337 ± 0.002	—	1.103 ± 0.002	—
Acetylene (r_g)	—	—	1.209 ± 0.001	—	1.077 ± 0.002
	∠(C=C–C)	∠(C–C≡C)	∠(C=C–H)		
Vinylacetylene (r_{av})	123.1 ± 0.5	177.9 ± 1.2	120.6 ± 1.5[a]		
Vinylcyanide (r_s)	122.6	—	121.7		
Propynal (r_s)	—	178.4 ± 0.2	—		
Ethylene (r_α^0)	—	—	121.4 ± 0.6		

a) Average value of the three angles.

calculated difference $r_g - r_\alpha^0$. It is shown in Table 4. This structure is considered to be appropriate for comparison of the bond lengths for different molecules.5) On the other hand, the angles are given in the r_{av} structure, which is suitable for the description of the shape of a molecule.5)

Discussion

The structure of vinylacetylene shown in Table 1 is close to that given by Bastiansen, although it is not clear whether they are of comparable physical significance.

Table 4 lists the structures of vinylacetylene, vinylcyanide, and propynal. It must be emphasized that the latter molecules are described in the r_s structure whereas the parameters for vinylacetylene are given in the r_g or r_{av} structure. Although no quantitative relation connecting the r_g with the r_s distances has been set forth, there is little doubt in that the former is longer than the latter. The difference is expected to be in the range of several thousandths of an angstrom. In this consideration, it is probable that the r_g(C–C) of propynal is longer than that of vinylacetylene by more than 0.01 Å. Thus the present system provides another example of the lengthening of a C–C bond adjacent to a heteroatom. On the other hand, it is premature to draw any conclusion about whether or not a similar heteroatom effect also exists between vinylacetylene and vinylcyanide, since the r_g(C–C) of vinylcyanide may be close to 1.430 Å. In order to elucidate this point, and to grasp the heteroatom effect more quantitatively, an electron-diffraction investigation of vinylcyanide and propynal is now under way in our laboratory.

It is interesting in this connection to note that molecular-orbital calculations of bond orders have been reported by Moffat,17) who has shown that the bond order for the C–C bond in vinylacetylene is smaller than that for the corresponding bond in vinylcyanide. According to his calculations, the C–C bond of vinylacetylene should be longer than that of vinylcyanide. He has asserted the agreement of his prediction with the experimental results by comparing directly the electron-diffraction structure of vinylacetylene with the r_s structure of vinylcyanide. This comparison may not be justified in view of the difference between r_g and r_s stated above. Our preliminary calculation by the Pariser-Parr-Pople method shows that the relative magnitude of the C–C bond orders for these molecules depends on the integral parameters, and especially, on the core resonance integral β used in the calculation. It is likely, however, that for any choice of parameters the difference in the observed sp^2-sp C–C bond lengths is larger than that predicted by the bond order-bond length correlation curve proposed by Julg and Pellégatti.18) The same tendency has been pointed out for butadiene, acrolein, and glyoxal.3)

The lengths of C=C and C≡C are slightly larger than those of ethylene and acetylene, respectively. A similar lengthening of the C=C double bond has been observed for butadiene (r_g(C=C) = 1.345 ± 0.002 Å3)), and that of the triple bond for diacetylene (r_g(C≡C) = 1.218 ± 0.001 Å6)). These results are suspected as indications of the conjugation effect. On the other hand, the C–H lengths and C=C–H angles are close to those in ethylene or acetylene. The angles C=C–C in butadiene and acrolein are different beyond the limit of uncertainty, as pointed out in Ref. 3. (123.3° and 121.0°, respectively). The corresponding angle in vinylacetylene is found to be close to the former. A slight bend is observed in the C–C≡C chain of vinylacetylene, while C≡C–H is linear within the limit of error. The ethynyl group of propynal has been shown to have a similar r_s structure.7)

The authors are indebted to Dr. Chiaki Hirose for providing them with the rotational constants for vinylacetylene before publication. Their thanks are also due to Mr. Koichi Abe who offered the vinylacetylene sample and who supplied the force constants for the molecule before publication.

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