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Molecular Structure of Ethynylbenzene from Electron Diffraction and Ab Initio Molecular Orbital Calculations

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The molecular structure and benzene ring distortions of ethynylbenzene have been investigated by gas-phase electron diffraction and ab initio MO calculations at the HF/6-31G* and 6-31G** levels. Least-squares refinement of a model with C_{2v} symmetry, with constraints from the MO calculations, yielded the following important bond distances and angles: $r_g(C_i-C_o) = 1.407 \pm 0.003$ Å, $r_g(C_o-C_m) = 1.397 \pm 0.003$ Å, $r_g(C_m-C_p) = 1.400 \pm 0.003$ Å, $r_g(C_i-CCH) = 1.436 \pm 0.004$ Å, $r_g(C\equiv C) = 1.205 \pm 0.005$ Å, $\angle C_o-C_i-C_o = 119.8 \pm 0.4^\circ$. The deformation of the benzene ring of ethynylbenzene given by the MO calculations, including $\angle C_o-C_i-C_o = 119.4^\circ$, is insensitive to the basis set used and agrees with that obtained by low-temperature X-ray crystallography for the phenylethynyl fragment, $C_6H_5-C\equiv C-$, in two different crystal environments. The partial substitution structure of ethynylbenzene from microwave spectroscopy is shown to be inaccurate in the ipso region of the benzene ring.

KEY WORDS: Substituted benzenes; gas-phase electron diffraction; ethynylbenzene; benzene ring deformation.

INTRODUCTION

Our gas-phase studies on the deformation of the benzene ring in simple monosubstituted derivatives (toluene [1, 2], trifluorotoluene [3], fluorobenzene [4], cyanobenzene [5], phenol [6], and nitrobenzene [7]) have now been extended to ethynylbenzene (phenylacetylene, $C_6H_5-C\equiv CH$). The ring geometry of this molecule has not yet been established with certainty: op-

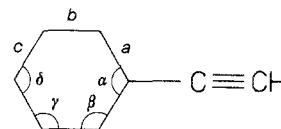


Fig. 1. Lettering of the ring parameters in ethynylbenzene. C_{2v} symmetry has been assumed.

posite ring deformations have been obtained by using different techniques. The internal angle at the *ipso* position, α (see Fig. 1)—a parameter quite sensitive to the presence and nature of the substituent [8–10]—is reported as $120.8 \pm 0.4^\circ$ in a study by microwave spectroscopy [11], while ab initio MO calculations at the HF/4-21G [12] and 6-31G [13] levels yield values of 119.4 and 119.3° , respectively. (Here and throughout this paper estimated total errors are given as error limits; least-squares standard deviations are given in parentheses as units in the last digit.) Contrasting results are also obtained for the variation of the a bond distances with respect to b and c . Accurate low-temperature X-ray diffraction studies of molecules containing the $C_6H_5-C\equiv C-$ fragment apparently support the MO

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Fig. 3. Radial distribution curves (E , experimental; T , theoretical for the model obtained from refinement B). The positions of the most important distances are marked with vertical bars, the heights of which are proportional to the weights of the distances. Also shown is the difference curve (experimental - theoretical).

tering functions and phase shifts were taken from Refs. 23 and 24, respectively.

The molecule was assumed to have C_{2v} symmetry. The five C—H bonds of the phenyl group were assumed to have equal length and to bisect the corresponding C—C—C angles. Under these constraints the geometry of the molecule is described by nine independent geometrical parameters. We have chosen to define these as follows (see Fig. 3 for the numbering of atoms): (i) three bond distances: $r(\text{C1—C2})$, $r(\text{C7}\equiv\text{C8})$, and $r(\text{C2—H2})$; (ii) four differences between bond distances: $\Delta_1(\text{C—C}) = r(\text{C1—C2}) - r(\text{C2—C3})$, $\Delta_2(\text{C—C}) = r(\text{C1—C2}) - r(\text{C3—C4})$, $\Delta_3(\text{C—C}) = r(\text{C1—C7}) - r(\text{C1—C2})$, and $\Delta(\text{C—H}) = r(\text{C2—H2}) - r(\text{C8—H8})$; (iii) two bond angles: $\angle \text{C2—C1—C6}$ and $\angle \text{C1—C2—C3}$. The difference $\Delta(\text{C—H})$ was kept fixed throughout the analysis at $+0.015 \text{ \AA}$, a value consistent with the results of the MO calculations.

In addition to geometrical parameters, 16 amplitudes of vibration were refined as independent variables. They were coupled in blocks to other amplitudes with fixed differences. All amplitudes but those associated with H...H distances were involved in the coupling. Initial values of the amplitudes were taken from calculations carried out by Dr. Attila Császár of Eötvös University, based on the force field and geometry of Ref. 12.

Selected geometric parameters from three refinements are presented in Table I. In refinement A the six C—C bonds of the benzene ring were assumed to have equal length [$\Delta_1(\text{C—C}) = \Delta_2(\text{C—C}) = 0$]; in B their differences were fixed in accordance with the results of the MO calculations [$\Delta_1(\text{C—C}) = +0.010 \text{ \AA}$, $\Delta_2(\text{C—C}) = +0.007 \text{ \AA}$]; in C the differences were taken from the microwave study [11] [$\Delta_1(\text{C—C}) = -0.008 \text{ \AA}$, $\Delta_2(\text{C—C}) = -0.010 \text{ \AA}$]. The molecular parameters from refinement B are reported in more detail in Table II, which also shows the coupling scheme of the vibrational amplitudes. Correlation matrix elements having absolute values greater than 0.5 are given in Table III.

An attempt to refine $\Delta_1(\text{C—C})$ and $\Delta_2(\text{C—C})$ as independent variables led to unsatisfactory results. Although causing a minor decrease of the R factor (0.0326 versus 0.0332), the refinement gave an unreasonably large value of $\Delta_1(\text{C—C})$, $+0.027(5) \text{ \AA}$. A similar result was obtained when the distances $r(\text{C2—C3})$ and $r(\text{C3—C4})$ were assumed to be equal and only one difference, $\Delta_1(\text{C—C}) = \Delta_2(\text{C—C})$, was refined. This reinforces our previous experience that differences between aromatic C—C bond lengths in benzene derivatives can-

Table I. Selected Geometrical Parameters^a and R Factors for Ethynylbenzene, as Obtained from Refinements A–C^b

Parameter	Refinements		
	A	B	C
$\Delta_1(\text{C—C}) = a - b$	0.0000 ^c	+0.0100 ^c	−0.0080 ^c
$\Delta_2(\text{C—C}) = a - c$	0.0000 ^c	+0.0070 ^c	−0.0100 ^c
$r(\text{C1—C2})$ (a)	1.3997(3)	1.4052(3)	1.3939(3)
$r(\text{C2—C3})$ ^d (b)	1.3997(3)	1.3952(3)	1.4019(3)
$r(\text{C3—C4})$ ^d (c)	1.3997(3)	1.3982(3)	1.4039(3)
$r(\text{C1—C7})$ ^d	1.433(2)	1.434(2)	1.431(3)
$r(\text{C7}\equiv\text{C8})$	1.204(1)	1.204(1)	1.204(1)
$\angle \text{C2—C1—C6}$ (α)	119.4(3)	119.8(3)	119.0(3)
$\angle \text{C1—C2—C3}$ (β)	120.5(3)	120.0(3)	121.3(3)
$\angle \text{C2—C3—C4}$ ^d (γ)	119.6(4)	120.1(4)	118.9(4)
$\angle \text{C3—C4—C5}$ ^d (δ)	120.3(5)	120.1(5)	120.6(5)
R factor	0.0345	0.0332	0.0361

^aBond distances (r_a) and their differences are given in \AA , angles in degrees. Least-squares standard deviations are given in parentheses as units in the last digit.

^bRefinements A, B, and C differ in the constraints on the bond lengths in the benzene ring. A: equilateral benzene ring; B: $\Delta_1(\text{C—C})$ and $\Delta_2(\text{C—C})$ taken from the ab initio MO calculations; C: $\Delta_1(\text{C—C})$ and $\Delta_2(\text{C—C})$ taken from the microwave study [11].

^cAssumed.

^dDependent parameter.

not be determined reliably from electron-diffraction data alone [25].

With the aim of reducing the number of independent variables, refinement B was repeated under either of the following constraints: (i) the internal ring angle β was linked to α by the equation $\Delta\beta = -0.591\Delta\alpha - 0.301^\circ$, where $\Delta\alpha$ and $\Delta\beta$ are differences from 120° (this empirical relationship is firmly established; it has been obtained by regression ($R = -0.991$) from a large sample of monosubstituted benzene rings, mostly studied by X-ray crystallography [9]); (ii) the internal ring angle at the *para* position, δ , was fixed at the value 119.9° , obtained by the ab initio MO calculations as well as by microwave spectroscopy. In both cases, the R factors and the refined parameters were only marginally different from those of refinement B. Repetition of refinements A and C under constraint (i) led, however, to unacceptable values of γ and δ . This points to the superiority of model B in describing the geometry of the molecule.

An attempt was eventually made to refine the shrinkage parameter that is expected to have the largest value, $\delta(\text{C4...C8})$. However, this did not result in a decrease of the R factor, and the value obtained for

Table II. Final Molecular Parameters for Ethynylbenzene, as Obtained from Refinement B^a

Distances and amplitudes of vibration (Å)				
Atomic pair	Multiplicity	r_a	l	Key to the coupling scheme
C1—C2 (<i>a</i>)	2	1.4052(3)	0.0472(5)	i
C2—C3 ^b (<i>b</i>)	2	1.3952(3)	0.0472	i
C3—C4 ^b (<i>c</i>)	2	1.3982(3)	0.0472	i
C1—C7 ^b	1	1.434(2)	0.0532	i
C2—H2	5	1.096(2)	0.077(2)	ii
C8—H8 ^b	1	1.081(2)	0.074	ii
C7≡C8	1	1.204(1)	0.036	ii
C1···C3 ^b	2	2.425(3)	0.0546(6)	iii
C1···C4 ^b	1	2.798(5)	0.064(1)	iv
C2···C4 ^b	2	2.421(5)	0.0545	iii
C2···C5 ^b	2	2.799(3)	0.064	iv
C2···C6 ^b	1	2.431(4)	0.0550	iii
C3···C5 ^b	1	2.423(6)	0.0546	iii
C7···C2 ^b	2	2.460(2)	0.0756	iii
C7···C3 ^b	2	3.736(3)	0.068(3)	v
C7···C4 ^b	1	4.232(5)	0.067(6)	vi
C8···C1 ^b	1	2.638(2)	0.051(3)	vii
C8···C2 ^b	2	3.557(3)	0.104(4)	viii
C8···C3 ^b	2	4.890(3)	0.089(6)	ix
C8···C4 ^b	1	5.436(5)	0.063(8)	x
C1···H2 ^b	2	2.171(2)	0.091(2)	xi
C1···H3 ^b	2	3.418(4)	0.091	viii
C1···H4 ^b	1	3.894(5)	0.115(13)	xii
C1···H8 ^b	1	3.718(3)	0.086	v
C2···H3 ^b	2	2.162(3)	0.091	xi
C2···H4 ^b	2	3.413(5)	0.091	viii
C2···H5 ^b	2	3.895(3)	0.116	xii
C2···H6 ^b	2	3.425(4)	0.091	viii
C2···H8 ^b	2	4.587(3)	0.15(2)	xiii
C3···H2 ^b	2	2.162(2)	0.091	xi
C3···H4 ^b	2	2.164(3)	0.091	xi
C3···H5 ^b	2	3.415(6)	0.091	viii
C3···H6 ^b	2	3.895(3)	0.115	xii
C3···H8 ^b	2	5.943(4)	0.12(5)	xiv
C4···H2 ^b	2	3.414(5)	0.091	viii
C4···H3 ^b	2	2.164(3)	0.091	xi
C4···H8 ^b	1	6.517(5)	0.14(5)	xv
C7···H2 ^b	2	2.689(2)	0.148	vii
C7···H3 ^b	2	4.619(4)	0.12	xiii
C7···H4 ^b	1	5.328(5)	0.090	x
C7···H8 ^b	1	2.285(2)	0.0773	iii
C8···H2 ^b	2	3.538(2)	0.206	viii
C8···H3 ^b	2	5.711(4)	0.12(5)	xvi
C8···H4 ^b	1	6.532(5)	0.14	xv

Angles (degrees) and differences between bond distances (Å)

Parameter	Value
∠ C2—C1—C6 (α)	119.8(3)
∠ C1—C2—C3 (β)	120.0(3)
∠ C2—C3—C4 ^b (γ)	120.1(4)
∠ C3—C4—C5 ^b (δ)	120.1(5)
$\Delta_1(\text{C—C})^c$ ($a - b$)	0.0100 ^d

Table II. Continued

Angles (degrees) and differences between bond distances (Å)	
Parameter	Value
$\Delta_2(\text{C}-\text{C})^e$ ($a - c$)	0.0070 ^d
$\Delta_3(\text{C}-\text{C})^f$	0.028(2)
$\Delta(\text{C}-\text{H})^g$	0.015 ^d

^aLeast-squares standard deviations are given in parentheses as units in the last digit. The H···H interactions are not shown; they have been given fixed amplitudes of 0.12–0.26 Å.

^bDependent distance (or angle).

^c $\Delta_1(\text{C}-\text{C}) = r(\text{C1}-\text{C2}) - r(\text{C2}-\text{C3})$.

^dAssumed from the ab initio MO calculations.

^e $\Delta_2(\text{C}-\text{C}) = r(\text{C1}-\text{C2}) - r(\text{C3}-\text{C4})$.

^f $\Delta_3(\text{C}-\text{C}) = r(\text{C1}-\text{C7}) - r(\text{C1}-\text{C2})$.

^g $\Delta(\text{C}-\text{H}) = r(\text{C2}-\text{H2}) - r(\text{C8}-\text{H8})$.

$\delta(\text{C4} \dots \text{C8})$ under the conditions of refinement B, 0.012(10) Å, was not significantly different from zero.

RESULTS AND DISCUSSION

The molecular geometry of ethynylbenzene obtained by electron diffraction using MO constraints on bond length differences (refinement B) is compared in Table IV with those obtained by microwave spectroscopy [11] and ab initio MO calculations with various basis sets. The calculated values of the ring angles and of the differences between the ring C—C distances are virtually unaffected by the choice of the basis set, including the addition of polarization functions. This suggests that the deformation of the benzene ring caused by the ethynyl substituent is determined accurately by the calculations, in spite of neglecting electron correlation.

The value of the angle α from the present electron-

diffraction study, $119.8 \pm 0.4^\circ$, is consistent with the result of the MO calculations, 119.4° . The agreement between experiment and calculation is even better for the other ring angles, with differences not exceeding 0.2° . On the other hand, the results of refinement C (see Table I) indicate that the geometry of the *ipso* region of the ring obtained by microwave spectroscopy [11] is incompatible with the electron-diffraction data.

It seems likely that the results of the microwave study are affected by some systematic error, arising from the fact that atoms C1, C2, and H2 have small a coordinates in the principal axes system. The same problem has occurred in the microwave studies of chlorobenzene [27] and nitrobenzene [28], where the geometry of the *ipso* region of the ring has been shown to be in error [7, 10, 29].

The molecular structure of ethynylbenzene in the crystal has not yet been studied by X-ray diffractometry. However, the low-temperature studies of 2-phenylethynyl-*N,N*-dimethylaniline [14] and diphenylacetylene [15] provide accurate geometries for the phenylethynyl fragment, $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-$, in two different crystal environments. The geometries of the benzene ring obtained from these studies are compared in Table V with that of free ethynylbenzene from MO calculations. There is excellent agreement between the ring angles as well as between the differences of bond distances. Thus, the deformation of the benzene ring caused by the ethynyl substituent is reproduced by the calculations, and the effects of crystal environment on the ring geometry are of marginal importance in this system. On the other hand, effects of crystal environment occur markedly in benzene derivatives with highly polar functional groups, which take part in intermolecular hydrogen bonding or

Table III. Correlation Matrix Elements with Absolute Values Greater than 0.5, as Obtained from Refinement B

i	j	x_{ij} ($i \neq j$)
$r(\text{C1}-\text{C2})$	$\Delta_3(\text{C}-\text{C})$	-0.65
$\angle \text{C2}-\text{C1}-\text{C6}$	$\angle \text{C1}-\text{C2}-\text{C3}$	-0.92
$r(\text{C2}-\text{H2})$	$l(\text{C2}-\text{H2})$	0.51
$l(\text{C1}-\text{C2})$	$l(\text{C1} \dots \text{C3})$	0.54
$l(\text{C1}-\text{C2})$	S_{19}^a	0.78
$l(\text{C1} \dots \text{C3})$	S_{19}^a	0.59
$l(\text{C8} \dots \text{C3})$	$l(\text{C2} \dots \text{H8})$	0.56
$l(\text{C3} \dots \text{H8})$	$l(\text{C8} \dots \text{H3})$	0.65

^aScale factor for the 19-cm data set.

Table IV. Bond Distances(Å) and Internal Ring Angles (degrees) of Ethynylbenzene

Parameter	Electron diffraction ^{a,b}	Microwave spectroscopy ^c	Ab initio MO calculations			
			4-21G ^d	6-31G ^e	6-31G* ^f	6-31G** ^f
$r(\text{C1}-\text{C2})$ (a)	1.407	1.388 ± 0.004	1.392	1.395	1.393	1.392
$r(\text{C2}-\text{C3})$ (b)	1.397	1.396 ± 0.005	1.382	1.385	1.383	1.383
$r(\text{C3}-\text{C4})$ (c)	1.400	1.398 ± 0.001	1.385	1.388	1.386	1.386
$r(\text{C1}-\text{C7})$	1.436 ± 0.004	1.448 ± 0.005	1.438	1.437	1.443	1.443
$r(\text{C7}\equiv\text{C8})$	1.205 ± 0.005	1.208 ± 0.001	1.188	1.196	1.188	1.189
$r(\text{C2}-\text{H2})$	1.101 ± 0.014	—	1.071	1.072	1.074	1.075
$r(\text{C3}-\text{H3})$		—	1.072	1.073	1.075	1.076
$r(\text{C4}-\text{H4})$		—	1.072	1.073	1.075	1.076
$r(\text{C8}-\text{H8})$	1.086 ± 0.014 ^b	1.055 ± 0.001	1.051	1.053	1.057	1.057
$\angle \text{C2}-\text{C1}-\text{C6}$ (α)	119.8 ± 0.4	120.8 ± 0.4	119.4	119.3	119.4	119.4
$\angle \text{C1}-\text{C2}-\text{C3}$ (β)	120.0 ± 0.4	119.8 ± 0.4	120.2	120.3	120.2	120.2
$\angle \text{C2}-\text{C3}-\text{C4}$ (γ)	120.1 ± 0.5	119.9 ± 0.2	120.2	120.2	120.2	120.2
$\angle \text{C3}-\text{C4}-\text{C5}$ (δ)	120.1 ± 0.7	119.9 ± 0.2	119.9	119.9	119.9	119.9

^aThis work, refinement B. Bond distances are r_g values. Total errors are given as error limits; they have been calculated according to the expressions $\sigma_T = [2\sigma_{LS}^2 + (0.002r)^2]^{1/2}$ (for bond distances) and $\sigma_T = [2\sigma_{LS}^2]^{1/2}$ (for bond angles), where σ_{LS} is the least-squares standard deviation [26]. For $r(\text{C7}\equiv\text{C8})$ and the $r(\text{C}-\text{H})$ distances we have added 0.002 Å and 0.010 Å, respectively, to the total error to account for the sensitivity of these parameters to background changes.

^bThe differences $r(\text{C1}-\text{C2}) - r(\text{C2}-\text{C3})$, $r(\text{C1}-\text{C2}) - r(\text{C3}-\text{C4})$, and $r(\text{C2}-\text{H2}) - r(\text{C8}-\text{H8})$ were constrained from the MO calculations.

^cRef. 11. This is a partial substitution structure, since the coordinates of atoms C1, C2, H2, H3, and H4 are not substitution coordinates.

^dRef. 12. To facilitate comparison, bond distances are reported here without the offset corrections applied in the original paper.

^eRef. 13.

^fThis work.

Table V. Benzene Ring Deformation in the Phenylethynyl Fragment, $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-$, from Low-Temperature Crystallographic Studies^a

Parameter ^b	2-Phenylethynyl- <i>N,N</i> -dimethylaniline ^c	Diphenylacetylene ^d	Ethynylbenzene (ab initio MO geometry) ^e
<i>a</i>	1.401	1.406	1.392
<i>b</i>	1.388	1.394	1.383
<i>c</i>	1.389	1.395	1.386
α	119.5	119.4	119.4
β	120.0	120.1	120.2
γ	120.2	120.3	120.2
δ	120.1	119.9	119.9

^aBond distances are given in Å, angles in degrees.

^bBond distances and angles are labeled according to Fig. 1.

^cFrom an X-ray diffraction study at 98 K [14]. The refinement was based on all reflections ($\sin \theta/\lambda \leq 0.64$ Å⁻¹). Bond distances and angles are not corrected for thermal-motion effects; they have been averaged to be consistent with C_{2v} symmetry. Estimated standard deviations are 0.002–3 Å and 0.1–0.2°.

^dFrom an X-ray diffraction study at 123 K [15]. The refinement was based on high-order reflections ($\sin \theta/\lambda > 0.50$ Å⁻¹). Bond distances and angles are corrected for thermal-motion effects; they have been averaged to be consistent with C_{2v} symmetry. Estimated standard deviations are 0.002 Å and 0.1°.

^eThis work, 6-31G** level.

strong dipole-dipole interactions [5, 7, 10, 21, 30, 31]. The ethynyl substituent is slightly polar only, and the effects are expected to be small.

The horizontal variation in the absolute values of the C—C distances of Table V is not surprising. It originates from the different physical meaning that a bond distance has when determined by different techniques, and from the various systematic errors affecting its determination. Among these we mention the use of low-order intensity data and the lack of thermal-motion corrections in the X-ray diffraction study of 2-phenylethynyl-*N,N*-dimethylaniline [14], and the neglect of electron correlation in the MO calculations.

The equilibrium structure of acetylene has been determined from a combination of infrared and Raman spectroscopic data [32]; a value of 1.20241 ± 0.00009 Å was obtained for r_e (C≡C). The length of the same bond is calculated by us as 1.1861 Å at the HF/6-31G** level. This corresponds to an "offset" correction of +0.0163 Å, which can be transferred confidently to ethynylbenzene. As the C≡C bond distance in ethynylbenzene is 1.1886 Å at the HF/6-31G** level, the corresponding r_e value should be 1.205 Å. This compares well with the C≡C distance from the microwave study, $r_s = 1.208 \pm 0.001$ Å [11], which we expect to be accurate since the two atoms involved have large a coordinates in the principal axes system of the molecule. The value of r_g (C≡C) from the present electron-diffraction study is 1.205 ± 0.005 Å. This is a little small, as r_g should always be larger than r_e . Due to the stiffness of the triple bond, however, r_g (C≡C) is expected to be only a few thousandths of an angström larger than r_e (C≡C); thus the experimental result is compatible with the estimated r_e value, especially taking into account the relatively large experimental uncertainty.

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SUPPLEMENTARY MATERIAL AVAILABLE

A listing of total electron-diffraction intensities of ethynylbenzene for two camera distances (two pages). Supplementary material may be obtained from the authors upon request.

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