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Molecular Structure and Benzene Ring Deformation of Three Ethynylbenzenes from Gas-Phase Electron Diffraction and Quantum Chemical Calculations

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The molecular structures of ethynylbenzene and *s*-triethynylbenzene have been accurately determined by gas-phase electron diffraction and ab initio/DFT MO calculations and are compared to that of *p*-diethynylbenzene from a previous study [Domenicano, A.; Arcadi, A.; Ramondo, F.; Campanelli, A. R.; Portalone, G.; Schultz, G.; Hargittai, I. *J. Phys. Chem.* **1996**, *100*, 14625]. Although the equilibrium structures of the three molecules have C_{2v}, D_{3h}, and D_{2h} symmetry, respectively, the corresponding average structures in the gaseous phase are best described by nonplanar models of C_s, C_{3v}, and C_{2v} symmetry, respectively. The lowering of symmetry is due to the large-amplitude motions of the substituents out of the plane of the benzene ring. The use of nonplanar models in the electron diffraction analysis yields ring angles consistent with those from MO calculations. The molecular structure of ethynylbenzene reported from microwave spectroscopy studies is shown to be inaccurate in the ipso region of the benzene ring. The variations of the ring C−C bonds and C−C−C angles in *p*-diethynylbenzene and *s*-triethynylbenzene are well interpreted as arising from the superposition of independent effects from each substituent. In particular, experiments and calculations consistently show that the mean length of the ring C−C bonds increases by about 0.002 Å per ethynyl group. MO calculations at different levels of theory indicate that though the length of the C≡C bond of the ethynyl group is unaffected by the pattern of substitution, the $C_{ipso}-C_{ethynyl}$ bonds in *p*-diethynylbenzene are 0.001−0.002 Å shorter than the corresponding bonds in ethynylbenzene and *s*-triethynylbenzene. This small effect is attributed to conjugation of the two substituents through the benzene ring. Comparison of experimental and MO results shows that the differences between the lengths of the $C_{ipso}-C_{ethynyl}$ and $C_{ipso}-C_{ortho}$ bonds in the three molecules, 0.023−0.027 Å, are correctly computed at the MP2 and B3LYP levels of theory but are overestimated by a factor of 2 when calculated at the HF level.

Introduction

Gas-phase electron diffraction and, increasingly, quantum chemical calculations, have been used extensively in our laboratories to investigate geometrical changes in benzene derivatives.[1] We have shown that the geometry of a monosubstituted benzene ring contains valuable information on the electronegativity, resonance, and steric effects of the substituent, and also on other, more subtle electronic effects.[2] The geometrical parameters that are most sensitive to the impact of the substituent are the internal ring angles at the ipso and ortho positions (α and *β*, respectively, in Figure 1) and the $C_{ipso}-C_{ortho}$ bond distance, *a*. The changes of α and *a* have been rationalized in terms of either hybridization effects at the ipso carbon[3] or valence-shell electron-pair repulsions.[4] We have recently derived an electronegativity scale of functional groups, based on the ring angles of 100 monosubstituted benzene derivatives from quantum chemical calculations.[5]

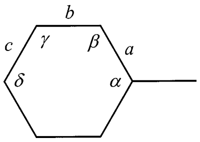

Figure 1. Lettering of the C−C bonds and C−C−C angles in a monosubstituted benzene ring of C_{2v} symmetry.

In polysubstituted benzene derivatives the distortion of the ring may be interpreted, to a good approximation, as arising from the superposition of independent contributions from each substituent.[4,6] Deviations from additivity may occur in ortho-disubstituted derivatives, due to interaction between substituents, and in some para-disubstituted derivatives, where the resonance interaction of each substituent with the ring is perturbed by the other substituent.[7]

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Some years ago, we reported the molecular structures of ethynylbenzene[8] and *p*-diethynylbenzene,[9] from electron diffraction and quantum chemical calculations. Here we present the results of (i) a gas-phase electron diffraction study of *s*-triethynylbenzene, (ii) a reanalysis of the gas electron diffraction intensities of ethynylbenzene, and (iii) a comparison of the molecular structures of ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene, as obtained from electron diffraction experiments and MO calculations at various levels of theory. The reliability of the comparison is enhanced by the fact that the experimental data are from the same laboratory, and have been produced, processed, and analyzed using identical procedures.

The rotational spectrum of ethynylbenzene was studied in 1975 by Cox et al.,[10] who determined a partial substitution structure from the spectra of six isotopomers. However, the accuracy of the parameters defining the geometry of the ipso region has been questioned,[8,11] because the reported ring deformation is opposite to that obtained by electron diffraction and quantum chemical calculations. Recently, the rotational spectrum of ethynylbenzene has been reinvestigated by Fourier transform microwave spectroscopy, measuring the spectra of 39 isotopomers, and using a variety of methods to derive the structure of the molecule from the inertial moments.[12] The geometry of the ipso region produced by the various methods supports the results of the earlier microwave study.[10] With regard to *p*-diethynylbenzene and *s*-triethynylbenzene, these molecules lack a permanent electric dipole moment and are therefore not amenable to microwave studies. On the other hand, the higher molecular symmetry makes them better suited for electron diffraction analysis than the monosubstituted derivative, because many of the atom−atom interactions double or treble in the scattering of electrons by these molecules.

The molecules considered in the present study are the building blocks of a number of highly conjugated systems with long electronic pathways.[13] These systems have important technological applications, such as liquid crystal displays, nonlinear optical devices, molecular wires and sensors, and self-assembling nanostructures.

Theoretical Calculations

Quantum chemical calculations on ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene (plus unsubstituted benzene, used as a reference) were carried out systematically and consistently at a series of levels of theory (HF, MP2(f.c.), and B3LYP) with the 6-31G* and 6-311++G** basis sets,[14] using the *Gaussian 98* package.[15] With *s*-triethynylbenzene convergence was slow, particularly at the MP2(f.c.)/6-311++G** level, where the standard convergence criterion had to be slightly released. Vibrational frequency calculations, run at the B3LYP/6-31G* level on the B3LYP/6-31G* geometries, showed the equilibrium structures of the three ethynylbenzenes to have C_{2v}, D_{2h}, and D_{3h} symmetry, respectively. Vibrational amplitudes for the electron diffraction least-squares refinements were calculated with the program ASYM40, version 3.2,[16] based on the B3LYP/6-31G* optimizations. Vibrational frequencies and amplitudes were also obtained from molecular mechanics calculations, using the MM3 force field.[17] Geometrical parameters from the MO calculations are provided as Supporting Information to this paper (Tables S1−S5; all tables containing an S in their identification label are deposited in the Supporting Information; see the relevant paragraph at the end of the paper).

TABLE 1: Low-Frequency Vibrational Modes (ν < 300 cm^{-1}) of *s*-Triethynylbenzene

description	symmetry	wavenumber (cm^{-1}) B3LYP/6-31G*[a]	wavenumber (cm^{-1}) MM3
symmetric $C-C_\alpha\equiv CH$ wag (mixed with CCC bending about C_α)	A_2'' (out-of-plane)	96	99
mixed asymmetric bendings (about C_{ipso} and C_α)	E' (in-plane)	112	110
asymmetric $C-C_\alpha\equiv CH$ wag (mixed with CCC bending about C_α)	E'' (out-of-plane)	162	176
mixed symmetric bendings (about C_{ipso} and C_α)	A_2' (in-plane)	204	206

[a] Unscaled frequencies.

Most calculations were run on a cluster of four AlphaServer COMPAQ/ES40 at the CASPUR Supercomputing Center, University of Rome “La Sapienza”.

Experimental Section

Synthesis. *s*-Triethynylbenzene was prepared according to the literature[18] from *s*-tribromobenzene and trimethylsilylacetylene, by means of a palladium-catalyzed coupling reaction. After workup, the raw product was purified by column chromatography and recrystallized from 70/30 ethanol/water solution (mp 103−104 °C, lit.[19] 105−107 °C). The purity was checked by thin-layer chromatography, gas chromatography, gas chromatography/mass spectrometry, and NMR spectroscopy, and was found to be better than 98%.

Electron Diffraction. The electron diffraction photographs of *s*-triethynylbenzene were taken with the Budapest EG-100A apparatus,[20] using a membrane nozzle[21] at a temperature of about 397 K. Nozzle-to-plate distances of about 50 and 19 cm were used. The tracing and data reduction were carried out according to our usual procedure.[7b,22] The ranges of the intensity data were $2.000 \le s \le 13.875$ Å^{-1} and $8.50 \le s \le 35.75$ Å^{-1}, with data intervals of 0.125 and 0.25 Å^{-1}, respectively. The total experimental intensities are deposited in Table S6.

Analysis of the Electron Diffraction Data

The least-squares method was applied to molecular intensities as in refs 7b and 22, using a modified version of the program by Seip and co-workers.[23] The inelastic and elastic scattering functions were taken from refs 24 and 25, respectively. The initial background lines were modified repeatedly in the course of the analysis.

***s*-Triethynylbenzene.** Already at an early stage of the analysis it became apparent that a model based on the equilibrium D_{3h} structure was inadequate to describe the average structure of the molecule, due to large-amplitude vibrational motions. According to vibrational frequency calculations, the lowest-frequency modes are two in-plane and two out-of-plane vibrations (Table 1). As with other benzene derivatives studied in our laboratories,[26] the MM3 and B3LYP/6-31G* frequencies are in close agreement, pointing to the suitability of the MM3 force field to obtain low-frequency modes. Only the out-of-plane vibrations (symmetric and asymmetric) contribute significantly to making the average structure of the present molecule different from the equilibrium structure. They involve principally the bending of the ethynyl groups as rigid entities about the respective ipso carbons (wagging), mixed with contributions from $C-C\equiv C$ bendings. The effect of the in-plane vibrations on the long C···C distances is much less pronounced and can safely be ignored. A substantial proportion of the effect

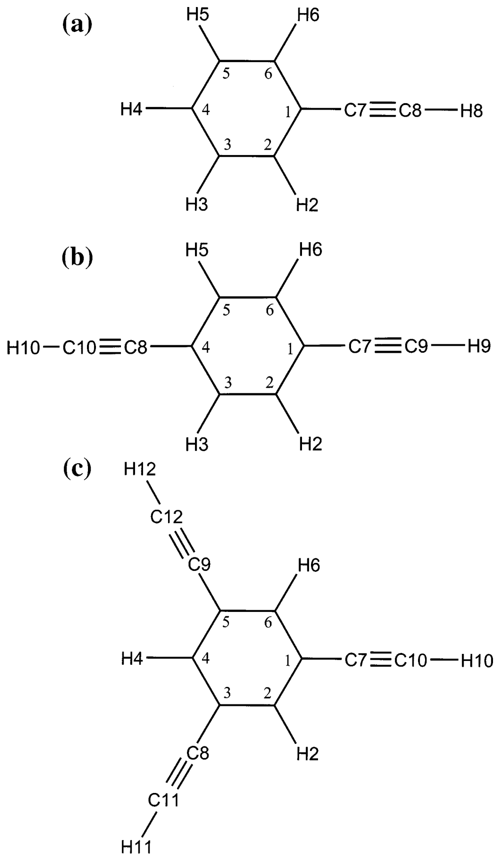

Figure 2. Numbering of atoms in (a) ethynylbenzene, (b) *p*-diethynylbenzene, and (c) *s*-triethynylbenzene.

that the asymmetric out-of-plane vibration has on the C···C distances is the same as that of the symmetric out-of-plane vibration.

Two simple models, A and B, were tested in the course of the analysis. Model A was based on the equilibrium structure, that is, on a planar molecule of D_{3h} symmetry. Model B consisted in a symmetrically out-of-plane bent molecule of C_{3v} symmetry, with local D_{3h} and $C_{\infty v}$ symmetries for the benzene ring and the C−C≡C−H groups, respectively. The six independent parameters to describe the geometry of model A were chosen as follows (see Figure 2c for the numbering of atoms): (i) the bond distances r(C1−C2) and r(C2−H2); (ii) the bond-distance differences[27] Δ_1(C−C) = r(C1−C7) − r(C1−C2), Δ_2(C−C) = r(C7≡C10) − r(C1−C2), and Δ(C−H) = r(C10−H10) − r(C2−H2); (iii) the bond angle ∠C2−C1−C6. Model B requires an additional parameter, the out-of-plane bending angle of the ethynyl groups about the ipso carbons, θ. This is defined as the angle that the C1···H10 line makes with the C1···C4 line. Of these parameters, r(C2−H2) was kept at 1.0935 Å, based on the fact that our r_a(C−H) value for benzene is 1.096 Å,[28] whereas r_e(C2−H2) is calculated to be ca. 0.0025 Å shorter than r_e(C−H) in benzene at the HF and B3LYP levels (see Tables S3 and S4). The difference Δ(C−H) was fixed at −0.019 Å, a value consistent with the results of MO calculations. The remaining geometrical parameters were refined as independent variables.

Eleven mean amplitudes of vibration, l, were also treated as independent parameters. Most of them were coupled in groups to other amplitudes with constrained differences, Δl. These Δl's and some other amplitudes that were not refined were taken from spectroscopic calculations based on the B3LYP/6-31G* optimization. Using Δl values from calculations with the MM3 force field[17] had no effect on the geometrical parameters.

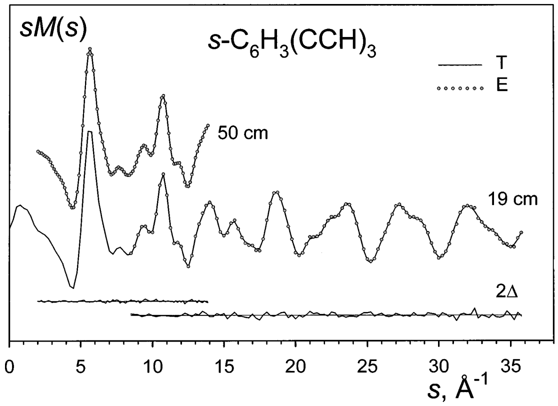

Figure 3. Molecular intensity curves of *s*-triethynylbenzene for the two camera distances (E, experimental; T, theoretical for model B). Also shown are the difference curves (E − T).

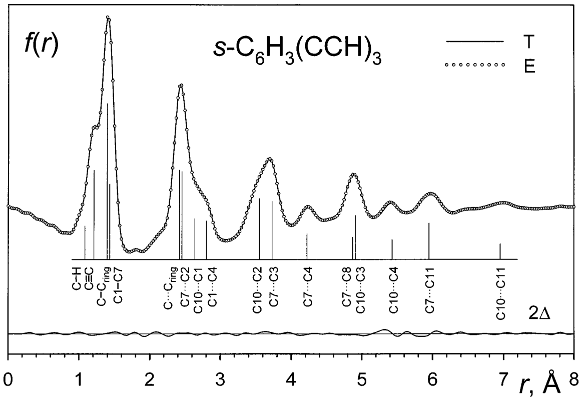

Figure 4. Radial distribution curves of *s*-triethynylbenzene (E, experimental; T, theoretical for model B). They were calculated using an artificial damping factor exp(−0.002s^2); theoretical values were used in the 0.00 ≤ s ≤ 1.75 Å^{-1} region. The positions of the most important distances are marked with vertical bars, whose heights are proportional to the relative weights of the atomic pairs. Also shown is the difference curve (E − T).

Model B fits the experimental data better than model A (R = 0.0300 vs 0.0364), yielding an effective bending angle of the ethynyl groups of 8.7 ± 0.6°.[29] This compares well with the value of the corresponding angle in *p*-diethynylbenzene, 6.8 ± 1.7° from our electron diffraction study.[9] The value of the internal ring angle at the ipso carbon, 119.6 ± 0.2°, is consistent with the results of MO calculations (Table S3), whereas the corresponding value of model A is unacceptably large, 120.7°. Using more sophisticated models, such as an out-of-plane bent molecule with nonlinear C−C≡C−H groups, or a 1:1 mixture of symmetrically and asymmetrically out-of-plane bent molecules, did not result in further improvement of the fit, nor in significant changes in the molecular parameters. Final molecular parameters from model B are reported in Tables 2 and S7, showing also the coupling of vibrational amplitudes. Molecular intensities and radial distributions are presented in Figures 3 and 4, respectively. Correlation matrix elements with absolute values greater than 0.5 are given in Table S8.

Ethynylbenzene. The accurate determination of the molecular structure of ethynylbenzene by the electron diffraction technique is a demanding task, due to the relatively low symmetry of the molecule. The present reanalysis of the experimental data from the previous study,[8] collected at about 319 K with the Budapest apparatus,[20] was aimed at improving the accuracy of the results by (i) appropriately treating the large-amplitude out-of-plane motion of the substituent (which was ignored in the previous study), (ii) imposing more accurate constraints from other

TABLE 2: Molecular Parameters of *s*-Triethynylbenzene from Electron Diffraction[a]

Distances and Mean Amplitudes of Vibration (Å)[b]

atom pair	multiplicity	r_a	l exp	l calc[c]	coupling scheme[d]
C1−C2	6	1.4023(4)	0.0469(4)	0.0458	i
C1−C7	3	1.4294(9)[e]	0.0470	0.0459	i
C7≡C10	3	1.2114(4)[e]	0.0368(6)	0.0354	ii
C2−H2	3	1.0935[f]	0.0764	0.0750	ii
C10−H10	3	1.0745[e]	0.0738	0.0724	ii
C1⋯C3	3	2.434(2)[e]	0.0584(5)	0.0556	iii
C1⋯C4	3	2.805(1)[e]	0.065(1)	0.063	iv
C2⋯C4	3	2.424(2)[e]	0.0589	0.0561	iii
C7⋯C2	6	2.450(1)[e]	0.0697	0.0669	iii
C7⋯C3	6	3.732(1)[e]	0.067(1)	0.065	v
C7⋯C4	3	4.223(1)[e]	0.077(3)	0.067	vi
C10⋯C1	3	2.641(1)[e]	0.052	0.050	iv
C10⋯C2	6	3.553(1)[e]	0.099(2)	0.099	vii
C10⋯C3	6	4.889(1)[e]	0.089(1)	0.086	viii
C10⋯C4	3	5.430(2)[e]	0.085(4)	0.070	ix
C7⋯C8	3	4.881(2)[e]	0.089	0.086	viii
C7⋯C11	6	5.951(3)[e]	0.135(3)	0.128	x
C10⋯C11	3	6.955(4)[e]	0.186(10)	0.183	xi

Angles (deg) and Differences between Distances (Å)

∠C2−C1−C6	119.57(15)
Δ_1(C−C)[g]	0.0271(12)
Δ_2(C−C)[h]	−0.1910(5)
Δ(C−H)[i]	−0.019[j]
θ[k]	8.7(4)

[a] Least-squares standard deviations are in parentheses in units of the last digit. [b] To save space, only C−C, C−H, and C⋯C pairs are listed in this table. The unabridged list, reporting also C⋯H pairs, is provided in the Supporting Information (Table S7). [c] From spectroscopic calculations based on the B3LYP/6-31G* optimization. [d] The roman numerals indicate the groups within which the amplitudes were refined with constant differences between them. [e] Dependent parameter. [f] Assumed (see text). [g] Δ_1(C−C) = r(C1−C7) − r(C1−C2). [h] Δ_2(C−C) = r(C7≡C10) − r(C1−C2). [i] Δ(C−H) = r(C10−H10) − r(C2−H2). [j] Assumed from B3LYP/6-311++G** calculations. [k] Out-of-plane bending angle of the substituent about C1, defined as the angle that the C1⋯H10 line makes with the C1⋯C4 line.

TABLE 3: Low-Frequency Vibrational Modes (ν < 300 cm^{-1}) of Ethynylbenzene

		wavenumber (cm^{-1})				
		experimental		calculated		
description	symmetry	Bacon et al.[a]	King and So[b]	HF/ 4-21G[c]	B3LYP/ 6-31G*[d]	MM3[e]
C−C$_\alpha$≡CH wag (mixed with CCC bending about C$_\alpha$)	B$_1$ (out-of-plane)	140	162	130	146	155
mixed CCC bendings (about C$_{ipso}$ and C$_\alpha$)	B$_2$ (in-plane)	152	162[f]	146	159	159

[a] Reference 30. [b] Reference 31. [c] Reference 11, scaled frequencies. [d] This work, unscaled frequencies. [e] This work. [f] Double assignment, see ref 32.

techniques, and (iii) carefully redrawing the background lines. The ranges of the intensity data used in the present analysis were 2.000 ≤ s ≤ 14.125 Å^{-1} (50 cm data set) and 10.00 ≤ s ≤ 35.50 Å^{-1} (19 cm data set), with data intervals of 0.125 and 0.25 Å^{-1}, respectively. The total experimental intensities are deposited in Table S9.

The two lowest-frequency vibrational modes of ethynylbenzene are in-plane and out-of-plane vibrations (Table 3). The two modes are nearly degenerate, as shown consistently by experiment and theoretical calculations. They involve principally the bending of the ethynyl group as a rigid entity—an in-plane and an out-of-plane bend about the ipso carbon—mixed with contributions from C−C≡C bendings. Only the out-of-plane vibration contributes significantly to making the average structure of the molecule different from the equilibrium structure, as it shortens systematically all nonbonded interatomic distances between the substituent and the benzene ring. The resulting average structure is therefore nonplanar. We have based our model on an out-of-plane bent molecule of C_s symmetry, with local C_{2v} and $C_{\infty v}$ symmetries for the benzene ring and the C−C≡C−H group, respectively. Under these symmetry constraints the geometry of the molecule is described by 14 independent parameters, which we have chosen to define as follows (see Figure 2a for the numbering of atoms): (i) the bond distances r(C1−C2) and r(C4−H4); (ii) the bond-distance differences[27] Δ_1(C−C) = r(C2−C3) − r(C1−C2), Δ_2(C−C) = r(C3−C4) − r(C1−C2), Δ_3(C−C) = r(C1−C7) − r(C1−C2), Δ_4(C−C) = r(C7≡C8) − r(C1−C2), Δ_1(C−H) = r(C2−H2) − r(C4−H4), Δ_2(C−H) = r(C3−H3) − r(C4−H4), and Δ_3(C−H) = r(C8−H8) − r(C4−H4); (iii) the bond angles ∠C2−C1−C6(α) and ∠C3−C4−C5(δ); (iv) the bond-angle differences $\Delta\tau_1$ = ∠C1−C2−H2 − ∠C3−C2−H2 and $\Delta\tau_2$ = ∠C2−C3−H3 − ∠C4−C3−H3; and (v) the out-of-plane bending angle of the substituent about the ipso carbon, θ, defined as the angle that the C1⋯H8 line makes with the C1⋯C4 line.

An accurate determination of all these parameters is not feasible by electron diffraction alone. We have therefore imposed a number of geometrical constraints, based on reliable structural information from other techniques. The bond distance r(C4−H4) was assumed at 1.096 Å from our electron diffraction study of benzene,[28] because MO calculations give essentially equal values for r_e(C4−H4) in ethynylbenzene (Table S1) and r_e(C−H) in benzene (Table S4). The differences Δ_1(C−C), Δ_2(C−C), Δ_1(C−H), Δ_2(C−H), Δ_3(C−H), $\Delta\tau_1$, and $\Delta\tau_2$ were assumed from the B3LYP/6-311++G** calculations. The ring angle δ was kept at 119.9°, from the partial r_s structure of ethynylbenzene obtained by microwave spectroscopy.[10] This value is expected to be accurate, because the atomic coordinates of C3, C4, and C5 in the inertial reference framework are large and are thus well determined by the substitution method. The microwave result is also supported by MO calculations at various levels of theory, which yield δ values in the narrow range 119.8−119.9° (Table S1 and refs 8, 11, and 12). Simultaneously refining the ring angle α and the bending angle θ has proved unfeasible, due to high correlation between these parameters. We have found that the experimental data could be approximated equally well by either assuming different values for θ and allowing α to refine or vice versa. In view of the evidence for a pronounced out-of-plane motion of the substituent provided by spectroscopic calculations, we have eventually fixed θ at 8.0°, a value consistent with our experimental results for *p*-diethynybenzene[9] and *s*-triethynylbenzene. The remaining variables, namely r(C1−C2), Δ_3(C−C), Δ_4(C−C), and the ring angle α, were refined as independent parameters. Eleven mean amplitudes of vibration were also treated as independent parameters, in the same manner as with *s*-triethynylbenzene. Under the above conditions, the ring angle α refines to 119.2 ± 0.2°, a value consistent with the results of MO calculations. If the model is constrained to the C_{2v} symmetry of the equilibrium structure, α increases to 120.0°.

Molecular parameters from the final refinement are reported in Tables 4 and S10, showing also the coupling of vibrational amplitudes. Molecular intensities and radial distributions are presented in Figures 5 and 6, respectively. Correlation matrix

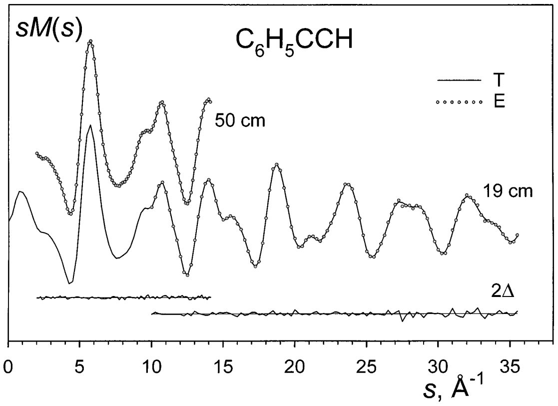

Figure 5. Molecular intensity curves of ethynylbenzene for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (E − T).

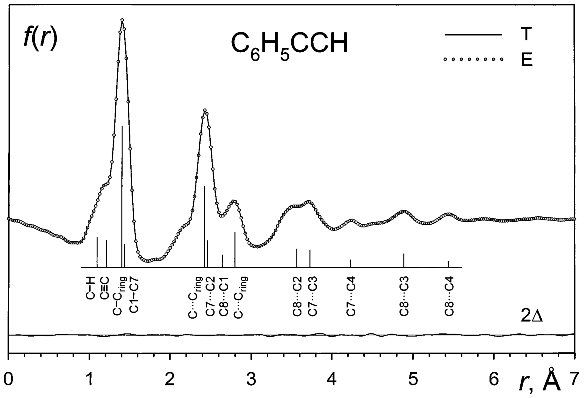

Figure 6. Radial distribution curves of ethynylbenzene (E, experimental; T, theoretical). They were calculated using an artificial damping factor $\exp(-0.002s^2)$; theoretical values were used in the $0.00 \leq s \leq 1.75$ Å^{-1} region. The positions of the most important distances are marked with vertical bars, whose heights are proportional to the relative weights of the atomic pairs. Also shown is the difference curve (E − T).

elements with absolute values greater than 0.5 are given in Table S11.

Results and Discussion

The present study provides conclusive evidence that the average structures of ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene in the gaseous phase are best described by nonplanar models of C_s, C_{2v}, and C_{3v} symmetry, respectively, although the corresponding equilibrium structures have C_{2v}, D_{2h}, and D_{3h} symmetry, respectively.[33] This is due to the large-amplitude motions of the substituents out of the plane of the benzene ring. The use of nonplanar models in the present electron diffraction studies yielded ring angles consistent with the results of MO calculations, as well as the expectation for this type of substituent (p 4945 of ref 5).

Benzene Ring Deformation in Ethynylbenzene. Accurate determination of the deformation of the benzene ring in monosubstituted derivatives is important as it conveys information on the nature of the interaction between the ring and the substituent.[2,5] In the case of ethynylbenzene the ring deformation is small, with the C−C bond distances and C−C−C angles differing by less than 0.011 Å and 1.0°, respectively, from the reference values of unsubstituted benzene. Our MO calculations, carried out at different levels of theory, consistently reveal the trends of distortion (Table S5). The actual geometrical variations, however, depend slightly on the level of theory in the calculations. Table S5 shows that bond distance changes become less pronounced as one moves from the ipso to the para carbon. Thus the *a* bonds are 0.006−0.010 Å longer than the C−C bond of unsubstituted benzene, the *b* bonds are 0.003−0.004 Å shorter, and the variation of the *c* bonds is negligibly small. The angular deformation is also more pronounced at the ipso carbon, with α decreasing by 0.4−0.9° from the reference value of 120.0°. The largest value in each range is produced by B3LYP calculations. As regards the other ring angles, all MO calculations point to a tiny increase of γ (0.2−0.3°) and an even smaller decrease of δ (0.1−0.2°). The angle β is calculated to be nearly equal to γ at the HF and B3LYP level, whereas MP2 calculations yield values closer to 120.0°.

The electron diffraction study gives accurate ring angles, whose values ($\alpha = 119.2$, $\beta = 120.2$, $\gamma = 120.2$, and $\delta = 119.9$°) are in closer agreement with the results of HF and B3LYP calculations than those from the previous study.[8] As reliable information on the differences between the lengths of the *a*, *b*, and *c* bonds in ethynylbenzene could not be obtained from the experiment, these were assumed from the MO calculations.

In their reinvestigation of the microwave rotational spectra of ethynylbenzene Dreizler et al.[12] used a number of different procedures to derive the structure of the molecule from the inertial moments. In all cases, however, the ring angle α turned out to be larger than 120°, in agreement with the earlier work by Cox et al.[10] Also, the *a* bonds came up to be shorter than the *b* bonds in many cases. This is contrary to the results of MO calculations carried out at various levels of theory (Table S1 and refs 8, 11, and 12). The present electron diffraction experimental results further support the view[8,11] that the geometry of the ipso region of the benzene ring obtained by microwave spectroscopy[10,12] is affected by some systematic error, related to the small *a* coordinates of atoms C1, C2, and H2 in the principal axis system of the molecule. Quoting from ref 12, "The determination of atomic positions with small coordinates in the principal inertial axis system of the molecule admittedly remains an inherent weakness of molecular structure determination from inertial moments alone." Whenever experimental data from one technique do not provide enough information to determine the structure of a molecule, the use of appropriate constraints from other techniques (such as imposing fixed values to angles and differences between bond distances) may substantially improve the accuracy of the results. This procedure is commonplace in gas-phase electron diffraction work and has started to be applied to rotational spectroscopy studies as well.[12] However, imposing fixed values to bond distances in a least-squares refinement, as done in some instances in ref 12, may introduce systematic errors, due to the different physical meaning that a bond distance has in different techniques of structure determination. At this point we note that Dreizler et al.'s direct comparison (pp 22−23 of ref 12) of various experimental bond distances with the results of MO calculations may be misleading. Such comparisons beyond certain accuracy levels, as in the case of these studies, can be made properly by first applying all necessary vibrational corrections to bring all data to a common basis.

Benzene Ring Deformation in *p*-Diethynylbenzene and *s*-Triethynylbenzene. In most polysubstituted derivatives of benzene, the deformation of the ring with respect to unsubstituted benzene may be interpreted to a good approximation as arising from the superposition of separate effects from each substituent.[4,6] Using the Δa, Δb, Δc, $\Delta\alpha$, $\Delta\beta$, $\Delta\gamma$, and $\Delta\delta$ values from Table S5 (where $\Delta a = a - r(\mathrm{C{-}C})_{\mathrm{benzene}}$, etc., $\Delta\alpha = \alpha$

− 120°, etc.), the lengths of the C−C bonds and the values of the C−C−C angles in *p*-diethynylbenzene and *s*-triethynylbenzene can be well predicted. For instance, r(C2−C3) in *p*-diethynylbenzene should be $r(\mathrm{C{-}C})_{\mathrm{benzene}} + 2\Delta b$, and ∠C2−C1−C6 in *s*-triethynylbenzene should be $120° + \Delta\alpha + 2\Delta\gamma$. Comparison with geometrical parameters from the actual optimizations (Tables S2 and S3) shows that the differences between predicted and optimized geometries are negligibly small at the HF level, not exceeding 0.0003 Å for bond distances and 0.05° for bond angles. Somewhat larger differences are calculated at the MP2 (B3LYP) level, up to 0.0010 Å (0.0007 Å) for bond distances and 0.21° (0.17°) for bond angles. In the case of *p*-diethynylbenzene, the optimized ring geometry is slightly more distorted than the predicted geometry.

The present experimental study of ethynylbenzene yields $\Delta\alpha = -0.8$, $\Delta\beta = +0.2$, $\Delta\gamma = +0.2$, and $\Delta\delta = -0.1°$. From these values, the ring angles at the place of substitution are predicted to be 119.1° for *p*-diethynylbenzene and 119.6° for *s*-triethynylbenzene. The corresponding experimental values are 119.2 ± 0.2°[9] and 119.6 ± 0.2°, respectively.

The MO calculations consistently indicate that the mean length of the ring C−C bonds in ethynylbenzene, $\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$, exceeds by 0.001−0.002 Å that in benzene. This is a consequence of the lengthening of the *a* bonds caused by the ethynyl substituent being more pronounced than the shortening of the *b* bonds. Due to the additivity of the deformations, we expect $\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$ to increase gradually as the number of ethynyl groups increases. Table 5 shows this to be the case, not only with the computed r_e values but also with the experimental r_g values. Although the small differences between the lengths of the ring C−C bonds are hard to measure by electron diffraction, $\langle r_g(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$ is accurately determined.

Comparison with Solid-State Results. Comparing geometrical parameters from gas-phase electron diffraction with those from X-ray crystallography is by no means straightforward, because different physical meanings are involved.[6e,g] The r_g bond distances obtained by electron diffraction are thermal-average internuclear separations. The bond distances obtained by X-ray crystallography are separations between average atomic positions and refer to the centroids of electron density distribution rather than to the nuclei. Moreover, the motion of a molecule in a crystal has substantial contributions from librational rigid body motions, which may seriously affect the observed geometry. Last, but not least, intermolecular interactions in the solid state may perturb the geometry of the molecule. It appears, however, that the internal angles of the benzene ring are less affected than bond distances by these effects, so that gas-phase and solid-state results of the accuracy of 0.1−0.2° can be safely compared,[6g] unless strong intermolecular interactions involve the substituent in the crystal. Here we will limit our comparison to the ring angles at the place of substitution.

The crystal structures of ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene have been determined by Weiss et al. by low-temperature (125 K) X-ray crystallography.[34] In crystalline ethynylbenzene the asymmetric unit contains two independent molecules in general position; a third molecule is disordered over a crystallographic center of inversion. The two nondisordered molecules have ipso angles of 119.3(2) and 119.5(2)°.[35] The *p*-diethynylbenzene molecule has C_i crystallographic symmetry in the solid state; the ipso angle is 119.4(2)°.[35] A value of 118.9(2)°[35] is obtained for the same angle in a molecular complex of *p*-diethynylbenzene with *p*-dinitrobenzene, studied by room-temperature X-ray crystallography.[36] In the case of *s*-triethynylbenzene the low-temperature study[34] was apparently carried out by imposing a D_{6h} symmetry constraint to the benzene ring in the least-squares refinement. A room-temperature study[37] yields values of the ipso angles in the range 119.5−119.8(2)°.[38]

TABLE 4: Molecular Parameters of Ethynylbenzene from Electron Diffraction[a]

Distances and Mean Amplitudes of Vibration (Å)[b]

atom pair	multiplicity	r_a	l exp	l calc[c]	coupling scheme[d]
C1−C2 (*a*)	2	1.4072(2)	0.0455(4)	0.0456	i
C2−C3 (*b*)	2	1.3932(2)[e]	0.0447	0.0448	i
C3−C4 (*c*)	2	1.3972(2)[e]	0.0449	0.0450	i
C1−C7	1	1.4320(15)[e]	0.0453	0.0454	i
C7≡C8	1	1.2114(8)[e]	0.0358(10)	0.0354	ii
C2−H2	2	1.095[e]	0.075[c]	0.075	
C3−H3	2	1.096[e]	0.075[c]	0.075	
C4−H4	1	1.096[f]	0.075[c]	0.075	
C8−H8	1	1.074[e]	0.072[c]	0.072	
C1···C3	2	2.428(2)[e]	0.0548(4)	0.0542	iii
C1···C4	1	2.805(2)[e]	0.0605(10)	0.0605	iv
C2···C4	2	2.420(1)[e]	0.0549	0.0543	iii
C2···C5	2	2.795(1)[e]	0.0610	0.0610	iv
C2···C6	1	2.428(2)[e]	0.0555	0.0549	iii
C3···C5	1	2.419(1)[e]	0.0550	0.0544	iii
C7···C2	2	2.460(1)[e]	0.0644	0.0638	iii
C7···C3	2	3.730(1)[e]	0.059(2)	0.062	v
C7···C4	1	4.227(1)[e]	0.064(4)	0.064	vi
C8···C1	1	2.643(2)[e]	0.046(2)	0.049	vii
C8···C2	2	3.563(1)[e]	0.091(3)	0.092	viii
C8···C3	2	4.889(1)[e]	0.086(3)	0.080	ix
C8···C4	1	5.435(1)[e]	0.062(5)	0.066	x

Angles (deg) and Differences between Distances (Å) or Angles (deg)

Δ_1(C−C)[g]	−0.014[h]
Δ_2(C−C)[i]	−0.010[h]
Δ_3(C−C)[j]	0.0247(17)
Δ_4(C−C)[k]	−0.1958(7)
Δ_1(C−H)[l]	−0.001[h]
Δ_2(C−H)[m]	0.000[h]
Δ_3(C−H)[n]	−0.022[h]
∠C2−C1−C6 (α)	119.23(17)
∠C1−C2−C3 (*β*)	120.20(13)[e]
∠C2−C3−C4 (*γ*)	120.24(4)[e]
∠C3−C4−C5 (*δ*)	119.90[o]
$\Delta\tau_1$[p]	−1.2[h]
$\Delta\tau_2$[q]	−0.4[h]
θ[r]	8.0[s]

[a] Least-squares standard deviations are in parentheses in units of the last digit. [b] To save space, only C−C, C−H, and C···C pairs are listed in this table. The unabridged list, reporting also C···H pairs, is provided in the Supporting Information (Table S10). [c] From spectroscopic calculations based on the B3LYP/6-31G* optimization. [d] The roman numerals indicate the groups within which the amplitudes were refined with constant differences between them. [e] Dependent parameter. [f] Assumed from our electron diffraction study of benzene[28] (see text). [g] Δ_1(C−C) = r(C2−C3) − r(C1−C2). [h] Assumed from B3LYP/6-311++G** calculations. [i] Δ_2(C−C) = r(C3−C4) − r(C1−C2). [j] Δ_3(C−C) = r(C1−C7) − r(C1−C2). [k] Δ_4(C−C) = r(C7≡C8) − r(C1−C2). [l] Δ_1(C−H) = r(C2−H2) − r(C4−H4). [m] Δ_2(C−H) = r(C3−H3) − r(C4−H4). [n] Δ_3(C−H) = r(C8−H8) − r(C4−H4). [o] Assumed from the partial r_s structure obtained by microwave spectroscopy.[10] [p] $\Delta\tau_1$= ∠C1−C2−H2 − ∠C3−C2−H2. [q] $\Delta\tau_2$ = ∠C2−C3−H3 − ∠C4−C3−H3. [r] Out-of-plane bending angle of the substituent about C1, defined as the angle that the C1···H8 line makes with the C1···C4 line. [s] Assumed (see text).

The above results agree with those from the present study. They provide further evidence of the fact that replacing an hydrogen atom of the benzene ring with the ethynyl substituent causes the ipso angle to become slightly but unambiguously smaller than 120°.

TABLE 5: Mean Lengths (Å) of the Ring C−C Bonds in Mono-, *p*-Di-, and *s*-Triethynylbenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments[a]

level/basis set	distance type	benzene	mono	para	sym
HF/6-31G*	r_e	1.386	1.387	1.389	1.390
HF/6-311++G**	r_e	1.386	1.387	1.388	1.389
MP2(f.c.)/6-31G*	r_e	1.397	1.399	1.401	1.403
MP2(f.c.)/6-311++G**	r_e	1.400	1.402	1.405	1.406
B3LYP/6-31G*	r_e	1.397	1.399	1.402	1.404
B3LYP /6-311++G**	r_e	1.395	1.397	1.399	1.402
experimental values[b]	r_g	1.398[c]	1.401	1.402[d]	1.404

[a] Also shown is the length of the C−C bond in unsubstituted benzene. [b] All ±0.003 Å. [c] From our electron diffraction study of benzene.[28] [d] From ref 9.

TABLE 6: Lengths (Å) of the $C_{ipso}-C_{ethynyl}$ Bonds in Mono-, *p*-Di-, and *s*-Triethynylbenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	sym
HF/6-31G*	r_e	1.442_5	1.441_6	1.442_2
HF/6-311++G**	r_e	1.441_6	1.440_5	1.441_2
MP2(f.c.)/6-31G*	r_e	1.431_9	1.430_2	1.431_5
MP2(f.c.)/6-311++G**	r_e	1.432_6	1.430_7	1.432_1
B3LYP/6-31G*	r_e	1.430_6	1.428_8	1.430_0
B3LYP/6-311++G**	r_e	1.428_7	1.426_9	1.428_5
experimental values[a]	r_g	1.433	1.431[b]	1.431

[a] All ±0.003 Å. [b] From ref 9.

TABLE 7: Differences between the Lengths (Å) of the $C_{ipso}-C_{ethynyl}$ and $C_{ipso}-C_{ortho}$ Bonds in Mono-, *p*-Di-, and *s*-Triethynylbenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	sym
HF/6-31G*	r_e	0.050	0.049	0.052
HF/6-311++G**	r_e	0.050	0.049	0.052
MP2(f.c.)/6-31G*	r_e	0.027	0.024	0.029
MP2(f.c.)/6-311++G**	r_e	0.024	0.021	0.026
B3LYP/6-31G*	r_e	0.023	0.021	0.026
B3LYP/6-311++G**	r_e	0.024	0.022	0.027
experimental values[a]	r_g	0.025	0.023[b]	0.027

[a] All ±0.002 Å. [b] From ref 9.

Ethynyl Substituent. Calculated and experimental values of $r(C_{ipso}-C_{ethynyl})$ in the three molecules are reported in Table 6. It appears that in *p*-diethynylbenzene the calculated values are 0.001−0.002 Å shorter than in the mono and sym-trisubstituted derivatives, at all levels of theory. This small effect is likely to arise from through-conjugation, that is, in valence bond terms, a contribution from quinoidal canonical forms such as $H-C^+=C=C_6H_4=C=C^--H$ to the electronic structure of the molecule, implying a more extensive delocalization of the π-electron system than would otherwise be the case. As pointed out in the preceding section, the deformation of the benzene ring in *p*-diethynylbenzene is slightly more pronounced than expected from the superposition of separate distortions from each substituent—again a sign of through-conjugation.

The difference between the lengths of the $C_{ipso}-C_{ethynyl}$ and $C_{ipso}-C_{ortho}$ bonds is well determined from electron diffraction. The values obtained are 0.025 Å for ethynylbenzene, 0.023 Å for *p*-diethynylbenzene, and 0.027 Å for *s*-triethynylbenzene, all ±0.002 Å. Table 7 shows that these values agree with those calculated at the MP2 and B3LYP levels, whereas the values from HF calculations are about twice as large—a rather serious discrepancy.

The lengths of the $C\equiv C$ bonds in the three molecules are compared in Table 8. The differences between r_e values calculated at the same level of theory using the same basis set do not exceed 0.001 Å and do not show any definite pattern of variation. The differences between the experimental r_g values are also small, 0.001−0.002 Å, which is within experimental uncertainty. It can be concluded that, at the 0.001 Å level of accuracy, the lengths of the $C\equiv C$ bonds of the ethynyl groups are the same in the three molecules. The fact that in *p*-diethynylbenzene the lengths of the $C\equiv C$ bonds are apparently unaffected by through-conjugation is not surprising. It is well-known that the effect of resonance interactions on the lengths of multiple bonds is much less pronounced than on the lengths of single bonds.[39]

TABLE 8: Lengths (Å) of the $C\equiv C$ Bonds in Mono-, *p*-Di-, and *s*-Triethynylbenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	sym
HF/6-31G*	r_e	1.188	1.188	1.188
HF/6-311++G**	r_e	1.186	1.186	1.186
MP2(f.c.)/6-31G*	r_e	1.223	1.223	1.223
MP2(f.c.)/6-311++G**	r_e	1.222	1.223	1.222
B3LYP/6-31G*	r_e	1.210	1.210	1.209
B3LYP /6-311++G**	r_e	1.205	1.205	1.204
experimental values[a]	r_g	1.212	1.211[b]	1.213

[a] All ±0.003 Å. [b] From ref 9.

As regards the terminal C−H bonds of the ethynyl substituents, inspection of Tables S1−S3 shows that their lengths are also unaffected by the pattern of substitution.

Conclusions

(1) Although the equilibrium structures of ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene have C_{2v}, D_{2h}, and D_{3h} symmetry, respectively, the corresponding average structures in the gaseous phase are best described by nonplanar models of C_s, C_{2v}, and C_{3v} symmetry, respectively. The lowering of symmetry is due to the large-amplitude motions of the substituents out of the plane of the benzene ring. The use of nonplanar models in the electron diffraction analysis yields ring angles consistent with the results of MO calculations.

(2) The geometry of the ipso region of the benzene ring reported from microwave spectroscopy studies,[10,12] with the *a* bonds shorter than the *b* bonds and α larger than 120°, is affected by some systematic error, originating from the smallness of the *a* coordinates of atoms C1, C2, and H2 in the principal axis system of the molecule.

(3) The deformation of the ring C−C bonds and C−C−C angles in *p*-diethynylbenzene and *s*-triethynylbenzene may be well interpreted (within 0.001 Å and 0.2°) as arising from the superposition of independent effects from each substituent. In particular, the mean length of the ring C−C bonds increases gradually with the number of substituents. The increase amounts to about 0.002 Å per ethynyl group.

(4) Although the length of the $C\equiv C$ bond of the ethynyl group is unaffected by the pattern of substitution, the $C_{ipso}-C_{ethynyl}$ bonds in *p*-diethynylbenzene are 0.001−0.002 Å shorter than the corresponding bonds in ethynylbenzene and *s*-triethynylbenzene. This small effect is attributed to conjugation of the two substituents through the benzene ring.

(5) Comparison of experimental and MO results shows that the differences between the lengths of the $C_{ipso}-C_{ethynyl}$ and $C_{ipso}-C_{ortho}$ bonds, 0.023−0.027 Å, are correctly computed at the MP2 and B3LYP levels of theory but are overestimated by a factor of 2 when calculated at the HF level.

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Supporting Information Available: Tables S1−S4, equilibrium geometries of ethynylbenzene, *p*-diethynylbenzene, *s*-triethynylbenzene, and unsubstituted benzene, respectively, from quantum chemical calculations. Table S5, ring deformation parameters of ethynylbenzene from quantum chemical calculations. Table S6, total experimental electron diffraction intensities of *s*-triethynylbenzene for two camera distances. Table S7, interatomic distances and mean amplitudes of vibration of *s*-triethynylbenzene from electron diffraction. Table S8, correlation matrix elements with absolute values greater than 0.5 from the final refinement of *s*-triethynylbenzene. Table S9, total experimental electron diffraction intensities of ethynylbenzene for two camera distances. Table S10, interatomic distances and mean amplitudes of vibration of ethynylbenzene from electron diffraction. Table S11, correlation matrix elements with absolute values greater than 0.5 from the final refinement of ethynylbenzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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