

Molecular Structure and Large-Amplitude Motion of *p*-Diethynylbenzene from Gas-Phase Electron Diffraction and Theoretical Calculations

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Received: August 8, 1995; In Final Form: January 29, 1996[⊗]

The molecular structure of *p*-diethynylbenzene has been determined by gas-phase electron diffraction and ab initio MO calculations at the HF/6-31G* and MP2/6-31G*(fc) levels. The two ethynyl groups undergo large-amplitude bending motions, making the equilibrium D_{2h} model inadequate to describe the average structure from electron diffraction. Based on spectroscopic information on low-frequency modes, the electron diffraction data were approximated by a model consisting of a mixture of rigid conformers, differing only in the extent of the symmetric out-of-plane bending of the substituents. This gave the following geometrical parameters: $\angle C_{\text{ortho}}-C_{\text{ipso}}-C_{\text{ortho}} = 119.2 \pm 0.2^\circ$, $\langle r_g(\text{C}-\text{C}) \rangle = 1.402 \pm 0.003 \text{ \AA}$, $r_g(\text{C}_{\text{ring}}-\text{C}_{\text{sp}}) = 1.431 \pm 0.003 \text{ \AA}$, and $r_g(\text{C}\equiv\text{C}) = 1.211 \pm 0.003 \text{ \AA}$. The computed r_e values (MP2) are 119.2° , 1.401 \AA , 1.430 \AA , and 1.223 \AA , respectively, with the $C_{\text{ipso}}-C_{\text{ortho}}$ bond 0.016 \AA longer than the central C–C bond. The HF/6-31G* geometries of ethynylbenzene and *p*-diethynylbenzene indicate that the interaction of the ethynyl group with the ring is not affected by the presence of another ethynyl group in the *para* position. Comparison with solid-state results shows no appreciable effect of crystal environment on the ring deformation in these molecules.

Introduction

Substitution of a hydrogen atom of the benzene molecule by a functional group leads to variations in the ring geometry.^{1–4} With most substituents the ring symmetry is lowered from D_{6h} to C_{2v} ; the parameter which is most affected is the ring angle at the *ipso* position, α (Figure 1). A change in the electronegativity of the substituent changes α from 112° ($\text{C}_6\text{H}_5\text{Li}$)⁵ to 126° ($\text{C}_6\text{H}_5\text{N}_2^+$).⁶ The changes in the ring geometry have been rationalized by hybridization effects or valence-shell electron-pair repulsions.¹

Electron diffraction and microwave spectroscopy have provided accurate ring geometries for a number of monosubstituted benzene derivatives in the gas phase.^{3,4,7} Many ab initio MO studies have also appeared.⁸

In most polysubstituted benzene derivatives the angular distortion of the ring may be interpreted as a superposition of separate effects from each substituent.^{2,9} However, deviations from additivity occur when the electronic interaction between the ring and a substituent is perturbed by other substituents.^{10,11}

Symmetrically *para*-disubstituted derivatives, $p\text{-C}_6\text{H}_4\text{X}_2$, have been studied in our laboratories;^{11–22} here we report the results

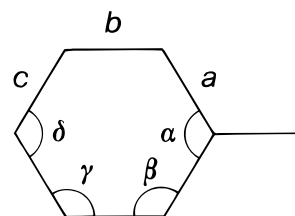


Figure 1. Lettering of bond distances and angles in a monosubstituted benzene ring of C_{2v} symmetry.

of a concerted study of *p*-diethynylbenzene, $\text{X} = \text{C}\equiv\text{CH}$, by electron diffraction and ab initio MO calculations.²³

Theoretical Calculations

Ab initio MO calculations on benzene (D_{6h} symmetry) and *p*-diethynylbenzene (D_{2h} symmetry) were carried out with the 6-31G* basis set²⁴ at the Hartree–Fock (HF) level and at the second order of the Møller–Plesset perturbation theory²⁵ (MP2, frozen-core approximation) by gradient optimization,²⁶ using the Gaussian 92/DFT package.²⁷ Vibrational frequency calculations for *p*-diethynylbenzene were run at the HF/6-31G* level on the optimized geometry. Molecular mechanics calculations were carried out with the MM3 force field,²⁸ using the 1992 version of the program. The geometrical parameters of *p*-

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[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

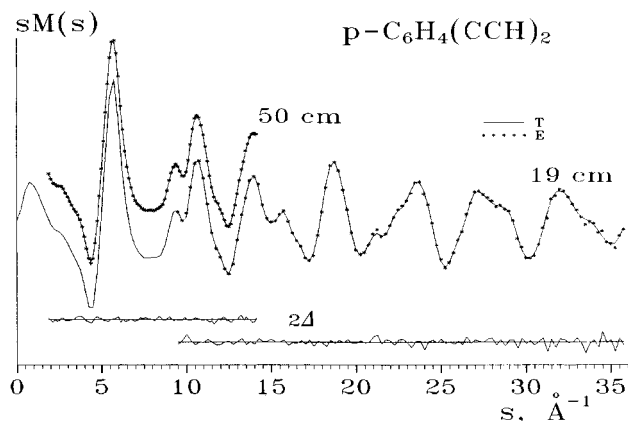


Figure 2. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical for the model obtained from refinement B). Also shown are difference curves (experimental – theoretical).

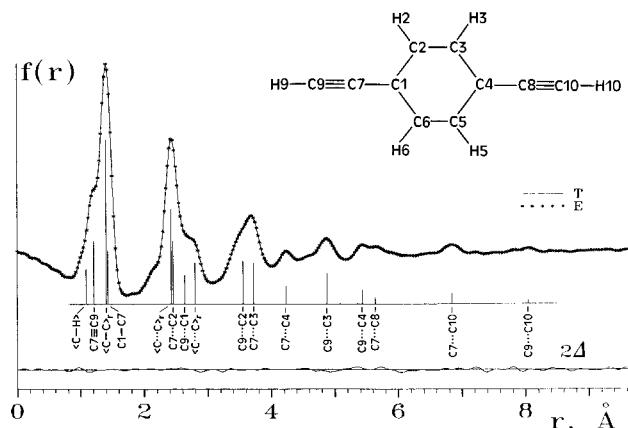


Figure 3. Radial distribution curves (E, experimental; T, theoretical for the model obtained from refinement B). The functions were calculated using an artificial damping factor $\exp(-0.002s^2)$; theoretical values were used in the $0.000 \leq s \leq 1.750 \text{ Å}^{-1}$ region. The positions of the most important distances are marked with vertical bars, whose heights are proportional to the relative weights of the distances. A difference curve (experimental – theoretical) and the numbering of atoms in the molecule are also shown.

diethynylbenzene from the MO calculations are listed in Table 3. The calculations on benzene yield $r_e(\text{C}–\text{C}) = 1.3862$ and 1.3968 Å , and $r_e(\text{C}–\text{H}) = 1.0756$ and 1.0874 Å , at the HF and MP2 levels, respectively.

Experimental Section

Synthesis. *p*-Diethynylbenzene was prepared from *p*-diiodobenzene and trimethylsilylacetylene by means of a palladium-catalyzed coupling reaction.²⁹ The raw product was purified by column chromatography and recrystallized from dichloromethane/*n*-hexane (mp 94 °C , lit.³⁰ 95 °C). The purity was checked by thin-layer chromatography, gas chromatography, and NMR spectroscopy and was found to be better than 99%.

Electron Diffraction. The electron diffraction photographs were taken with the Budapest EG-100A apparatus,³¹ using a membrane nozzle³² at a temperature of about 405 K , at nozzle-to-plate distances of about 50 and 19 cm . The ranges of intensity data were $1.875 \leq s \leq 14.125 \text{ Å}^{-1}$ and $9.50 \leq s \leq 35.75 \text{ Å}^{-1}$, with data intervals of 0.125 and 0.25 Å^{-1} , respectively. Total experimental intensities are collected in Table S1 (supporting information; see Supporting Information Available paragraph at the end of the paper). Molecular intensities and radial distributions are presented in Figures 2 and 3, respectively.

TABLE 1: Calculated Low-Frequency Bending Modes ($\bar{\nu} < 300 \text{ cm}^{-1}$) of the Ethynyl Substituents in *p*-Diethynylbenzene

bending mode	symmetry	wavenumber (cm^{-1})			
		Palmö <i>et al.</i> ^a	Arenas <i>et al.</i> ^b	this work MM3	MO ^c
out-of-plane, symmetric	B _{3u}	79	96	89	87
in-plane, symmetric	B _{2u}	128	193	119	135
out-of-plane, asymmetric	B _{2g}	186	196	198	213
in-plane, asymmetric	B _{3g}	193	201	186	208

^a Reference 33. ^b Reference 34. ^c HF/6-31G* level.

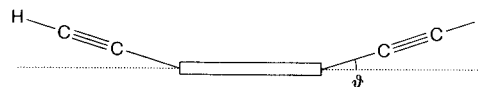


Figure 4. Dynamical model of *p*-diethynylbenzene.

Analysis of the Electron Diffraction Data

The initial stages of the analysis followed our usual routine.^{11,12} However, the large-amplitude motion of the two ethynyl groups makes the equilibrium D_{2h} model inadequate to describe the average structure of the molecule. According to vibrational frequency calculations the lowest-frequency mode, *ca.* 90 cm^{-1} , is the symmetric out-of-plane bending of the substituents. This and other low-frequency modes are identified in Table 1. Of these modes, only the symmetric bendings (in-plane and out-of-plane) contribute appreciably to making the average structure different from the equilibrium structure; they cause the same kind of change in the four longest $\text{C} \cdots \text{C}$ distances. The effect of the asymmetric bendings on these distances is much less pronounced. Thus we tested two dynamical models, both with C_{2v} symmetry, consisting of a D_{2h} benzene ring and two linear substituents equally bent from the $\text{C1} \cdots \text{C4}$ axis, either in the plane of the ring or perpendicular to it. However, only the out-of-plane model resulted in a bending angle significantly different from zero.

The geometry of the out-of-plane C_{2v} model is described by nine independent parameters, which were chosen as follows: (i) the bond distances $r(\text{C1}–\text{C2})$ and $r(\text{C2}–\text{H2})$; (ii) the bond-distance differences $\Delta_1(\text{C}–\text{C}) = r(\text{C2}–\text{C3}) - r(\text{C1}–\text{C2})$, $\Delta_2(\text{C}–\text{C}) = r(\text{C1}–\text{C7}) - r(\text{C1}–\text{C2})$, $\Delta_3(\text{C}–\text{C}) = r(\text{C7} \equiv \text{C9}) - r(\text{C1}–\text{C2})$, and $\Delta(\text{C}–\text{H}) = r(\text{C2}–\text{H2}) - r(\text{C9}–\text{H9})$; (iii) the bond angles $\angle \text{C2}–\text{C1}–\text{C6}$ and $\angle \text{C3}–\text{C2}–\text{H2}$; and (iv) the bending angle of the substituent, ϑ (see Figure 4). Of these parameters, $\Delta_1(\text{C}–\text{C})$, $\Delta(\text{C}–\text{H})$, and $\angle \text{C3}–\text{C2}–\text{H2}$ were assumed from the MP2 calculations; $r(\text{C2}–\text{H2})$ was assumed from our electron diffraction study of benzene,³⁵ as the MP2 calculations give equal values for $r_e(\text{C2}–\text{H2})$ in *p*-diethynylbenzene and $r_e(\text{C}–\text{H})$ in benzene.

Fifteen mean amplitudes of vibration were treated as independent variables. They were often coupled in groups to other amplitudes with constrained differences. Most of these differences and a few $\text{C} \cdots \text{H}$ amplitudes were taken from spectroscopic calculations based on the MM3 force field.²⁸

Selected geometrical parameters from three refinements, A–C, are reported in Table S2 (supporting information). They correspond to the D_{2h} model (refinement A), the out-of-plane C_{2v} model (refinement B), and a dynamical model based on a mixture of four rigid conformers, differing *only* in the extent of symmetric out-of-plane bending of the substituents (refinement C). The angle ϑ and the population of the four conformers were given the following values: 0° , 0.19 ; $\pm 5^\circ$, 0.38 ; $\pm 10^\circ$, 0.31 ; and $\pm 15^\circ$, 0.12 . Although not derived from the Boltzmann distribution, these populations were chosen so as to be consistent with the effective bending angle $\langle |\vartheta| \rangle$ obtained from refinement

TABLE 2: Important Molecular Parameters of *p*-Diethynylbenzene from Electron Diffraction^a

Distances and Mean Amplitudes of Vibration (Å) ^b					
atom pair	multiplicity	r_a	l		coupling scheme ^d
			exp	calc ^c	
C1–C2	4	1.4061(4)	0.0486(5)	0.046	i
C2–C3	2	1.3901(4) ^e	0.0486	0.046	i
C1–C7	2	1.429(1) ^e	0.0503	0.047	i
C2–H2	4	1.096 ^f	0.077(1)	0.077	ii
C9–H9	2	1.076 ^e	0.074	0.074	ii
C7≡C9	2	1.2100(6) ^e	0.036	0.037	ii
C1...C3	4	2.425(1) ^e	0.0568(6)	0.058	iii
C1...C4	1	2.808(5) ^e	0.064(2)	0.065	iv
C2...C5	2	2.798(3) ^e	0.065	0.066	iv
C2...C6	2	2.428(3) ^e	0.0574	0.059	iii
C7...C2	4	2.456(1) ^e	0.0738	0.074	iii
C7...C3	4	3.725(1) ^e	0.066(2)	0.072	v
C7...C4	2	4.231(3) ^e	0.071(4)	0.072	vi
C9...C1	2	2.639(1) ^e	0.048(2)	0.052	vii
C9...C2	4	3.558(1) ^e	0.101(3)	0.102	viii
C9...C3	4	4.883(2) ^e	0.094(4)	0.090	ix
C9...C4	2	5.438(3) ^e	0.066(5)	0.074	x
C7...C8	1	5.646(4) ^e	0.062(8)	0.078	xi
C7...C10	2	6.849(6) ^e	0.085(8)	0.080	xii
C9...C10	1	8.049(9) ^e	0.093(19)	0.083	xiii

Angles (deg) and Differences between Bond Distances (Å)			
∠C2–C1–C6	119.4(2)	Δ ₂ (C–C) ^j	0.0226(16)
∠C3–C2–H2	120.3 ^g	Δ ₃ (C–C) ^k	–0.1960(6)
θ ^h	6.8(12)	Δ(C–H) ⁱ	0.020 ^g
Δ ₁ (C–C) ⁱ	–0.016 ^g		

^a Refinement B. Least-squares standard deviations are given in parentheses as units in the last digit. ^b To save space, only C–C, C–H, and C...C pairs are included in this table. The unabridged table, reporting also C...H pairs, is available as supporting information (Table S3). ^c From molecular mechanics calculations (MM3 force field).²⁸ ^d The roman numerals indicate the groups within which the amplitudes were refined with constant differences between them. ^e Dependent parameter. ^f Assumed from an electron diffraction study of benzene.³⁵ ^g Assumed from ab initio MP2/6-31G* (fc) calculations. ^h Bending angle of the substituent (see Figure 4). ⁱ Δ₁(C–C) = $r(C2–C3) - r(C1–C2)$. ^j Δ₂(C–C) = $r(C1–C7) - r(C1–C2)$. ^k Δ₃(C–C) = $r(C7≡C9) - r(C1–C2)$. ^l Δ(C–H) = $r(C2–H2) - r(C9–H9)$.

B, 6.8(12)°.³⁶ Using slightly different populations has practically no effect on the results.

Important molecular parameters from refinement B are reported in Table 2, showing also the coupling of vibrational amplitudes; the complete list is given in Table S3 (supporting information). (The least-squares standard deviations in these tables are merely indicators of *precision*; they are sometimes unrealistically small due to the constraints.) Correlation matrix elements with absolute values greater than 0.5 are given in Table S4 (supporting information); it is comforting that there are only six such elements, and none of them exceeds 0.82 in absolute value.

Results and Discussion

The three models (*vide supra*) all fit the electron diffraction intensities and give the same bond distances. However, the *ring angle C2–C1–C6 gradually decreases as the quality of the model improves* [refinement A, 119.94(13)°; B, 119.42(22)°; C, 119.20(13)°]. The angle obtained for the dynamical model based on a mixture of rigid conformers (refinement C) coincides with that from the MO calculations.

Our discussion of the molecular structure of *p*-diethynylbenzene is based on the results of refinement C.³⁷ This geometry is compared with the geometry from MO calculations in Table 3. Notwithstanding the difference in physical meaning, the

TABLE 3: Molecular Geometry of *p*-Diethynylbenzene: ab Initio MO and Electron Diffraction Results^a

parameter	ab initio MO calculations ^b		electron diffraction ^c
	HF/6-31G*	MP2/6-31G* (fc)	
$\langle r(C–C) \rangle$	1.3886	1.4012	1.402 ± 0.003
$r(C1–C2)$	1.393	1.407	1.408 ^d
$r(C2–C3)$	1.381	1.391	1.392 ^d
$r(C1–C7)$	1.442	1.430	1.431 ± 0.003
$r(C7≡C9)$	1.188	1.223	1.211 ± 0.003
$r(C2–H2)$	1.074	1.087	1.101 ^{d,e}
$r(C9–H9)$	1.057	1.067	1.081 ^d
∠C2–C1–C6	119.26	119.21	119.2 ± 0.2
∠C3–C2–H2	120.1	120.3	120.3 ^f

^a Bond distances are given in ångströms, angles in degrees. ^b r_c values. ^c From refinement C; bond distances are r_g values. Total errors are given as error limits, and were estimated as $\sigma_T = [2\sigma_{LS}^2 + (0.002r)^2 + (\Delta/2)^2]^{1/2}$ (for bond distances) and $\sigma_T = [2\sigma_{LS}^2 + (\Delta/2)^2]^{1/2}$ (for angles),^{21,38} where σ_{LS} is the least-squares standard deviation, and $\Delta/2$ is the effect of the constraints adopted in the refinement.²¹ ^d The differences $r(C2–C3) - r(C1–C2)$ and $r(C2–H2) - r(C9–H9)$ have been constrained from the MP2 calculations. ^e $r_a(C2–H2)$ was assumed at 1.096 Å from an electron diffraction study of benzene.³⁵ ^f Assumed from the MP2 calculations.

experimental and calculated (MP2) values of $r(C1–C2)$, $r(C2–C3)$, and $r(C1–C7)$ are in close agreement, while the MP2 value of $r(C7≡C9)$ is too large, as expected for a multiple bond.³⁹

Benzene Ring Deformation. The C2–C1–C6 angle of *p*-diethynylbenzene is 119.2° from both theory and experiment. The MO calculations show that the C1–C2 bond is longer than the C2–C3 bond by 0.012 Å (HF) or 0.016 Å (MP2). This small difference was assumed in the electron diffraction study.⁴⁰

In ethynylbenzene, the values of the ring angles α and δ are 119.4 and 119.9°, respectively, from HF/6-31G* MO calculations.⁴¹ Assuming additivity of angular distortions the C2–C1–C6 angle of *p*-diethynylbenzene is predicted to be 119.3°, coinciding with the value obtained here from HF/6-31G* calculations. As for bond-distance changes, the *a* and *c* bonds of ethynylbenzene are longer than the *b* bonds by 0.010 and 0.003 Å, respectively.⁴¹ Assuming additivity of bond-distance distortions, the C1–C2 bond of *p*-diethynylbenzene is predicted to be 0.013 Å longer than the C2–C3 bond, again in excellent agreement with the present HF calculations.

The mean length of the ring C–C bonds in *p*-diethynylbenzene, $\langle r_g(C–C) \rangle = 1.402 \pm 0.003$ Å,⁴² is determined accurately by electron diffraction. The corresponding distance in benzene is 1.399 ± 0.003 Å.³⁵ Although the difference is within experimental error, the effect may be real, since much of the error comes from systematic errors and both experiments were done in the same laboratory. Our MO calculations on *p*-diethynylbenzene and benzene yield similar differences.

In symmetrically *para*-disubstituted benzene derivatives the variation of the ring angle ∠C2–C1–C6 is accompanied by a change in the $r(C1...C4)$ nonbonded distance.^{3,4} Figure 5 shows a scatterplot of ∠C2–C1–C6 vs $r_g(C1...C4)$, based on electron diffraction results. The least-squares line has a correlation coefficient –0.995 on 15 data points. The chemical implication is that while the most electronegative functional groups *push* C1 and C4 toward the ring center, the least electronegative *pull* C1 and C4 away from it. The relatively large variation of $r(C1...C4)$, ca. 0.19 Å in Figure 5, is accompanied by only minor changes in the lengths of the C–C bonds.

Ethynyl Substituent. The values of $r_c(C1–C7)$ and $r_c(C7≡C9)$ obtained for *p*-diethynylbenzene from HF/6-31G* MO calculations are 1.442 and 1.188 Å, respectively. They are the same as for ethynylbenzene.⁴¹

The experimental C1–C7 bond distance, $r_g = 1.431 \pm 0.003$ Å, agrees, within the combined total errors, with the corre-

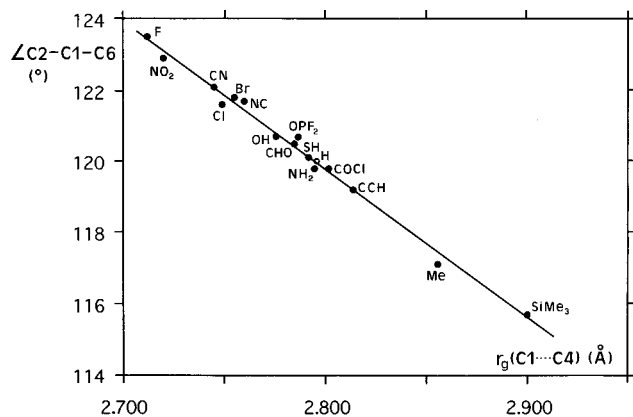


Figure 5. Scatterplot of the angle C2–C1–C6 against the nonbonded distance $r_g(\text{C1}\cdots\text{C4})$ in symmetrically *para*-disubstituted benzene derivatives from electron diffraction studies.^{11–22,43,44} Also shown is the reference point of benzene (H).³⁵

sponding distance for ethynylbenzene, $r_g = 1.436 \pm 0.004$ Å.⁴¹ The experimental C7≡C9 bond distance is $r_g = 1.211 \pm 0.003$ Å. Values of $r_g(\text{C}\equiv\text{C})$ for noncyclic alkynes studied by electron diffraction are compiled in Table S5 (supporting information). They fall in the interval 1.205–1.221 Å, with a mean value of 1.214(1) Å.⁴⁵

Comparison with Solid-State Results. A study of the crystal and molecular structure of *p*-diethynylbenzene was published in 1972, in a work of low accuracy by today's standards.⁴⁶ More recently, the structure of diphenylacetylene ($\text{C}_6\text{H}_5\text{—C}\equiv\text{C—C}_6\text{H}_5$) was determined by modern X-ray crystallographic techniques.⁴⁷ The interaction of the $\text{HC}\equiv\text{C—}$ and $\text{C}_6\text{H}_5\text{—C}\equiv\text{C—}$ substituents with the benzene ring is virtually the same, and the bond angles are especially little affected by systematic errors.⁴ Thus a comparison with the present results is warranted. The α and δ angles in crystalline diphenylacetylene are 119.4(1) and 119.9(1)°, respectively,⁴⁷ showing no appreciable effect of crystal environment on the ring deformation. This seems generally valid for substituents of low polarity.^{4,7} On the other hand, appreciable effects have been documented for highly polar substituents.^{3,4,11,16,48,49} Also the bond-distance differences in the benzene ring of crystalline diphenylacetylene, $a - b = 0.012$ Å and $c - b = 0.001$ Å,⁴⁷ are similar to those calculated for free ethynylbenzene⁴¹ and *p*-diethynylbenzene.

The ethynyl bond distances in crystalline diphenylacetylene, $r(\text{C}_{\text{ring}}\text{—C}_{\text{sp}}) = 1.426(2)$ Å and $r(\text{C}\equiv\text{C}) = 1.212(2)$ Å,⁴⁷ are also in good agreement with those of free *p*-diethynylbenzene, notwithstanding the difference in physical meaning (r_α vs r_g).

Conclusions

1. A dynamical model, based on spectroscopic information on low-frequency modes, has improved the electron diffraction analysis of *p*-diethynylbenzene. It made it possible to determine accurately the *ipso* ring angle, $\angle\text{C2—C1—C6} = 119.2 \pm 0.2^\circ$, in agreement with the results of *ab initio* MO calculations at the HF/6-31G* and MP2/6-31G*(fc) levels.

2. The introduction of a second ethynyl group in the *para* position does not affect the interaction of the first ethynyl group with the benzene ring, as shown by both the additivity of the ring deformation and the constancy of the lengths of the exocyclic carbon-carbon bonds.

3. The effect of crystal environment on the ring deformation is negligibly small in these systems, due to the low polarity of the ethynyl group, as shown by comparison of gas-phase and solid-state results.

Acknowledgment. We thank Mrs. Mária Kolonits (Budapest) for electron diffraction experimental work. This research was carried out in the framework of the Scientific Cooperation Agreement between the National Research Council of Italy and the Hungarian Academy of Sciences and has also been supported by the Hungarian National Scientific Research Foundation (OTKA, grant No. T014945).

Supporting Information Available: Table S1 giving the total experimental electron diffraction intensities of *p*-diethynylbenzene for two camera distances, Table S2 comparing selected geometrical parameters of *p*-diethynylbenzene from three different refinements, Table S3 reporting the complete list of molecular parameters (this is an unabridged version of Table 2 of the text), Table S4 showing the correlation matrix elements with absolute values greater than 0.5, and Table S5 reporting the length of the $\text{C}\equiv\text{C}$ bond in alkynes from electron diffraction studies (11 pages). Ordering information is given in any current masthead page.

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