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

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Received: April 20, 2008; Revised Manuscript Received: July 6, 2008

The molecular structures of cyanobenzene, *p*-dicyanobenzene, and 1,2,4,5-tetracyanobenzene have been accurately determined by gas-phase electron diffraction and ab initio/DFT MO calculations. The equilibrium structures of these molecules are planar, but their average geometries in the gaseous phase are nonplanar because of large-amplitude vibrational motions of the substituents out of the plane of the benzene ring. The use of nonplanar models in electron diffraction analysis is necessary to yield ring angles consistent with the results of MO calculations. The angular deformation of the benzene ring in the three molecules is found to be much smaller than obtained from previous electron diffraction studies, as well as from microwave spectroscopy studies of cyanobenzene. While the deformation of the ring C—C bonds and C—C—C angles in *p*-dicyanobenzene is well interpreted as arising from the superposition of independent effects from each substituent, considerable deviation from additivity occurs in 1,2,4,5-tetracyanobenzene. The changes in the ring geometry and $C_{ipso}-C_{cyano}$ bond lengths in this molecule indicate an enhanced ability of the cyano group to withdraw π-electrons from the benzene ring, compared with cyanobenzene and *p*-dicyanobenzene. In particular, gas-phase electron diffraction and MP2 or B3LYP calculations show a small but consistent increase in the mean length of the ring C—C bonds for each cyano group and a further increase in 1,2,4,5-tetracyanobenzene. Comparison with accurate results from X-ray and neutron crystallography indicates that in *p*-dicyanobenzene the internal ring angle at the place of substitution opens slightly as the molecule is frozen in the crystal. The small geometrical change, about 0.6°, is shown to be real and to originate from intermolecular $-C{\equiv}N\cdots H-C$ interactions in the solid state.

Introduction

The variation of the benzene ring geometry upon substitution provides important structural information on substituent effects[1] (including electronegativity,[1b,f] resonance,[1c–e] steric,[1e] and field[1g] effects) as well as on substituent—substituent interactions.[2] Gas-phase electron diffraction and, increasingly, quantum chemical calculations have been used in our laboratories to measure these geometrical changes.[3] The accuracy requirements for such studies are quite stringent, as discussed in ref 4.

We have recently shown that although ethynylbenzene, *p*-diethynylbenzene, and *s*-triethynylbenzene have planar equilibrium structures, their average geometries in the gaseous phase are best represented by nonplanar models.[5] This is due to the large-amplitude vibrational motions of the substituents out of the plane of the benzene ring, causing a shortening of most ring—substituent internuclear separations. The nonplanar models in the electron diffraction analysis yield internal ring angles in better agreement with equilibrium values from quantum chemical calculations than the planar models.[5]

We have now applied this approach to improve the information on the variation of the benzene ring geometry caused by the cyano group, a linear substituent isoelectronic with the ethynyl group. Some time ago, the gas-phase molecular structures of cyanobenzene,[6] *p*-dicyanobenzene,[7] and 1,2,4,5-tetracyanobenzene[8] were determined in our laboratories by electron diffraction, based on intensity data collected with the Budapest apparatus. In cyanobenzene[6] and *p*-dicyanobenzene[7] the internal ring angle at the place of substitution was found to be significantly larger than 120°, 121.9 ± 0.3° and 122.1 ± 0.2°, respectively.[9] These values are in agreement with the value of 121.82(5)° obtained for cyanobenzene by the isotopic substitution method of microwave spectroscopy.[10a] (A slightly smaller value, 121.16°, was obtained by remeasuring some transitions in the microwave spectra of cyanobenzene and its isotopomers.[10b]) On the other hand, they differ appreciably from the values of 120.0−120.6° obtained for cyanobenzene by quantum chemical calculations at various levels of theory and with different basis sets.[1e,2c,11,12] Accumulating computational evidence (see also ref 13) has pointed to the need of reanalyzing

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10.1021/jp803425h CCC: $40.75

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

	wavenumber (cm^{-1})					
	experimental (vapor), Green and Harrison[a]		calculated			
symmetry	infrared	Raman	Császár and Fogarasi[b]	Dimitrova[c]	Carniato et al.[d]	Rastogi et al.[e] and this work[f]
B_1 (out-of-plane)	141	143−147	136	162	145	147
B_2 (in-plane)	158−167	163	159	184	156	165

[a] Reference 27. [b] Reference 11, HF/4-21G calculations. [c] Reference 28, HF/6-31G** calculations. [d] Reference 29, B3LYP/6-311G* calculations (the IGLOO-III basis set was used for nitrogen). [e] Reference 12g, B3LYP/6-31G** calculations. [f] B3LYP/6-31G* calculations.

our previously collected electron diffraction data in order to enhance the reliability of the experimental geometries.

Here, we present the results of a reanalysis of the electron diffraction intensities of the three molecules. It is stressed that the experimental data were of high quality, but an improved approach in data treatment and conditions and assumptions in their analysis gave hope for better results. The following measures were taken: (i) the large-amplitude out-of-plane motion of the substituents (which had been ignored previously) was taken into account; (ii) more accurate geometrical constraints were included from other techniques than previously; (iii) better initial values of the vibrational amplitudes were used; (iv) the background lines were carefully redrawn. Independent information on the average structure of free cyanobenzene was obtained by molecular dynamics simulations, and equilibrium geometries were determined by quantum chemical calculations at various levels of theory. The enhanced reliability of the comparison of the experimental geometries was due to the fact that the electron diffraction intensities were from the same apparatus and have been processed and analyzed using identical procedures. Gas-phase electron diffraction studies of cyanobenzenes from other laboratories have been reported for *o*-dicyanobenzene[14] and *s*-tricyanobenzene.[15]

Theoretical Calculations

Quantum chemical calculations on cyanobenzene, *p*-dicyanobenzene, and 1,2,4,5-tetracyanobenzene (plus unsubstituted benzene, used as reference) were carried out at the HF and B3LYP levels of theory with the 6-31G* and 6-311++G** basis sets[16] and at the MP2(f.c.) level with Dunning's cc-pVTZ and aug-cc-pVTZ basis sets,[17] using the Gaussian 03 package.[18] The correlation-consistent basis sets used at the MP2 level contain high angular momentum functions that prevent aromatic nuclear frameworks from becoming artificially nonplanar.[19] Vibrational frequency calculations, run at the B3LYP/6-31G* and MP2(f.c.)/cc-pVTZ levels on the respective geometries, showed the equilibrium structures of the three cyanobenzenes to have C_{2v}, D_{2h}, and D_{2h} symmetry, respectively. Vibrational amplitudes for the electron diffraction least-squares refinements were calculated with the program ASYM40, version 3.2,[20] based on the B3LYP/6-31G* optimizations. 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).

The dynamics of free cyanobenzene was simulated by the molecular dynamics approach atom-centered density matrix propagation (ADMP),[21] as implemented in the Gaussian 03 package,[18] at the B3LYP/6-31G* level of theory. The system was simulated under constant temperature conditions for a trajectory duration of 8.5 ps and with a time step of 0.25 fs.

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

Electron Diffraction Data

The total experimental electron diffraction intensities of cyanobenzene, *p*-dicyanobenzene, and 1,2,4,5-tetracyanobenzene were those used in the previous studies.[6−8] They were collected with the Budapest apparatus[22] at nozzle temperatures of about 351, 468, and 505 K, respectively, with nozzle-to-plate distances of about 50 and 19 cm. The ranges of the intensity data actually used in the present work were $1.875 \le s \le 13.750$ Å^{-1} and $9.25 \le s \le 35.75$ Å^{-1} for cyanobenzene, $2.125 \le s \le 13.875$ Å^{-1} and $9.00 \le s \le 35.25$ Å^{-1} for *p*-dicyanobenzene, and $1.875 \le s \le 13.500$ Å^{-1} and $8.25 \le s \le 36.00$ Å^{-1} for 1,2,4,5-tetracyanobenzene, with data intervals of 0.125 and 0.25 Å^{-1} for the 50 and 19 cm data sets, respectively. The total experimental intensities are given in Tables S6−S8.

Analysis of the Electron Diffraction Data

The least-squares method was applied to molecular intensities as in refs 2b and 23, using a modified version of the program by Seip and co-workers.[24] The inelastic and elastic scattering functions were taken from refs 25 and 26, respectively. The initial background lines were modified repeatedly in the course of the analysis. We used geometrical constraints from computations, carefully examining their effects on the refined parameters by systematically testing the assumed values in reasonable ranges. The effects were found to be marginal in all cases and were taken into account in the final estimate of total errors.[9]

Cyanobenzene. The two lowest-frequency vibrational modes of cyanobenzene are an in-plane and an out-of-plane vibration (Table 1). The two modes are nearly degenerate,[30] as shown consistently by experiment and theoretical calculations. They involve the bending of the cyano group as a rigid entity (an in-plane bend and an out-of-plane wag about the ipso carbon) mixed with contributions from $C_{ipso}{-}C_\alpha{\equiv}N$ bending about C_α. Much of the deviation of the electron diffraction average structure compared with the equilibrium structure originates from the out-of-plane vibration, which shortens all but one of the nonbonded internuclear separations between the substituent and the benzene ring. The resulting average structure is therefore nonplanar. This is supported by molecular dynamics calculations on free cyanobenzene. The simulation indicates that the average structure of the molecule has an almost linear $C{-}C{\equiv}N$ system, making an angle of about 8° with the plane of the benzene ring at the temperature of the electron diffraction experiment.

We have therefore 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 $C{-}C{\equiv}N$ group, respectively. Under these symmetry constraints the geometry of the molecule is described by 13 independent parameters that were defined as follows (see Figure 1a for the numbering of atoms and Figure 2 for the lettering of the C−C bonds and C−C−C angles of the benzene ring): (i) the bond distances r(C1−C2) and r(C4−H4); (ii) the bond-distance differences $\Delta_1(C{-}C) = r(C1{-}C2) - r(C2{-}C3)$, $\Delta_2(C{-}C) = r(C1{-}C2) - r(C3{-}C4)$,

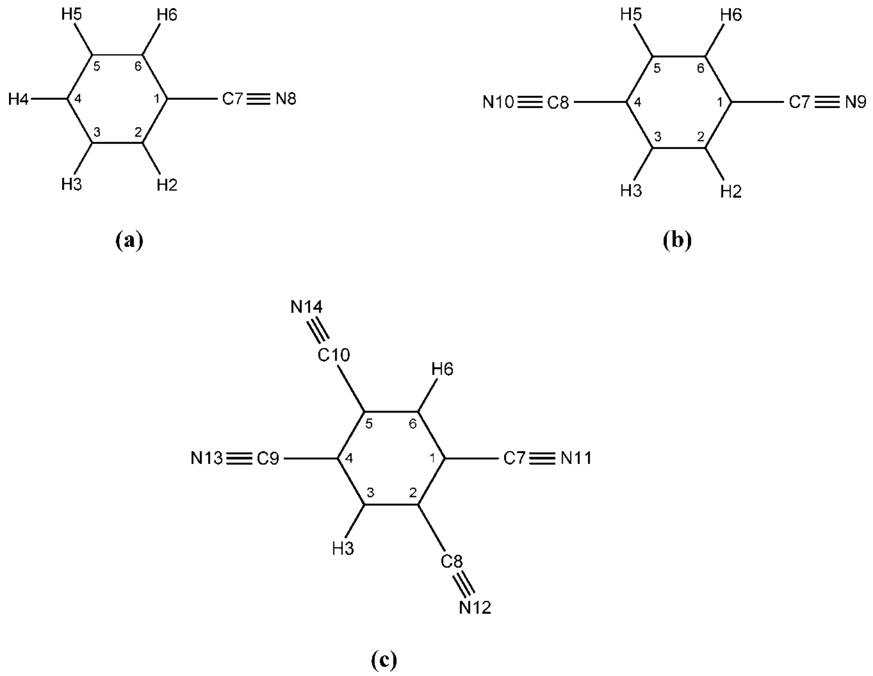

Figure 1. Numbering of atoms in (a) cyanobenzene, (b) *p*-dicyanobenzene, and (c) 1,2,4,5-tetracyanobenzene.

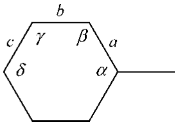

Figure 2. Lettering of the C—C bonds and C—C—C angles in a monosubstituted benzene ring of C_{2v} symmetry.

Δ_3(C—C) = r(C1—C7) − r(C1—C2), Δ(C≡N) = r(C1—C2) − r(C7≡N8), Δ_1(C—H) = r(C4—H4) − r(C2—H2), and Δ_2(C—H) = r(C4—H4) − r(C3—H3); (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 wagging angle of the substituent about the ipso carbon, θ, defined as the angle that the C1···N8 line makes with the C1···C4 line.

A 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 kept at 1.0955 Å, based on the fact that our r_a(C—H) value for benzene is 1.096 Å[31] while r_e(C4—H4) in cyanobenzene is about 0.0005 Å shorter than r_e(C—H) in benzene at all levels of calculations (see Tables S1 and S4). The differences Δ_1(C—C), Δ_2(C—C), Δ_1(C—H), Δ_2(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 120.05°, from the r_s structure of cyanobenzene obtained by microwave spectroscopy.[10a] This value is expected to be accurate, since the atomic coordinates of C3, C4, and C5 in the inertial reference framework are large and are thus well determined by the isotopic substitution method. It is also supported by MP2 and B3LYP calculations, yielding δ values in the range 120.03−120.15° (Table S1). Simultaneously refining the ring angle α and the wagging angle θ proved inappropriate because of high correlation between these parameters (the correlation matrix element is −0.96). 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 and molecular dynamics calculations, we have eventually fixed θ at 8.0°, the value indicated by molecular dynamics calculations. The remaining variables, namely, r(C1—C2), Δ_3(C—C), Δ(C≡N), and the ring angle α, were refined as independent parameters. 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 values and a few other amplitudes that were not refined were taken from spectroscopic calculations based on the B3LYP/6-31G* optimization.

Under the above conditions, the ring angle α refines to 120.2 ± 0.2°, a value consistent with the results of MO calculations (Table S1). If the model is constrained to the C_{2v} symmetry of the equilibrium structure, α increases to 121.0°.

Molecular parameters from the final refinement are reported in Tables 2 and S9, 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 S10.

***p*-Dicyanobenzene.** According to vibrational frequency calculations, the four lowest-frequency modes of *p*-dicyanobenzene are two in-plane and two out-of-plane vibrations (Table 3). Only the out-of-plane vibrations contribute significantly to making the average structure of the molecule different from the equilibrium structure. They involve the wagging of the cyano groups about the respective ipso carbons, mixed with contributions from C_{ipso}—C_α≡N bendings about C_α. The effect of the in-plane vibrations on the long C···C distances is much less pronounced and can be ignored. Much of the effect that the B_{2g} vibration has on the C···C distances is the same as that of the B_{3u} vibration.

The model used in the refinement was based on a nonplanar molecule of C_{2v} symmetry, with the two substituents bent on the same side of the benzene ring, as in the lowest-frequency vibrational mode ($\nu = 80$ cm^{-1}, B_{3u} symmetry). Local D_{2h} and $C_{\infty v}$ symmetries were assumed for the benzene ring and the C—C≡N groups, respectively. The eight independent parameters describing the geometry of this model were chosen as follows

TABLE 2: Molecular Parameters of Cyanobenzene from Electron Diffraction[a]

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

atom pair	multiplicity	r_a	l exptl	l calcd[c]	coupling scheme[d]
C1—C2 (*a*)	2	1.4042(1)	0.0460(3)	0.0456	i
C2—C3 (*b*)	2	1.3922(1)[e]	0.0453	0.0449	i
C3—C4 (*c*)	2	1.3962(1)[e]	0.0455	0.0451	i
C1—C7	1	1.4326(11)[e]	0.0463	0.0459	i
C7≡N8	1	1.1582(5)[e]	0.0333(5)	0.0338	ii
C2—H2	2	1.0945[e]	0.0745	0.075	ii
C3—H3	2	1.0955[e]	0.0745	0.075	ii
C4—H4	1	1.0955[f]	0.0745	0.075	ii
C1···C3	2	2.417(1)[e]	0.0554(3)	0.0547	iii
C1···C4	1	2.790(1)[e]	0.0612(6)	0.0614	iv
C2···C4	2	2.419(1)[e]	0.0555	0.0548	iii
C2···C5	2	2.798(1)[e]	0.0616	0.0618	iv
C2···C6	1	2.435(2)[e]	0.0559	0.0552	iii
C3···C5	1	2.419(1)[e]	0.0556	0.0549	iii
C7···C2	2	2.452(1)[e]	0.0669	0.0662	iii
C7···C3	2	3.719(1)[e]	0.067(2)	0.064	v
C7···C4	1	4.213(1)[e]	0.058(3)	0.065	vi
N8···C1	1	2.591(1)[e]	0.0485	0.0487	iv
N8···C2	2	3.504(1)[e]	0.097(1)	0.095	vii
N8···C3	2	4.826(1)[e]	0.079(2)	0.082	viii
N8···C4	1	5.368(1)[e]	0.074(4)	0.067	ix

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

Δ_1(C—C)[g]	0.012[h]
Δ_2(C—C)[i]	0.008[h]
Δ_3(C—C)[j]	0.0284(11)
Δ(C≡N)[k]	0.2460(4)
Δ_1(C—H)[l]	0.001[h]
Δ_2(C—H)[m]	0.000[h]
∠C2—C1—C6 (α)	120.19(12)
∠C1—C2—C3 (β)	119.58(9)[e]
∠C2—C3—C4 (γ)	120.30(3)[e]
∠C3—C4—C5 (δ)	120.05[n]
$\Delta\tau_1$[o]	−1.1[h]
$\Delta\tau_2$[p]	−0.5[h]
θ [q]	8.0[r]

[a] Least-squares standard deviations are in parentheses in units of the last digit. [b] To save space, C···H, N···H and H···H pairs are not listed in this table. The unabridged list is provided in the Supporting Information (Table S9). [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—C2) − r(C2—C3). [h] Assumed from B3LYP/6-311++G** calculations. [i] Δ_2(C—C) = r(C1—C2) − r(C3—C4). [j] Δ_3(C—C) = r(C1—C7) − r(C1—C2). [k] Δ(C≡N) = r(C1—C2) − r(C7≡N8). [l] Δ_1(C—H) = r(C4—H4) − r(C2—H2). [m] Δ_2(C—H) = r(C4—H4) − r(C3—H3). [n] Assumed from the r_s structure obtained by microwave spectroscopy.[10a] [o] $\Delta\tau_1$ = ∠C1—C2—H2 − ∠C3—C2—H2. [p] $\Delta\tau_2$ = ∠C2—C3—H3 − ∠C4—C3—H3. [q] Wagging angle of the substituent about C1, defined as the angle that the C1···N8 line makes with the C1···C4 line. [r] Assumed from molecular dynamics calculations.

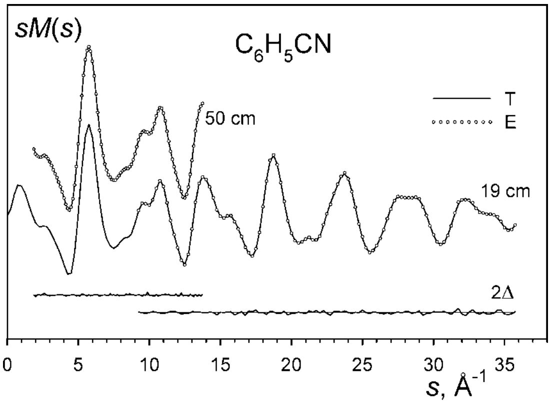

Figure 3. Molecular intensity curves of cyanobenzene for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (E − T).

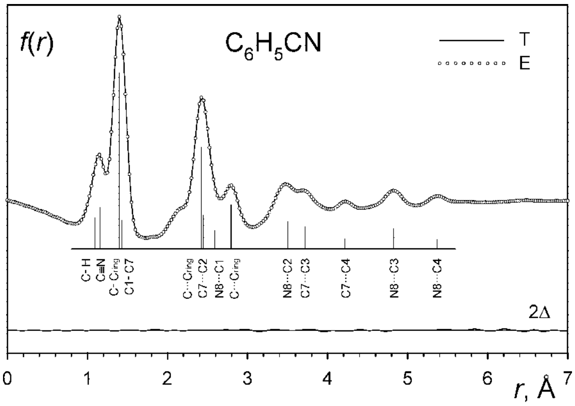

Figure 4. Radial distribution curves of cyanobenzene (E, experimental; T, theoretical). They were calculated using an artificial damping factor exp($-0.002s^2$); theoretical values were used in the $0.00 \le s \le 1.75$ Å^{-1} region. The positions of the most important distances are marked with vertical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

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

	wavenumber (cm^{-1})			
	experimental (solid state)[a]		calculated	
symmetry	infrared	Raman	Higgins et al.[b]	this work[c]
B_{3u} (out-of-plane)	109[d]		77	80
B_{2u} (in-plane)	155[e]		119	124
	165[d]			
B_{3g} (in-plane)		206[e]	183	190
B_{2g} (out-of-plane)		213[d,f]	190	198

[a] Gas-phase data are not available. The assignment is in accordance with ref 13; see ref 32 for an alternative assignment. [b] Reference 13, BLYP/6-31G* calculations. [c] B3LYP/6-31G* calculations. [d] Reference 33. [e] Reference 34. [f] Reference 35.

(see Figure 1b for the numbering of atoms): (i) the bond distances r(C1—C2) and r(C2—H2); (ii) the bond-distance differences Δ_1(C—C) = r(C1—C2) − r(C2—C3), Δ_2(C—C) = r(C1—C7) − r(C1—C2), and Δ(C≡N) = r(C1—C2) − r(C7≡N9); (iii) the bond angle ∠C2—C1—C6; (iv) the bond-angle difference $\Delta\tau$ = ∠C1—C2—H2 − ∠C3—C2—H2; and (v) the wagging angle of the substituent about the ipso carbon, θ, defined as the angle that the C1···N9 line makes with the C1···C4 line. Of these parameters, r(C2—H2) was kept at 1.094 Å, based on the fact that our r_a(C—H) value for benzene is 1.096 Å,[31] while r_e(C2—H2) in *p*-dicyanobenzene is calculated to be about 0.002 Å shorter than r_e(C—H) in benzene at the HF and B3LYP levels (see Tables S2 and S4). The differences Δ_1(C—C) and $\Delta\tau$ were assumed from the B3LYP/6-311++G** calculations. The remaining five variables, namely, r(C1—C2), Δ_2(C—C), Δ(C≡N), the ring angle ∠C2—C1—C6, and the wagging angle θ, were refined as independent parameters. Thirteen mean amplitudes of vibration were also treated as independent parameters, in the same manner as with cyanobenzene.

This model fits the experimental data, yielding an effective bending angle of the cyano groups of 7.3 ± 0.9°, which

TABLE 4: Molecular Parameters of *p*-Dicyanobenzene from Electron Diffraction[a]

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

atom pair	multiplicity	r_a	l exptl	l calcd[c]	coupling scheme[d]
C1—C2	4	1.4040(2)	0.0470(3)	0.0463	i
C2—C3	2	1.3880(2)[e]	0.0460	0.0453	i
C1—C7	2	1.4355(8)[e]	0.0477	0.0470	i
C7≡N9	2	1.1560(3)[e]	0.0344(5)	0.0338	ii
C2—H2	4	1.094[f]	0.0756	0.075	ii
C1···C3	4	2.414(1)[e]	0.0576(4)	0.0571	iii
C1···C4	1	2.778(3)[e]	0.064(1)	0.065	iv
C2···C5	2	2.807(2)[e]	0.065	0.066	iv
C2···C6	2	2.440(2)[e]	0.0581	0.0576	iii
C7···C2	4	2.452(1)[e]	0.0719	0.0714	iii
C7···C3	4	3.718(1)[e]	0.069(1)	0.069	v
C7···C4	2	4.206(2)[e]	0.074(3)	0.070	vi
N9···C1	2	2.592(1)[e]	0.049	0.050	iv
N9···C2	4	3.502(1)[e]	0.108(1)	0.106	vii
N9···C3	4	4.822(1)[e]	0.093(2)	0.091	viii
N9···C4	2	5.359(2)[e]	0.072(3)	0.072	ix
C7···C8	1	5.626(2)[e]	0.068(5)	0.075	x
C7···N10	2	6.774(3)[e]	0.075(4)	0.077	xi
N9···N10	1	7.919(4)[e]	0.098(10)	0.079	xii

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

Δ_1(C—C)[g]	0.016[h]
Δ_2(C—C)[i]	0.0315(9)
Δ(C≡N)[j]	0.2480(3)
∠C2—C1—C6	120.65(13)
∠C1—C2—C3	119.67(6)[e]
$\Delta\tau$[k]	−0.54[h]
θ[l]	7.3(6)

[a] Least-squares standard deviations are in parentheses in units of the last digit. [b] To save space, C···H, N···H and H···H pairs are not listed in this table. The unabridged list is provided in the Supporting Information (Table S11). [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—C2) − r(C2—C3). [h] Assumed from B3LYP/6-311++G** calculations. [i] Δ_2(C—C) = r(C1—C7) − r(C1—C2). [j] Δ(C≡N) = r(C1—C2) − r(C7≡N9). [k] $\Delta\tau$ = ∠C1—C2—H2 − ∠C3—C2—H2. [l] Wagging angle of the substituent about C1, defined as the angle that the C1···N9 line makes with the C1···C4 line.

compares well with the corresponding angle in *p*-diethynylbenzene, 6.8 ± 1.7° from our electron diffraction study.[5b] The ∠C2—C1—C6 angle refines to 120.6 ± 0.2°, a value consistent with the results of MO calculations (Table S2). Constraining the model to the D_{2h} symmetry of the equilibrium structure causes an appreciable worsening of the fit, with ∠C2—C1—C6 increasing to 121.2°. Using more sophisticated models, such as an out-of-plane bent molecule with nonlinear C—C≡N groups or a mixture of symmetrically and antisymmetrically out-of-plane bent pseudoconformers, did not result in further improvement of the fit or in significant changes in the molecular parameters. Final molecular parameters are reported in Tables 4 and S11, showing also the coupling of vibrational amplitudes. Molecular intensities and radial distributions are presented in Figures 5 and 6, respectively. Correlation matrix elements with absolute values greater than 0.5 are given in Table S12.

1,2,4,5-Tetracyanobenzene. Vibrational frequency calculations show that the eight lowest-frequency modes of 1,2,4,5-tetracyanobenzene are four in-plane and four out-of-plane vibrations (Table 5). Only the out-of-plane vibrations contribute significantly to making the electron diffraction average structure of the molecule different from the equilibrium structure. They involve the wagging of the cyano groups about the respective ipso carbons, mixed with contributions from $C_{ipso}—C_\alpha≡N$ bendings about C_α. As with cyanobenzene and *p*-dicyanobenzene, the effect of the in-plane vibrations on the long C···C distances is much less pronounced and can be ignored.

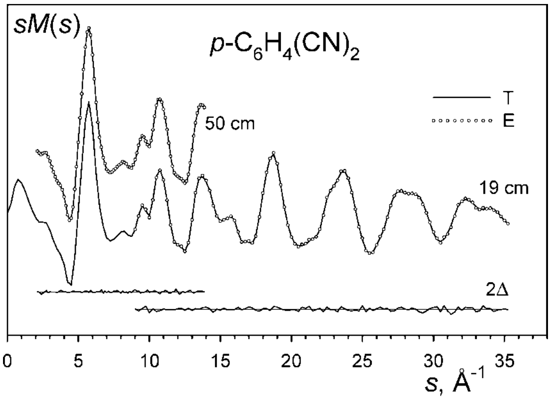

Figure 5. Molecular intensity curves of *p*-dicyanobenzene for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (E − T).

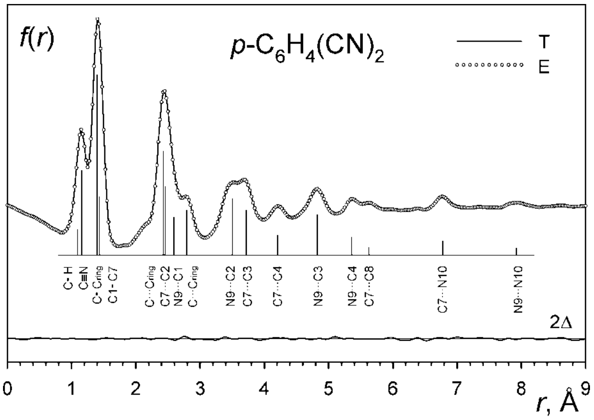

Figure 6. Radial distribution curves of *p*-dicyanobenzene (E, experimental; T, theoretical). They were calculated using an artificial damping factor $\exp(-0.002s^2)$; theoretical values were used in the $0.00 \le s \le 2.00$ Å^{-1} region. The positions of the most important distances are marked with vertical bars whose heights are proportional to the relative weights of the atomic pairs. Also shown is the difference curve (E − T).

TABLE 5: Low-Frequency Vibrational Modes (ν < 300 cm^{-1}) of 1,2,4,5-Tetracyanobenzene

symmetry	wavenumber[a] (cm^{-1})
A_u (out-of-plane)	61
B_{3u} (out-of-plane)	95
A_g (in-plane)	110
B_{2u} (in-plane)	118
B_{1u} (in-plane)	123
B_{2g} (out-of-plane)	158
B_{1g} (out-of-plane)	219
B_{3g} (in-plane)	221

[a] From B3LYP/6-31G* calculations.

Three models, A, B, and C, were tested in the analysis. Model A was based on the equilibrium structure, that is, on a planar molecule of D_{2h} symmetry. Model B was based on a 3:2 mixture of two nonplanar pseudoconformers, having D_2 and C_{2v} symmetry, respectively. In the D_2 pseudoconformer two opposite substituents were bent about the respective ipso carbons on one

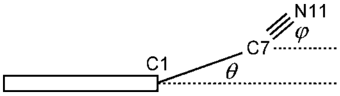

Figure 7. Definition of angles θ and φ in 1,2,4,5-tetracyanobenzene.

side of the benzene ring, while the other two were bent on the other side, as in the lowest-frequency vibrational mode (ν = 61 cm^{-1}, A_u symmetry). In the C_{2v} pseudoconformer all substituents were bent on the same side of the ring, as in the second lowest-frequency mode (ν = 95 cm^{-1}, B_{3u} symmetry). The two pseudoconformers were otherwise assumed to have identical geometries, with local D_{2h} and $C_{\infty v}$ symmetries for the benzene ring and the C—C≡N groups, respectively. Model C differed from model B in that the four C—C≡N groups were assumed to be nonlinear, as indicated by vibrational frequency calculations. The independent parameters describing the geometry of these models were chosen as follows (see Figure 1c for the numbering of atoms): (i) the bond distances r(C1—C6) and r(C3—H3); (ii) the bond-distance differences Δ_1(C—C) = r(C1—C2) − r(C1—C6), Δ_2(C—C) = r(C1—C7) − r(C1—C6), and Δ(C≡N) = r(C1—C6) − r(C7≡N11); (iii) the bond angle ∠C1—C6—C5; (iv) the bond-angle difference $\Delta\tau$ = ∠C2—C1—C7 − ∠C6—C1—C7; (v) the wagging angle of the four substituents about the respective ipso carbons, θ, defined as the angle that the C1—C7 line makes with the ring plane; and (vi) the ratio φ/θ, where φ is the angle that the C7—N11 line makes with the ring plane; see Figure 7. (In model A $\varphi = \theta = 0$ and in model B $\varphi/\theta = 1$ because of symmetry constraints.) Of these parameters, r(C3—H3) was kept at 1.093 Å, based on the fact that our r_a(C—H) value for benzene is 1.096 Å,[31] while r_e(C3—H3) is calculated to be about 0.003 Å shorter than r_e(C—H) in benzene at the HF and B3LYP levels (see Tables S3 and S4). The bond-distance difference Δ_1(C—C) was assumed from the B3LYP/6-311++G** calculations. In model C the ratio of the two out-of-plane angles, φ/θ, was assumed to be 1.5, as suggested by the analysis of the two lowest-frequency modes. The remaining geometrical parameters were refined as independent variables. Fourteen mean amplitudes of vibration were also treated as independent parameters in the same manner as with cyanobenzene.

Model B fits the experimental data better than model A, and further improvement is obtained with model C, which yields an effective θ value of 6.3 ± 1.0°. The value of the internal ring angle at the ipso carbon, 120.2 ± 0.3° from model C, is smaller than the corresponding value from model A, 120.8°, and in better agreement with the results of MO calculations (see Table S3). Changes in the composition of the mixture of pseudoconformers (from 3:2 to 1:1 or 3:1) or in the angular ratio φ/θ (from 1.5 to 1.3 or 1.7) did not result in further improvement of the fit or in appreciable changes of geometrical parameters. Final molecular parameters from model C are reported in Tables 6 and S13, showing also the coupling of vibrational amplitudes. Molecular intensities and radial distributions are presented in Figures 8 and 9, respectively. Correlation matrix elements with absolute values greater than 0.5 are given in Table S14.

TABLE 6: Molecular Parameters of 1,2,4,5-Tetracyanobenzene from Electron Diffraction[a]

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

atom pair[c]	multiplicity	r_a	l exptl	l calcd[d]	coupling scheme[e]
C1—C2	2	1.4144(6)[f]	0.0492(6)	0.0474	i
C1—C6	4	1.3974(6)	0.0481	0.0463	i
C1—C7	4	1.4298(10)[f]	0.0490	0.0472	i
C7≡N11	4	1.1555(4)[f]	0.0355(7)	0.0338	ii
C3—H3	2	1.093[g]	0.0767	0.075	ii
C1···C3	4	2.438(3)[f]	0.059(1)	0.059	iii
C1···C4	2	2.799(3)[f]	0.065(3)	0.066	iv
C1···C5	2	2.416(4)[f]	0.058	0.058	iii
C3···C6	1	2.820(8)[f]	0.066	0.067	iv
C7···C2	4	2.471(2)[f]	0.072	0.071	iii
C7···C3	4	3.744(3)[f]	0.073(2)	0.070	v
C7···C4	4	4.223(2)[f]	0.069(3)	0.072	vi
C7···C5	4	3.712(3)[f]	0.073	0.070	v
C7···C6	4	2.433(2)[f]	0.072	0.072	iii
N11···C1	4	2.584(1)[f]	0.054(2)	0.051	vii
N11···C2	4	3.520(3)[f]	0.107(2)	0.105	viii
N11···C3	4	4.847(4)[f]	0.090(2)	0.090	ix
N11···C4	4	5.372(2)[f]	0.072(4)	0.074	x
N11···C5	4	4.810(2)[f]	0.096	0.096	ix
N11···C6	4	3.478(3)[f]	0.112	0.110	viii
C7···C8 (a)	2	2.889(7)[f]	0.125	0.126	iv
C7···C8 (b)	2	2.872(7)[f]	0.125	0.126	iv
C7···C9	2	5.642(2)[f]	0.075(9)	0.077	xi
C7···C10 (a)	2	4.866(5)[f]	0.095	0.095	ix
C7···C10 (b)	2	4.856(4)[f]	0.095	0.095	ix
C7···N12 (a)	4	3.627(9)[f]	0.207	0.204	v
C7···N12 (b)	4	3.597(9)[f]	0.207	0.204	v
C7···N13	4	6.784(4)[f]	0.089(5)	0.079	xii
C7···N14 (a)	4	5.886(5)[f]	0.134(9)	0.144	xiii
C7···N14 (b)	4	5.867(5)[f]	0.134	0.144	xiii
N11···N12 (a)	2	4.099(14)[f]	0.308	0.311	vi
N11···N12 (b)	2	4.040(13)[f]	0.308	0.311	vi
N11···N13	2	7.922(7)[f]	0.120(14)	0.081	xiv
N11···N14 (a)	2	6.849(7)[f]	0.218	0.208	xii
N11···N14 (b)	2	6.814(9)[f]	0.218	0.208	xii

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

Δ_1(C—C)[h]	0.017[i]
Δ_2(C—C)[j]	0.032(2)
Δ(C≡N)[k]	0.2419(6)
∠C2—C1—C6	120.2(2)[f]
∠C1—C6—C5	119.6(3)
$\Delta\tau$ [l]	1.9(3)
θ [m]	6.3(7)
φ/θ [n]	1.5[g]

[a] Least-squares standard deviations are in parentheses in units of the last digit. [b] To save space, C···H, N···H, and H···H pairs are not listed in this table. The unabridged list is provided in the Supporting Information (Table S13). [c] Atom pairs having different distances in the D_2 and C_{2v} pseudoconformers are denoted as (a) and (b), respectively. [d] From spectroscopic calculations based on the B3LYP/6-31G* optimization. [e] The roman numerals indicate the groups within which the amplitudes were refined with constant differences between them. [f] Dependent parameter. [g] Assumed (see text). [h] Δ_1(C—C) = r(C1—C2) − r(C1—C6). [i] Assumed from B3LYP/6-311++G** calculations. [j] Δ_2(C—C) = r(C1—C7) − r(C1—C6). [k] Δ(C≡N) = r(C1—C6) − r(C7≡N11). [l] $\Delta\tau$ = ∠C2—C1—C7 − ∠C6—C1—C7. [m] Wagging angle of the substituent about C1, defined as the angle that the C1—C7 line makes with the ring plane. [n] Ratio of the angles that the C7—N11 and C1—C7 lines make with the ring plane (see Figure 7).

Results and Discussion

The present study provides conclusive evidence that the average structures of cyanobenzene, p-dicyanobenzene, and 1,2,4,5-tetracyanobenzene in the gaseous phase are best represented by nonplanar models, although the equilibrium structures are planar. 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 electron diffraction analysis yielded internal ring angles consistent with the results of MO calculations (Table 7).

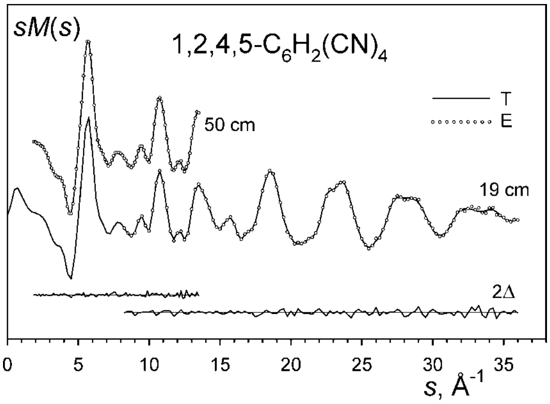

Figure 8. Molecular intensity curves of 1,2,4,5-tetracyanobenzene for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (E − T).

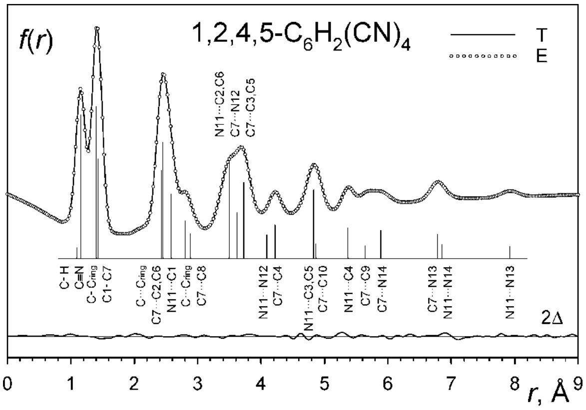

Figure 9. Radial distribution curves of 1,2,4,5-tetracyanobenzene (E, experimental; T, theoretical). They were calculated using an artificial damping factor exp($-0.002s^2$); theoretical values were used in the 0.00 ≤ s ≤ 1.75 Å^{-1} region. The positions of the most important distances are marked with vertical bars whose heights are proportional to the relative weights of the atomic pairs. Also shown is the difference curve (E − T).

TABLE 7: Internal Ring Angles (deg) at the Place of Substitution in Mono-, *p*-Di-, and 1,2,4,5-Tetracyanobenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	mono	para	tetra
HF/6-31G*	120.5	120.7	119.9
HF/6-311++G**	120.5	120.7	119.9
MP2(f.c.)/cc-pVTZ	120.4	120.4	119.9
MP2(f.c.)/aug-cc-pVTZ	120.5	120.4	119.9
B3LYP/6-31G*	120.0	120.1	119.7
B3LYP/6-311++G**	120.0	120.1	119.7
exptl values	120.2 ± 0.2	120.6 ± 0.2	120.2 ± 0.3

Benzene Ring Deformation in Cyanobenzene. The angular deformation of the benzene ring in cyanobenzene is found to be much smaller than reported in previous experimental studies.[6,10] Quantum chemical calculations (Table S5) and gas-phase electron diffraction (Table 2) consistently indicate that none of the internal ring angles (α, β, γ, and δ in Figure 2) differ from the reference value of 120° by more than 0.5°. The small angular changes, however, depend somewhat on the level of theory in the calculations: for instance, $\Delta\alpha = \alpha - 120°$ is about +0.5° at the HF and MP2 levels but is 0.0° at the B3LYP level; $\Delta\gamma = \gamma - 120°$ is 0.0° at the HF level, +0.3° at the MP2 level, and +0.2° at the B3LYP level. At each level of theory the effect of the basis set used is marginal. The experimental ring angles ($\alpha = 120.2 \pm 0.2°$, $\beta = 119.6 \pm 0.2°$, $\gamma = 120.3 \pm 0.1°$, and $\delta = 120.05°$ (assumed)) are within ±0.2° from those calculated at the MP2(f.c.)/cc-pVTZ, B3LYP/6-31G*, and B3LYP/6-311++G** levels.

The variation of the C—C bond distances (*a*, *b*, and *c* in Figure 2) with respect to unsubstituted benzene becomes less pronounced as one moves from the ipso to the para carbon (see Table S5). Thus, the *a* bonds are 0.003−0.008 Å longer than the C—C bond of unsubstituted benzene, the *b* bonds are 0.003−0.005 Å shorter, and the variation of the *c* bonds is negligibly small. The largest value in each range is produced by the B3LYP calculations. This pattern of bond-distance changes is remarkably similar to that reported for ethynylbenzene.[5a] Because reliable information on the differences between the lengths of the *a*, *b*, and *c* bonds in cyanobenzene could not be obtained from the experiment, these were assumed from the MO calculations.

The molecular structure of free cyanobenzene was determined twice by the isotopic substitution method of microwave spectroscopy.[10] The "substitution structure" obtained by this method is often considered to be a good approximation to the equilibrium structure of the molecule (but see ref 36 for a critical discussion). The deformation of the ipso region of the benzene ring in the substitution structure of cyanobenzene [α = 121.82(5)°, with the *a* bonds shorter than the *b* bonds by 0.008 Å from ref 10a; α = 121.16°, with the *a* bonds longer than the *b* bonds by 0.003 Å from ref 10b] is different from that obtained here. Yet the atom C2 is close to the *b* axis of the principal inertial system of the molecule, and thus, its *a* coordinate is small, less than 0.2 Å, and hard to determine accurately. Also rather small are the *a* coordinates of C1 (about −0.5 Å) and H2 (about −0.4 Å). It is well-known[4,5,37,38] that the determination of atomic positions with small coordinates is an inherent weakness of molecular structure determination from inertial moments alone. In many monosubstituted derivatives of benzene the atoms C1 and/or C2 are close to the *b* axis of the inertial reference framework, which makes microwave spectroscopy inadequate to determine accurately the geometry of the ipso region. This is rather unfortunate, as the largest geometrical changes caused by substitution tend to occur in that region. Serious discrepancies between the values of the α angle obtained by microwave spectroscopy and those obtained by gas-phase electron diffraction have been reported for chlorobenzene,[4b,39] nitrobenzene,[4a,40] and ethynylbenzene.[5a] On the other hand, the geometry of the para region of the ring is accurately determined by the isotopic substitution method.

Benzene Ring Deformation in *p*-Dicyanobenzene and 1,2,4,5-Tetracyanobenzene. 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.[1a,2c,4,40,41] 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*-dicyanobenzene and 1,2,4,5-tetracyanobenzene can be predicted. For instance, $r(\mathrm{C2{-}C3})$ in *p*-dicyanobenzene should be $r(\mathrm{C{-}C})_{\mathrm{benzene}} + 2\Delta b$ while ∠C2—C1—C6 in 1,2,4,5-tetracyanobenzene should be $120° + \Delta\alpha + \Delta\beta + \Delta\gamma + \Delta\delta$. Comparison with geometrical parameters from the actual optimizations (Tables S2 and S3) shows that with *p*-dicyanobenzene the differences between predicted and optimized geometries are small, not exceeding 0.0014 Å for bond distances and 0.10° for bond angles. This is not the case of 1,2,4,5-tetracyanobenzene, where the optimized values of the two nonequivalent bond distances, C1—C2 and

TABLE 8: Mean Lengths (Å) of the Ring C−C Bonds in Mono-, *p*-Di-, and 1,2,4,5-Tetracyanobenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments[a]

level/basis set	distance type	benzene	mono	para	tetra
HF/6-31G*	r_e	1.386	1.387	1.387	1.390
HF/6-311++G**	r_e	1.386	1.386	1.386	1.388
MP2(f.c.)/cc-pVTZ	r_e	1.393	1.395	1.396	1.400
MP2(f.c.)/aug-cc-pVTZ	r_e	1.394	1.395	1.396	1.400
B3LYP/6-31G*	r_e	1.397	1.398	1.400	1.405
B3LYP/6-311++G**	r_e	1.395	1.396	1.397	1.402
exptl values[b]	r_g	1.398[c]	1.399	1.400	1.405

[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.[31]

C1−C6, exceed the predicted values by 0.001−0.005 Å and the optimized ring angles at the place of substitution are 0.3−0.5° smaller than predicted. The deviations from additivity are likely to originate from the repulsion between adjacent cyano groups. This notion is supported by the fact that the external ring angle ∠C2−C1−C7 is larger than ∠C6−C1−C7, the difference amounting to 1.9 ± 0.5° from electron diffraction and 0.4−2.4° from MO calculations. Moreover, the C1−C7≡N11 system is not perfectly linear in the equilibrium structure produced by the MO calculations, the C7≡N11 bond being bent toward H6 by 0.6−1.3°.

The MO calculations indicate that the mean length of the ring C−C bonds in cyanobenzene, $\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$, exceeds that in benzene by ca. 0.001 Å. This is very little but still may be interpreted as a consequence of the lengthening of the *a* bonds caused by the cyano substituent being more pronounced than the shortening of the *b* bonds. We thus expect $\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$ to increase gradually as the number of cyano groups increases, with an additional increase in 1,2,4,5-tetracyanobenzene. Table 8 shows this to be the case with nearly all the computed r_e values and also with the experimental r_g values. The overall increase of $\langle r(\mathrm{C{-}C})_{\mathrm{ring}}\rangle$ from benzene to 1,2,4,5-tetracyanobenzene amounts to about 0.007 Å from both calculations (MP2 and B3LYP levels) and experiment. Although the small differences between the lengths of the ring C−C bonds are hard to measure by electron diffraction, their mean value is accurately determined.

Comparison with Solid-State Results. Comparing geometrical parameters from gas-phase electron diffraction with those from X-ray or neutron crystallography is by no means straightforward because of differences in physical meaning and averaging processes. However, the internal angles of the benzene ring are less affected than bond distances by such differences (the angles being related to ratios of distances) so that gas-phase and solid-state results of an accuracy of 0.1−0.2° can be safely compared.[4] Such comparisons may disclose the consequences of intermolecular interactions on the benzene ring geometry.

Cyanobenzene has been studied by low-temperature X-ray crystallography,[42] but the limited number of reflections used in the analysis has prevented an accurate determination of the benzene ring deformation. This is not the case of *p*-dicyanobenzene, which has been studied repeatedly in the solid state. A triclinic and a monoclinic form are known for this species. Apart from two earlier studies of lower accuracy,[43] the triclinic form has been studied at room temperature by both X-ray[7] and neutron crystallography.[44] The two studies yield almost the same value for the internal ring angle at the place of substitution, 121.2(1) and 121.3(2)°, respectively. The monoclinic form has also been studied by room temperature X-ray crystallography,[45] yielding 121.1(1)° for the ring angle at the place of substitution.

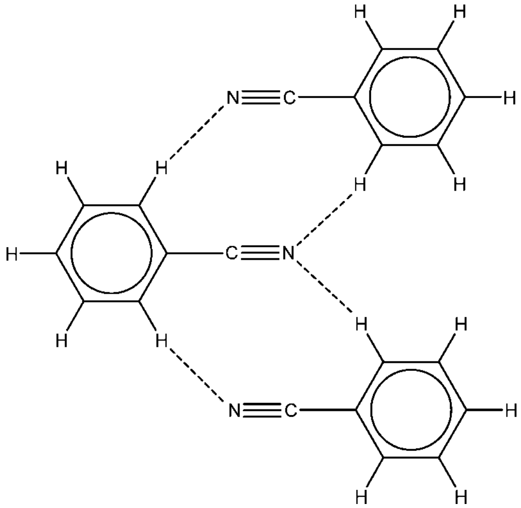

Figure 10. Structure of a cyanobenzene trimer of C_2 symmetry, from B3LYP/6-31G* calculations (after ref 47b). The N···H separations are 2.44−2.45 Å.

Comparison with the present experimental result, ∠C2−C1−C6 = 120.6 ± 0.2°, indicates that in crystalline *p*-dicyanobenzene the internal ring angle at the place of substitution is slightly larger than in the free molecule. The small difference, about 0.6°, can be explained in terms of polar interactions between adjacent molecules in the crystal. These interactions are of the same nature as the through-space polar effects, or field effects, described in ref 1g.

The following features are found in both crystal forms of *p*-dicyanobenzene: (i) a system of dipole−dipole interactions between parallel and antiparallel −C≡N groups and (ii) a network of −C≡N···H−C contacts, involving all the H atoms of the molecule, with N···H separations of 2.61−2.77 Å from the two X-ray diffraction studies.[7,45] (More accurate values, 2.503(5) and 2.577(5) Å, are calculated from the atomic and unit cell parameters given in the neutron diffraction study of the triclinic form.)[44] The lone pair of electrons and partial negative charge on the N atom are expected to polarize the H−C bond, causing an increase of electron density in the valence shell of carbon. According to the VSEPR model,[46] this gives rise in turn to a decrease of the ring angles at the four ortho positions and hence to an increase of the ring angles at the two places of substitution. Here, we provide sound evidence of the existence of this effect.

With cyanobenzene the intermolecular interactions described above lead to the formation of dimers and trimers, which have been the subject of a number of experimental and computational studies.[47] From the atomic coordinates given in ref 47b (produced by MO calculations at the B3LYP/6-31G* level) we have calculated the internal angles of the benzene ring in free cyanobenzene ($\alpha = 120.08°$, $\beta = 119.69°$, $\gamma = 120.19°$, and $\delta = 120.16°$) and in the central molecule of the cyanobenzene trimer of Figure 10 ($\alpha = 120.86°$, $\beta = 119.10°$, $\gamma = 120.32°$, and $\delta = 120.29°$). It appears that upon interaction with the two adjacent molecules the α and β angles of the central molecule of the trimer vary by +0.78 and −0.59°, respectively, from the corresponding angles of the free molecule. This indicates that the minute difference between the experimental ring angles of free and crystalline *p*-dicyanobenzene is real and supports our interpretation of its origin.

Cyano Substituent. The difference between the lengths of the $C_{\mathrm{ipso}}-C_{\mathrm{cyano}}$ and $C_{\mathrm{ipso}}-C_{\mathrm{ortho}}$ bonds is well determined

TABLE 9: Differences between the Lengths (Å) of the $C_{ipso}-C_{cyano}$ and $C_{ipso}-C_{ortho}$ Bonds in Mono-, *p*-Di-, and 1,2,4,5-Tetracyanobenzene,[a] from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	tetra
HF/6-31G*	r_e	0.055	0.055	0.057
HF/6-311++G**	r_e	0.054	0.055	0.056
MP2(f.c.)/cc-pVTZ	r_e	0.031	0.030	0.032
MP2(f.c.)/aug-cc-pVTZ	r_e	0.032	0.030	0.032
B3LYP/6-31G*	r_e	0.029	0.029	0.033
B3LYP/6-311++G**	r_e	0.028	0.029	0.033
exptl values	r_g	0.028 ± 0.002	0.032 ± 0.002	0.032 ± 0.003

[a] For 1,2,4,5-tetracyanobenzene the difference considered is $r(C1-C7) - r(C1-C6)$.

TABLE 10: Lengths (Å) of the $C_{ipso}-C_{cyano}$ Bonds in Mono-, *p*-Di-, and 1,2,4,5-Tetracyanobenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	tetra
HF/6-31G*	r_e	1.445	1.445	1.443
HF/6-311++G**	r_e	1.443	1.444	1.441
MP2(f.c.)/cc-pVTZ	r_e	1.431	1.430	1.427
MP2(f.c.)/aug-cc-pVTZ	r_e	1.431	1.430	1.427
B3LYP/6-31G*	r_e	1.434	1.434	1.432
B3LYP/6-311++G**	r_e	1.431	1.431	1.429
exptl values	r_g	1.434 ± 0.003	1.437 ± 0.003	1.431 ± 0.003

from the present electron diffraction studies. The values obtained for the three molecules are similar, 0.028 ± 0.002 Å for cyanobenzene, 0.032 ± 0.002 Å for *p*-dicyanobenzene, and 0.032 ± 0.003 Å for 1,2,4,5-tetracyanobenzene. Table 9 shows that these values agree with those calculated at the MP2 and B3LYP levels while the values from HF calculations are overestimated by a factor of almost 2. A similar situation was reported for the difference between the lengths of the $C_{ipso}-C_{ethynyl}$ and $C_{ipso}-C_{ortho}$ bonds in ethynylbenzenes.[5a]

Calculated and experimental values of $r(C_{ipso}-C_{cyano})$ in the three molecules are reported in Table 10. At all levels of theory, the $C_{ipso}-C_{cyano}$ bonds in 1,2,4,5-tetracyanobenzene are 0.002−0.004 Å shorter than in cyanobenzene or *p*-dicyanobenzene. As regards the experimental values, that for 1,2,4,5-tetracyanobenzene is also slightly smaller than the others.

When compared with cyanobenzene and *p*-dicyanobenzene, the 1,2,4,5-tetracyanobenzene molecule has shorter $C_{ipso}-C_{cyano}$ bonds, longer ring C−C bonds, and ring angles at the place of substitution smaller than expected on the basis of additivity of angular distortions. These small structural differences are all indicative of an increased aptitude of the cyano group to withdraw electron density from the π system of the benzene ring.[1c−e,4a] The lengthening of the ring C−C bonds is of course instrumental in relieving the strain caused by repulsive interactions between adjacent cyano groups. The ability of 1,2,4,5-tetracyanobenzene to act as a π-acceptor in organic charge-transfer complexes has been long recognized.[48]

The lengths of the C≡N bonds in the three molecules are compared in Table 11. The differences between r_e values calculated at the same level of theory using the same basis set do not exceed 0.002 Å and do not show any pattern of variation. The differences between the three r_g values are also small and well within experimental uncertainty. In cyanobenzene, r_g(C≡N) is 1.159 ± 0.002 Å, just marginally larger than the r_s values from the two studies by microwave spectroscopy, 1.1581(2)[10a] and 1.156 Å.[10b] This is not surprising, as r_s is considered to be a good approximation to r_e and the stretching vibration of the strong C≡N bond is expected to be substantially harmonic. The r_g(C≡N) values from the present study agree with those reported for *o*-dicyanobenzene, 1.161 ± 0.002 Å,[14] and *s*-tricyanobenzene, 1.159(3) Å.[15]

TABLE 11: Lengths (Å) of the C≡N Bonds in Mono-, *p*-Di-, and 1,2,4,5-Tetracyanobenzene, from Quantum Chemical Calculations and Electron Diffraction Experiments

level/basis set	distance type	mono	para	tetra
HF/6-31G*	r_e	1.136	1.136	1.135
HF/6-311++G**	r_e	1.131	1.130	1.129
MP2(f.c.)/cc-pVTZ	r_e	1.173	1.174	1.174
MP2(f.c.)/aug-cc-pVTZ	r_e	1.174	1.174	1.175
B3LYP/6-31G*	r_e	1.163	1.163	1.162
B3LYP/6-311++G**	r_e	1.156	1.155	1.154
exptl values	r_g	1.159 ± 0.002	1.157 ± 0.002	1.157 ± 0.002

Conclusions

(1) Although the equilibrium structures of cyanobenzene, *p*-dicyanobenzene, and 1,2,4,5-tetracyanobenzene are planar, their average structures in the gaseous phase are best represented by nonplanar models. 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 electron diffraction analysis improves the accuracy of the results and yields ring angles consistent with those from MO calculations.

(2) The angular deformation of the benzene ring in free cyanobenzene is smaller than reported in previous experimental studies.[6,10] Reanalysis of the electron diffraction intensities from ref 6 and quantum chemical calculations at different levels of theory consistently indicate that none of the internal ring angles differ from 120° by more than 0.5°. The microwave spectroscopy results in determining the geometry of the ipso region of this and other monosubstituted benzene derivatives are not reliable, as some of the atoms involved have small coordinates in the inertial reference system. Thus, their value in the relevant comparisons is limited. The angular deformation of the ring in free *p*-dicyanobenzene and 1,2,4,5-tetracyanobenzene is also smaller than reported previously.[7,8]

(3) While the deformation of the ring C−C bonds and C−C−C angles in *p*-dicyanobenzene is well interpreted as arising from the superposition of independent effects from each substituent, considerable deviations from additivity occur with 1,2,4,5-tetracyanobenzene. The changes in the ring geometry and $C_{ipso}-C_{cyano}$ bond lengths occurring in this molecule indicate an enhanced ability of the cyano group to withdraw π-electrons from the benzene ring, compared with cyanobenzene and *p*-dicyanobenzene.

(4) The mean length of the ring C−C bonds is particularly well determined by the present study. Gas-phase electron diffraction and MP2 or B3LYP calculations consistently indicate that it increases by about 0.001 Å for each cyano group, plus a further increase by about 0.003 Å in the case of 1,2,4,5-tetracyanobenzene.

(5) Comparison of experimental and MO results shows that the differences between the lengths of the $C_{ipso}-C_{cyano}$ and $C_{ipso}-C_{ortho}$ bonds, 0.028−0.032 Å, are correctly computed at the MP2 and B3LYP levels of theory but are overestimated by a factor of almost 2 when calculated at the HF level.

(6) Comparison with accurate solid-state results from X-ray and neutron crystallography indicates that in *p*-dicyanobenzene the internal ring angle at the place of substitution increases slightly as the molecule is frozen in the crystal. The small geometrical change, about 0.6°, is shown to be real and to

originate from $-C\equiv N\cdots H-C$ intermolecular interactions in the solid state.

Acknowledgment. This work was supported by the Hungarian National Scientific Research Funds, OTKA Grant No. T46183.

Supporting Information Available: Tables S1−S4, equilibrium geometries of cyanobenzene, *p*-dicyanobenzene, 1,2,4,5-tetracyanobenzene, and unsubstituted benzene from quantum chemical calculations; Table S5, ring deformation parameters of cyanobenzene from quantum chemical calculations; Tables S6−S8, total experimental electron diffraction intensities of cyanobenzene, *p*-dicyanobenzene, and 1,2,4,5-tetracyanobenzene for two camera distances; Table S9, interatomic distances and mean amplitudes of vibration of cyanobenzene from electron diffraction; Table S10, correlation matrix elements with absolute values greater than 0.5 from the final refinement of cyanobenzene; Table S11, interatomic distances and mean amplitudes of vibration of *p*-dicyanobenzene from electron diffraction; Table S12, correlation matrix elements with absolute values greater than 0.5 from the final refinement of *p*-dicyanobenzene; Table S13, interatomic distances and mean amplitudes of vibration of 1,2,4,5-tetracyanobenzene from electron diffraction; Table S14, correlation matrix elements with absolute values greater than 0.5 from the final refinement of 1,2,4,5-tetracyanobenzene. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP803425H