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Molecular Structure of *p*-Diaminobenzene in the Gaseous Phase and in the Crystal

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The molecular structure of *p*-diaminobenzene has been determined by electron diffraction in the gas phase and by X-ray diffraction in the crystal, in order to measure accurately the distortions of the benzene ring caused by the substituents and to see whether these distortions are affected by intermolecular interactions in the solid state. The crystals of *p*-diaminobenzene are monoclinic, space group $P2_1/c$, with $a = 8.397(2)$ Å, $b = 5.974(6)$ Å, $c = 23.034(13)$ Å, and $\beta = 93.58(4)^\circ$. The asymmetric part of the unit cell contains one molecule in general position and parts of two molecules on crystallographic centers of inversion. Although the site symmetry of the molecules is at most C_i , deviations from C_{2h} symmetry are insignificant or of marginal importance. The horizontal mirror is perpendicular to the plane of the ring and contains the two nitrogen atoms. Each of the four crystallographically independent amino groups acts as a proton acceptor in an intermolecular hydrogen bond and as a proton donor in another. The nitrogen atoms are displaced by 0.066–0.086 Å out of the respective ring planes. The dihedral angles that the H–N–H planes make with the respective ring planes range from 43° to 46° . After correcting for the effects of libration and averaging chemically equivalent parameters, we obtained the following important bond distances and angles for the crystal molecule of *p*-diaminobenzene: $r(C_{\text{ipso}}-C_{\text{ortho}}) = 1.403(1)$ Å, $r(C_{\text{ortho}}-C_{\text{ortho}'}) = 1.389(2)$ Å, $r(N-C) = 1.422(2)$ Å, $\angle C-C(NH_2)-C = 117.9(1)^\circ$. In the gas-phase study the molecule was constrained to C_{2h} symmetry. Important bond distances and angles are $\langle r_g(C-C) \rangle = 1.397 \pm 0.003$ Å, $r_g(N-C) = 1.424 \pm 0.005$ Å, and $\angle C-C(NH_2)-C = 119.8 \pm 0.2^\circ$. The dihedral angle between the H–N–H plane and the ring plane is $43 \pm 4^\circ$. The internal ring angle at the place of substitution is 2° larger in the gas phase as compared with the crystal. The highly significant difference reflects an increase in π -donation from the amino group to the benzene ring in going from the free molecule to the crystal molecule. This is an effect of the formation of hydrogen bonds in the solid state. Comparison of the gas-phase geometries of aniline (as determined by microwave spectroscopy) and *p*-diaminobenzene shows that π -donation from the amino group to the benzene ring becomes less pronounced when a second amino group is introduced in the para position.

Introduction

Substitution of a hydrogen atom of the benzene molecule by a functional group, X, gives rise to distortions of the ring geometry. In the majority of cases the ring symmetry is lowered from D_{6h} to C_{2v} ; the parameters that are most affected are the angles α , β , and δ and the a bond distances (Figure 1). The distortions have been rationalized in terms of either hybridization effects¹ or valence-shell electron-pair repulsions;² their dependence upon the electronic properties of the substituent provides a novel, intriguing approach to the study of substituent effects in the benzene series.^{3–7}

A change in the electronegativity of the substituent is reflected by a remarkable variation of the angle α ,^{2,3} whose values range from 111.8° ($X = \text{Li}$)⁸ to 123.4° ($X = \text{F}$).⁹ The decrease

(increase) of α is associated with a lengthening (shortening) of the a bonds and with smaller changes of β and δ .^{2,5}

Increasing π -donation from the substituent to the ring gives rise to a different pattern of distortions, whereby the angles α and δ decrease by comparable amounts, and the a bonds become longer.⁴

In most polysubstituted benzene derivatives the angular distortion of the ring may be interpreted as arising from the superposition of separate effects from each substituent.^{7,10} It has been shown, however, that deviations from additivity occur in some para-disubstituted derivatives, due to cooperative interactions between functional groups with opposite π -electronic properties.^{7,11}

We have studied the molecular structures of a number of symmetrically para-disubstituted benzene derivatives, $p\text{-C}_6\text{H}_4\text{X}_2$ ($X = \text{Me},^{12} \text{Cl},^{13} \text{F},^{14} \text{SiMe}_3,^{15} \text{CN},^{16} \text{NC},^{17} \text{OH},^{18} \text{SH},^{18} \text{CHO},^{19}$

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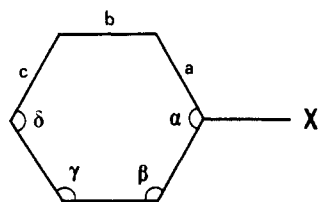


Figure 1. Labeling of the C-C bonds and C-C-C angles in monosubstituted benzene rings. C_{2v} symmetry has been assumed.

Br ,²⁰ NH_3^+ ,²¹ NO_2^{22}), by gas-phase electron diffraction and/or X-ray crystallography. Our aim is to examine the effect of various substituents on the geometry of the ring as a function of their electronic properties and to see whether additivity holds or not. The results of two such studies carried out in parallel by both techniques^{16,17} have outlined the possibility of determining subtle differences in the structure of the crystal molecule as compared with the free molecule.

In the present paper we report the molecular structure of *p*-diaminobenzene, as determined by gas-phase electron diffraction and X-ray crystallography.²³ A parallel gas-phase/crystal-phase investigation may reveal the presence of appreciable intermolecular interactions and their effect on the geometry of the molecule. Moreover, comparison with the molecular structure of aniline²⁴ should provide information on the additivity of the geometrical effects of substitution and, hence, on the nature of the interaction between the ring and the amino group.

Symmetrically para-disubstituted benzene derivatives are better suited for electron diffraction analysis than monosubstituted or other disubstituted derivatives, as many of the interactions double in electron scattering from a $p\text{-C}_6\text{H}_4\text{X}_2$ molecule. However, *p*-diaminobenzene is not an ideal subject for gas-phase electron diffraction. The presence of the amino substituents introduces interactions that give relatively small contributions to the total electron scattering intensities. Assumptions have to be made in the structure analysis, and the question has to be examined thoroughly as to what extent the parameters representing structural interest in our work are invariant to these assumptions.

An X-ray diffraction study of *p*-diaminobenzene was reported by Povet'eva and Zvonkova in 1975.²⁵ Three crystallographically independent molecules exist in the crystal, one in a general fourfold position (A) and the others in twofold positions with inversion symmetry (B, C); cf. our Figure 6. Although based on diffractometer data, the study was not accurate enough to allow a detailed analysis of the effects of substitution on the benzene ring geometry. The thermal motion of the atoms was treated only in the isotropic approximation; this may explain the rather high *R* factor, 0.082, on 1330 reflections. The benzene rings were found to be considerably distorted with respect to hexagonal symmetry, with the internal angles at the ipso positions ranging from 116.4° to 117.4° ²⁶ in the three independent molecules.

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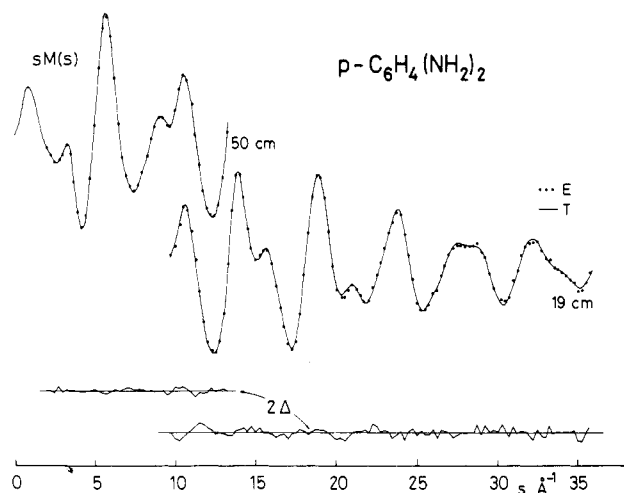


Figure 2. Molecular intensity curves for the two camera distances (E, experimental; T, theoretical). Also shown are the difference curves (experimental - theoretical).

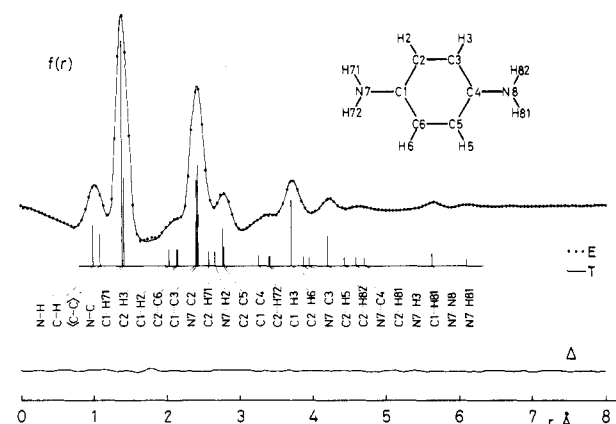


Figure 3. Radial distribution curves (E, experimental; T, theoretical). The functions were calculated with an artificial damping factor equal to $\exp(-0.002s^2)$; theoretical values were used in the $0.00 \leq s < 2.00 \text{ \AA}^{-1}$ region. The position of the most important distances is marked with vertical bars, whose height is proportional to the weight of the distances. Also shown is the difference curve (experimental - theoretical).

In the course of the analysis of the electron diffraction data it soon became apparent that the value of the internal ring angle at the ipso carbon in the free molecule, about 119.8° , was much higher than in the crystal. A new X-ray diffraction study was therefore mandatory, to check whether the large discrepancy in the values of the ipso angle in the two phases was real and also to improve the quality of the experimental data. We thus report here the results of our X-ray diffraction study. Though highly desirable, a low-temperature X-ray diffraction experiment could not be carried out, due to the lack of appropriate experimental facilities.

Experimental Section

Commercial *p*-diaminobenzene (Merck, 99%) was purified by column chromatography and crystallized from methylene chloride. The purity of the product used for the two experiments was checked by thin-layer chromatography.

Electron Diffraction Experiment. The electron diffraction photographs were taken in Budapest with a modified EG-100A apparatus,²⁷ using a so-called membrane nozzle system.²⁸ The nozzle temperature was about 431 K. Nozzle-to-plate distances of about 50 and 19 cm were used. The accelerating voltage of

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TABLE I: Crystal Data for *p*-Diaminobenzene

formula	C ₆ H ₈ N ₂	space group	P2 ₁ /c
mol wt	108.14	Z	8
mp	414–416 K		
parameter	Povet'eva and Zvonkova ^a	this work ^b	
<i>a</i> , Å	8.373 ± 0.004	8.397 (2)	
<i>b</i> , Å	5.970 ± 0.001	5.974 (6)	
<i>c</i> , Å	22.953 ± 0.006	23.034 (13)	
β, deg	93.58 ± 0.01	93.58 (4)	
<i>V</i> , Å ³	1145.1 ^c	1153.2 (14)	
<i>D</i> _{calcd} , g cm ⁻³	1.255 ^c	1.246	
<i>D</i> _{obsd} , g cm ⁻³		1.251 ^d	

^a Reference 25. ^b Measured at 299 K. Least-squares standard deviations are given in parentheses as units in the last digit. ^c Calculated from the given cell parameters. ^d Measured at 295 K by flotation in a mixture of carbon tetrachloride and *n*-hexane.

the electron beam was 60 kV. The electron wavelength was calibrated with a TlCl powder pattern ($a = 3.84145$ Å)²⁹ and was found to be $\lambda = 0.04897$ Å. Four photographic plates (Kodak electron image) for each camera distance were traced on a modified Zeiss GIII microphotometer.³⁰ Each plate was oscillated by approximately 20° about the center of the diffraction pattern during tracing. The ranges of intensity data used in the analysis were $2.000 \leq s \leq 13.250$ Å⁻¹ and $9.75 \leq s \leq 35.75$ Å⁻¹, with data intervals 0.125 and 0.25 Å⁻¹, respectively [$s = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle].

The experimental molecular intensities were derived according to the expression $sM(s) = s[I(s) - B(s)]/B(s)$, where $I(s)$ is the total experimental intensity and $B(s)$ the empirical background. The latter was drawn through the total experimental intensity curve of each camera distance as a smooth line, and has been slightly modified in the course of the analysis. Total experimental intensities are available as supplementary material. Experimental and calculated molecular intensities are presented in Figure 2. Experimental and calculated radial distributions are shown in Figure 3.

X-ray Diffraction Experiment. Several attempts were made to grow single crystals of *p*-diaminobenzene suitable for accurate X-ray diffraction work. The results were rather disappointing as the best crystals that we were able to grow were thin tablets. They were obtained by slowly cooling a warm benzene solution of the purified product.

Preliminary X-ray diffraction photographs confirmed the crystal system and space group given by Kitaigorodskii³¹ and by Povet'eva and Zvonkova.²⁵ A crystal, ca. $0.07 \times 0.32 \times 0.68$ mm³, was mounted on the Nicolet P3m diffractometer of the CNR Institute of Structural Chemistry (Mo K α radiation, graphite monochromator) and used for all subsequent work.

Accurate cell parameters were derived by least-squares techniques from the θ values of 18 reflections well distributed in reciprocal space (θ range 11–13°). Crystal data are presented in Table I.

Intensities were measured at room temperature (299 ± 2 K) in the θ - 2θ scan mode; the scanning interval was from $2\theta(K\alpha_1) - 1.1^\circ$ to $2\theta(K\alpha_2) + 1.2^\circ$. The scanning speed was varied according to intensity from 0.017 to 0.49 deg s⁻¹. The background was measured for half of the scanning time at each end of the scan. Four reference reflections, monitored periodically, showed a marked decrease of intensity, ca. 14% during the entire data collection, due to crystal decomposition in the X-ray beam. The intensities were corrected for the decrease and for Lorentz and polarization effects, but not for absorption [$\mu(\text{Mo K}\alpha) = 0.085$ mm⁻¹]. A total of 2625 reflections in the θ range 1.5–25° were measured; 1415 of these, having $I > 3.5\sigma_I$, were considered as nonzero. Because of its unfavorable shape, the crystal had a rather

small volume and gave virtually no reflections for $\theta > 25^\circ$. The reflections of the $h = 0$ layer were measured as $0kl$ and $0k\bar{l}$; averaging and merging (internal $R = 0.0323$) eventually led to a set of 1309 independent observations.

Analysis of the Electron Diffraction Data

The analysis was carried out by applying the least-squares method to the molecular intensities, as in our previous studies.^{12–17} Intensities in the overlapping s regions were treated as independent data; unit weights were used throughout. Calculations were carried out on the IBM 3031 computer of the Hungarian Academy of Sciences and on the Univac 1100/82 computer of the University of Rome "La Sapienza", using a modified version of the program by Seip and co-workers.³² The inelastic and the elastic scattering factors and phase shifts of the different atoms were taken from ref 33 and 34, respectively.

The benzene ring was assumed to have D_{2h} symmetry throughout the analysis. The molecule as a whole was initially constrained to C_{2h} symmetry, with the mirror perpendicular to the plane of the ring and passing through the two nitrogen atoms. Later on the symmetry constraint was partly released as the two amino groups were allowed to rotate about the C1...C4 axis. A model with C_{2v} symmetry was also tested.

Ten independent parameters are needed to describe the geometry of the *p*-diaminobenzene molecule if it has C_{2h} symmetry and contains a benzene ring with D_{2h} symmetry. We have chosen to define these parameters as follows (the numbering of atoms is given in Figure 3): (i) the C1–C2 bond distance; (ii) the difference between the two C–C bond distances of the benzene ring, $\Delta(\text{C–C}) = r(\text{C1–C2}) - r(\text{C2–C3})$; (iii) the C2–C1–C6 bond angle; (iv) the C1–N7 bond distance; (v) the N7–H71 bond distance; (vi) the difference between the C–H and N–H bond distances, $\Delta(\text{X–H}) = r(\text{C2–H2}) - r(\text{N7–H71})$; (vii) the C3–C2–H2 bond angle; (viii) the dihedral angle, ϕ , between the plane of the amino group and the plane of the ring; (ix) the H71–N7–H72 bond angle; and (x) the displacement of the N7 atom out of the plane of the ring.

Parameters i through viii were refined simultaneously as independent variables. Attempts to refine the H–N–H angle (parameter ix) led to unreasonable results in most cases, possibly because this parameter is highly correlated with the dihedral angle ϕ . (The corresponding correlation matrix element is -0.96 .) It was found safer to assume a value of 112° for the H–N–H angle. This choice is supported by the values that have been obtained by microwave spectroscopy for the corresponding angle in aniline (113.3°),²⁴ *p*-fluoroaniline (111.9°),³⁵ *m*-fluoroaniline (115.0°),³⁶ and *p*-chloroaniline (111.7°).³⁷ The value from the present X-ray diffraction study is 110 (1)°.

The displacement of the N7 atom out of the plane of the ring (parameter x) was varied stepwise under different refinement conditions. It was found that the experimental data could be fitted equally well by a model with a planar heavy-atom skeleton and by a model with the N atoms slightly (up to about 0.25 Å) displaced out of the ring plane, either on the same side (C_{2v} symmetry) or on opposite sides (C_{2h} symmetry).³⁸ Displacements

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TABLE II: Final Molecular Parameters^a from the Electron Diffraction Study

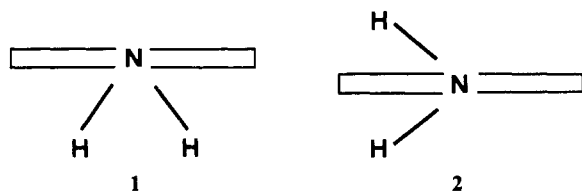
(a) Distances and Mean Amplitudes of Vibration (Å) ^b				
atom pair	multi- plicity	r_a	l	key to the coupling scheme
C1-C2	4	1.398 (1)	0.0458 (6)	i
C2-C3	2	1.391 (4) ^c	0.0458	i
N7-C1	2	1.422 (3)	0.0508	i
N7-H71	4	1.001 (6)	0.074 (5)	ii
C2-H2	4	1.081 (8) ^c	0.077	ii
C1...C3	4	2.416 (3) ^c	0.0621 (7)	iii
C1...C4	1	2.793 (5) ^c	0.069 (2)	iv
C2...C5	2	2.789 (2) ^c	0.069	iv
C2...C6	2	2.418 (2) ^c	0.0591	iii
N7...C2	4	2.444 (3) ^c	0.0661	iii
N7...C3	4	3.716 (2) ^c	0.069 (2)	v
N7...C4	2	4.215 (3) ^c	0.075 (4)	vi
N7...N8	1	5.638 (4) ^c	0.085 (10)	vii
C1...H2	4	2.175 (14) ^c	0.113 (6)	viii
C1...H3	4	3.380 (10) ^c	0.121 (8)	ix
C2...H3	4	2.121 (13) ^c	0.113	viii
C2...H5	4	3.870 (8) ^c	0.100 ^d	
C2...H6	4	3.412 (11) ^c	0.121	ix
C1...H71	4	2.044 (15) ^c	0.133	viii
C1...H81	4	4.711 (19) ^c	0.200 (18)	x
C2...H71	4	2.587 (16) ^c	0.155 ^d	
C2...H72	4	3.272 (14) ^c	0.151	ix
C2...H81	4	4.436 (17) ^c	0.190	x
C2...H82	4	3.958 (18) ^c	0.140 ^d	
N7...H2	4	2.705 (20) ^c	0.135 ^d	
N7...H3	4	4.564 (12) ^c	0.170	x
N7...H81	4	6.113 (19) ^c	0.114 (22)	xi

(b) Angles (deg) and Differences between Bond Distances (Å)			
parameter	value	parameter	value
$\angle C2-C1-C6$	119.8 (2)	ϕ^e	43 (3)
$\angle C3-C2-H2$	117.7 (10)	$\Delta(C-C)^f$	0.007 (4)
$\angle H71-N7-H72$	112 ^d	$\Delta(X-H)^g$	0.080 (14)

^a Least-squares standard deviations are given in parentheses as units in the last digit. ^b The H...H distances are not shown; they have been given fixed amplitudes of 0.130–0.150 Å. ^c Dependent parameter. ^d Assumed. ^e Dihedral angle between the plane of the amino group and the plane of the ring. ^f $\Delta(C-C) = r(C1-C2) - r(C2-C3)$. ^g $\Delta(X-H) = r(C2-H2) - r(N7-H71)$.

larger than about 0.25 Å caused a gradual, unacceptable worsening of the fit.

At an advanced stage of the analysis an attempt was made to ascertain whether the experimental data could reveal any twist of the amino groups from the conformation observed in the crystal and assumed so far for the isolated molecule, **1**. In this attempt



the two nitrogen atoms were constrained on the C1...C4 axis. The amino groups were rotated stepwise about that axis, with the molecule still preserving its center of symmetry; all the other parameters were refined at each step. The results show that conformation **2** can definitely be excluded. (It causes the *R* factor to increase from 0.0360 to 0.0425.) They also indicate, however, that a moderate twist of the amino groups, up to about 30° from conformation **1**, is compatible with the experimental data. The allowed conformations include that where two of the four N-H bonds lie in the plane of the ring.

In addition to geometrical parameters, 11 mean amplitudes of vibration were refined as independent variables. Four of these were refined individually, and seven were coupled in blocks to other amplitudes with constrained differences. The coupling scheme of the seven blocks is shown in Table II. As spectroscopically

calculated values were not available for this molecule, the differences within each block were carefully chosen, also on the basis of the values used with related molecules.¹²⁻¹⁷ Moreover, the effect that alternative choices might have on the geometry of the molecule was thoroughly investigated. The remaining amplitudes were given fixed values, and also the influence of these choices on the rest of the parameters was tested systematically.³⁹ Altogether some 150 refinements were carried out in order to sample the parameter space as extensively as possible. The results that we consider as final gave *R* = 0.0360 and are reported in Table II.

We present here some experience from our refinements to indicate the accuracy intervals of the various geometrical parameters, as appeared under the wide ranges of different conditions used in the analysis. These ranges centered around reasonable parameter values but extended to unreasonable ones so as to gain a complete picture of their influence.

Least-squares standard deviations are reported in Table II. They should be considered merely as indicators of precision and are sometimes unrealistically small because of the constraints.

Some of the geometrical parameters given in Table II are accurately determined by the present study. Some others have been found to depend on the conditions of the refinement, i.e., on the choice of those variables that were given a fixed value; they should not be considered as well determined.

The mean C-C bond distance of the benzene ring is remarkably constant. Even under extreme, highly improbable refinement conditions, it was never found to be smaller than 1.394 Å or larger than 1.398 Å. On the other hand, the difference $\Delta(C-C) = r(C1-C2) - r(C2-C3)$, although successfully refined as an independent parameter, converged to values that ranged from -0.018 to +0.018 Å, depending upon the conditions of the refinement. This parameter was found to be particularly sensitive to the values given to (i) the difference between the amplitudes $l(N7-C1)$ and $l(C1-C2)$, (ii) the difference between the amplitudes $l(N7-C2)$ and $l(C1-C3)$, (iii) the amplitudes $l(C2-H5)$, $l(C2-H71)$, and $l(N7-H2)$, and (iv) the extent of the displacement of the nitrogen atoms out of the plane of the ring.

A similar situation occurs with the N-H and C-H bond distances. Their mean value is certainly well determined: it ranged from 1.038 to 1.045 Å in the various refinements. On the other hand, the difference $\Delta(X-H) = r(C2-H2) - r(N7-H71)$ is much less accurate, as the corresponding range of values is 0.058–0.107 Å.

The accuracy in the determination of the N-C bond distance is fair, the range of values being 1.412–1.427 Å.

The values of the C2-C1-C6 angle obtained from most refinements fall in a rather narrow interval, 119.4–120.1°. Exceptions occur only when the nitrogen atoms are displaced out of the ring plane: displacements of 0.00, 0.10, 0.20, and 0.30 Å yield $\angle C2-C1-C6 = 119.8^\circ$, 119.6° , 119.2° , and 118.4° , respectively.

The interval of values for the C3-C2-H2 angle is again relatively narrow, 116.9–118.4°. Larger values are obtained, however, as the amino groups are rotated about the C1...C4 axis: twist angles of 0°, 20°, and 40° (relative to conformation **1**) yield $\angle C3-C2-H2 = 117.7^\circ$, 118.9° , and 121.5° , respectively.

Concerning the dihedral angle ϕ , values ranging from 31° to 58° have been obtained in the course of the analysis. The smallest values correspond to models where the nitrogen atoms are displaced (by as much as 0.30 Å) out of the plane of the ring. The largest values are given by models where the amino groups are rotated (by as much as 40°) about the C1...C4 axis. As pointed out earlier, the dihedral angle ϕ is strongly correlated with the H-N-H angle, which was assumed to be 112°. An increase (decrease) of $\angle H-N-H$ by 3° causes ϕ to decrease (increase) by the same amount.

(39) The influence of possible shrinkage effects on the geometry of the molecule was also investigated. Refinement of $\delta(N7-C3)$, $\delta(N7-C4)$, and $\delta(N7-N8)$ as additional parameters led to very small values, always less than one standard deviation, and had virtually no effect on the *R* factor and on the other molecular parameters.

TABLE III: Final Coordinates ($\times 10^5$) and Equivalent Isotropic Temperature Factors of the Non-Hydrogen Atoms in Crystalline *p*-Diaminobenzene^a

atom	x	y	z	$B_{eq}, \text{\AA}^2$
Molecule A				
C1	33 149 (19)	90 712 (32)	22 054 (7)	2.84
C2	28 666 (22)	97 314 (33)	27 544 (8)	3.11
C3	20 108 (22)	83 140 (33)	30 936 (8)	3.23
C4	15 668 (20)	61 781 (33)	29 005 (8)	3.12
C5	20 171 (22)	55 122 (33)	23 521 (8)	3.23
C6	28 775 (21)	69 334 (33)	20 139 (8)	3.13
N7	41 029 (20)	105 623 (32)	18 423 (7)	3.75
N8	7 803 (21)	46 788 (33)	32 639 (8)	4.00
Molecule B				
C1	7 949 (21)	134 873 (35)	3 909 (8)	3.37
C2	3 452 (24)	156 017 (36)	5 730 (8)	3.59
C6	4 331 (24)	129 199 (38)	-1 903 (8)	3.60
N7	15 098 (24)	119 117 (36)	7 886 (8)	4.54
Molecule C				
C1	44 272 (23)	37 529 (37)	45 149 (8)	3.53
C2	37 969 (25)	58 314 (40)	46 271 (9)	3.98
C6	56 415 (26)	29 401 (41)	48 916 (9)	4.12
N7	38 987 (26)	25 621 (43)	40 086 (9)	4.85

^a Least-squares standard deviations are given in parentheses as units in the last digit. ^b Defined as $(B_1 B_2 B_3)^{1/3}$, where $B_i = 8\pi^2 U_i$ ($i = 1, 2, 3$). The U_i are the mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid.

Analysis of the X-ray Diffraction Data

Refinement. The atomic coordinates given by Povet'eva and Zvonkova²⁵ for the nitrogen and carbon atoms of the three non-equivalent molecules were used as a starting set. Isotropic and then anisotropic block-diagonal least-squares refinement led to $R = 0.086$. At this stage a difference synthesis unequivocally showed all hydrogen atoms.

In the final refinement the matrix of the normal equations was factorized into two large blocks, one for the atomic coordinates and the other for the thermal parameters and the scale. The function minimized was $\sum w(|F_o| - K|F_c|)^2$. Weights were given according to the function $w = 1/(a + b|F_o| + c|F_c|^2)$,⁴⁰ with $a = 6.19$, $b = 1.00$, and $c = 0.0162$. The 16 hydrogen atoms were treated isotropically. The final R and R_w were 0.0327 and 0.0433, respectively, with all shifts less than 0.15σ . The number of observations per refined parameter was 1309/209 = 6.3. The final atomic coordinates are given in Tables III and IV; observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material.

Calculations were carried out on the Univac 1100/82 computer of the University of Rome "La Sapienza" and on the HP 21MX minicomputer of the CNR Research Area (Monterotondo Stazione), using programs from various sources.⁴¹ The scattering factors used were those of Cromer and Mann⁴² for the non-hydrogen atoms and those of Hanson, Herman, Lea, and Skillman⁴³ for the hydrogen atoms.

Thermal Motion Analysis. In the crystals of simple benzene derivatives studied at room temperature the thermal motion of the heavy-atom skeleton is due primarily to translational and librational rigid-body motions. Contributions from internal molecular motions are relatively small, except with the most

TABLE IV: Final Coordinates ($\times 10^3$) and Isotropic Temperature Factors of the Hydrogen Atoms in Crystalline *p*-Diaminobenzene^a

atom	x	y	z	$B, \text{\AA}^2$
Molecule A				
H2	320 (2)	1116 (3)	290 (1)	1.3 (4)
H3	168 (2)	881 (3)	347 (1)	1.3 (4)
H5	172 (2)	409 (3)	221 (1)	1.5 (4)
H6	321 (2)	645 (3)	164 (1)	1.4 (4)
H71	473 (3)	1157 (4)	204 (1)	2.7 (5)
H72	471 (3)	981 (4)	160 (1)	2.7 (5)
H81	19 (3)	366 (4)	306 (1)	2.8 (5)
H82	19 (2)	540 (3)	352 (1)	1.8 (4)
Molecule B				
H2	59 (3)	1605 (4)	99 (1)	2.8 (5)
H6	76 (2)	1148 (3)	-33 (1)	1.4 (4)
H71	213 (3)	1258 (4)	108 (1)	3.9 (6)
H72	205 (3)	1094 (4)	62 (1)	2.9 (6)
Molecule C				
H2	289 (3)	644 (4)	437 (1)	3.8 (6)
H6	609 (2)	150 (4)	482 (1)	2.0 (4)
H71	289 (4)	290 (5)	387 (1)	5.4 (8)
H72	409 (3)	108 (5)	406 (1)	4.0 (7)

^a Least-squares standard deviations are given in parentheses as units in the last digit.

peripheral atoms of polyatomic substituents.

Libration gives rise to apparent changes of molecular geometry; these must be accounted for if one wishes to compare the results of a crystal structure analysis with those obtained by gas-phase techniques. We have analyzed the thermal motion of the three crystallographically independent molecules of *p*-diaminobenzene in terms of rigid-body motions, following Schomaker and Trueblood.⁴⁴

The elements of the **T**, **L**, and **S** tensors of each molecule⁴⁵ have been derived by least-squares techniques from the elements of the atomic mean-square displacement tensors, **U**, using a program written by Gramaccioli and co-workers,^{41c} the elements of **T**, **L**, and **S** are available as supplementary material. The agreement between observed and calculated U_{ij} values is acceptable for molecules A and B and is less satisfactory for molecule C (see Table V). Inspection of the atomic vibration ellipsoids (Figure 4) shows that molecule C has a larger and more anisotropic motion than the other two.

The eigenvalues and eigenvectors of **T**, **L**, and the inertial tensor **I** of each molecule are given in Table V. Inspection of this table shows that the principal axes of libration are essentially parallel to those of the inertial tensor for molecules A and B. Thus, the principal components of libration of these two molecules are, in order of decreasing importance, (i) a "rolling" about the C1...C4 axis, (ii) a "pitching" about an axis parallel to C2...C6, and (iii) a "yawing" about an axis perpendicular to the plane of the ring.⁴⁶

The atomic coordinates of the heavy-atom skeleton have been corrected for libration;⁴⁴ the corrected and uncorrected geometries are compared in Table VI. The effect of the correction on the C-C and N-C bond distances is appreciable, 0.004–0.011 Å, while the effect on bond angles is small, 0.2° at most. The correction is probably unreliable for molecule C, where the rigid-body model is less satisfactory than with the other molecules.

Additional geometrical parameters, not corrected for thermal motion effects, are available as supplementary material.

Discussion

The Free Molecule. The geometry of the *p*-diaminobenzene molecule in the gas phase is reported in Figure 5a. The carbon

(40) Cruickshank, D. W. J. In *Computing Methods in Crystallography*; Rollett, J. S., Ed.; Pergamon: Oxford, 1965; p 112. See also ref 22.

(41) (a) Carruthers, J. R.; Spagna, R. Presented at the Seventh Meeting of the Italian Crystallographic Association, Bologna, Italy, 26–29 Oct. 1975; Abstracts, p 65. (b) Cerrini, S.; Spagna, R. Presented at the Fourth European Crystallographic Meeting, Oxford, England, 30 Aug.–3 Sept. 1977; Abstracts, p 7. (c) Filippini, G.; Gramaccioli, C. M. *Ric. Sci.* **1969**, *39*, 156. Filippini, G.; Gramaccioli, C. M.; Pilati, T., unpublished work. (d) Capitani, D.; Cerrini, S.; Spagna, R. Presented at the Fifteenth Meeting of the Italian Crystallographic Association, Monteporzio Catone, Italy, 2–5 Oct. 1984; Abstracts, p 85.

(42) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(43) Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040.

(44) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *24*, 63.

(45) The **S** tensor is identically zero for molecules B and C, which are located on crystallographic centers of inversion.

(46) The relationship of these sailing terms to librational motions of benzene derivatives is described in ref 5.

(47) Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *59*, 2513.

TABLE V: Analysis of Solid-State Thermal Motions

(a) Agreement between Observed and Calculated U_{ij} Values			
molecule	$\sum \Delta U_{ij} / \sum U_{ij}^{obsd} $	$\langle (\Delta U_{ij})^2 \rangle^{1/2}, \text{\AA}^2$	$\langle (\sigma U_{ij})^2 \rangle^{1/2}, \text{\AA}^2$
A	0.0522	0.001 46	0.000 89
B	0.0494	0.001 63	0.000 97
C	0.0665	0.002 46	0.001 10

(b) Eigenvalues and Eigenvectors of the Translational, Librational, and Inertial ^a Tensors				
tensor	eigenvalues	eigenvectors ^b ($\times 10^2$)		
Molecule A				
T	$T_1 = 0.047 \text{ \AA}^2$	-43	-65	63
	$T_2 = 0.035 \text{ \AA}^2$	20	-75	-64
	$T_3 = 0.020 \text{ \AA}^2$	88	-14	45
L	$L_1 = 0.0105 \text{ rad}^2$	40	63	-66
	$L_2 = 0.0042 \text{ rad}^2$	25	62	74
	$L_3 = 0.0020 \text{ rad}^2$	88	-46	9
I	$I_1 = 363.7 \text{ amu \AA}^2$	84	-35	40
	$I_2 = 295.2 \text{ amu \AA}^2$	5	-70	-71
	$I_3 = 68.7 \text{ amu \AA}^2$	54	62	-57
Molecule B				
T	$T_1 = 0.049 \text{ \AA}^2$	-23	90	-36
	$T_2 = 0.037 \text{ \AA}^2$	21	41	89
	$T_3 = 0.027 \text{ \AA}^2$	95	13	-28
L	$L_1 = 0.0129 \text{ rad}^2$	-32	64	-70
	$L_2 = 0.0050 \text{ rad}^2$	-18	68	71
	$L_3 = 0.0030 \text{ rad}^2$	93	36	-11
I	$I_1 = 363.9 \text{ amu \AA}^2$	91	35	-23
	$I_2 = 295.7 \text{ amu \AA}^2$	8	-67	-73
	$I_3 = 68.3 \text{ amu \AA}^2$	-41	65	-64
Molecule C				
T	$T_1 = 0.058 \text{ \AA}^2$	-59	80	-15
	$T_2 = 0.040 \text{ \AA}^2$	36	42	84
	$T_3 = 0.025 \text{ \AA}^2$	73	44	-53
L	$L_1 = 0.0126 \text{ rad}^2$	52	54	66
	$L_2 = 0.0068 \text{ rad}^2$	81	-7	-58
	$L_3 = 0.0034 \text{ rad}^2$	-27	84	-47
I	$I_1 = 360.1 \text{ amu \AA}^2$	72	44	-54
	$I_2 = 292.5 \text{ amu \AA}^2$	-63	73	-25
	$I_3 = 67.7 \text{ amu \AA}^2$	28	52	81

(c) RMS Amplitudes of Vibration along the Principal Axes of the Translational and Librational Tensors

molecule	rms amplitudes of translation, \AA			rms amplitudes of libration, deg		
A	0.22	0.19	0.14	5.9	3.7	2.5
B	0.22	0.19	0.16	6.5	4.1	3.2
C	0.24	0.20	0.16	6.4	4.7	3.3

^a Heavy-atom framework. ^b The orthonormal reference system used in the analysis (a' , b' , c') has the a' and b' axes coinciding with the a and b axes, respectively, of the monoclinic system (a , b , c).

skeleton of the ring is seen to be essentially undistorted with respect to unsubstituted benzene, $r_g(\text{C}-\text{C}) = 1.399 \pm 0.003 \text{ \AA}$.⁴⁸ As pointed out earlier, the small difference in the length of the two nonequivalent C-C bonds is not accurately determined, and even its sign is uncertain. However, its absolute value has been consistently small in most refinements, indicating that the two C-C bonds have nearly equal lengths.

Comparison with the gas-phase geometry of aniline, as determined by microwave spectroscopy²⁴ (Figure 5c), indicates that in *p*-diaminobenzene the mesomeric interaction of the amino group with the benzene ring is less pronounced than in aniline. The 0.022-\AA difference between the lengths of the respective N-C bonds is, in fact, well beyond experimental error, even though having r_g and r_s bond distances for *p*-diaminobenzene and aniline, respectively, may somewhat exaggerate this difference.⁴⁹ Ad-

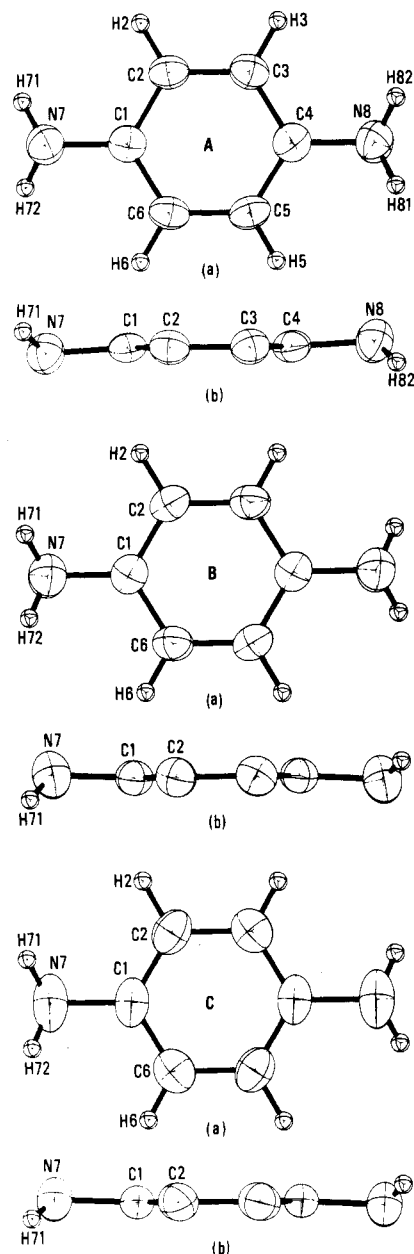


Figure 4. Anisotropy of thermal motion in the three crystallographically independent molecules of *p*-diaminobenzene. The thermal vibration ellipsoids of the non-hydrogen atoms have been scaled to 50% probability level. (a) Projection onto the plane of the benzene ring. (b) Projection onto a plane perpendicular to that of the ring and parallel to the long axis of the molecule. (The hydrogen atoms attached to C2 and C3 have been omitted for clarity.)

ditional evidence comes from the values of the internal ring angles in the two molecules.

It has been shown that in most para-disubstituted benzene derivatives the angular distortions of the ring may be reproduced to within experimental error by superimposing separate contributions from each functional group.⁷ Deviations from additivity have been found to occur only when the two groups interact with each other through the benzene ring: a reference case is that of *p*-nitroaniline, where π -donation from the amino group is strongly enhanced by the π -acceptor character of the para substituent.¹¹

In aniline the deviations from 120° of the internal ring angles at the ipso and para positions are $\Delta\alpha = -0.6^\circ$ and $\Delta\delta = -1.0^\circ$,

(48) Schultz, Gy.; Kolonits, M.; Hargittai, I. unpublished work. A value of $1.399 \pm 0.001 \text{ \AA}$ has been obtained by: Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243.

(49) Kuchitsu, K.; Cyvin, S. J. In *Molecular Structures and Vibrations*; Cyvin, S. J., Ed.; Elsevier: Amsterdam, 1972; pp 183-211. Robiette, A. G. In *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1973; Vol. 1, pp 160-197. Kuchitsu, K. In *Diffraction Studies on Non-Crystalline Substances*; Hargittai, I., Orville-Thomas, W. J., Eds.; Elsevier: Amsterdam, 1981; pp 63-116.

TABLE VI: Bond Distances (Å) and Angles (deg) of the Heavy-Atom Skeleton of Crystalline *p*-Diaminobenzene, with and without Correction for Libration^a

	molecule A		molecule B		molecule C	
	uncor	cor	uncor	cor	uncor	cor
C1-C2	1.399	1.406	1.391	1.400	1.381	1.392
C1-C6	1.393	1.401	1.396	1.405	1.385	1.396
C3-C4	1.394	1.402				
C4-C5	1.399	1.406				
C2-C3	1.383	1.388	1.383	1.389	1.387	1.395
C5-C6	1.386	1.390				
N7-C1	1.414	1.419	1.420	1.426	1.414	1.421
N8-C4	1.417	1.422				
C2-C1-C6	117.7	117.8	117.6	117.8	118.3	118.5
C3-C4-C5	117.8	118.0				
C1-C2-C3	121.1	121.0	121.0	120.9	120.7	120.6
C1-C6-C5	121.3	121.3	121.5	121.4	121.0	120.9
C2-C3-C4	121.2	121.1				
C4-C5-C6	120.9	120.8				
N7-C1-C2	121.3	121.2	121.3	121.2	120.2	120.1
N7-C1-C6	120.9	120.9	121.0	120.9	121.4	121.3
N8-C4-C3	121.0	120.9				
N8-C4-C5	121.1	121.0				

^a Estimated standard deviations are 0.003 Å for bond distances and 0.2° for bond angles.

respectively (Figure 5c). Decreasing π -donation from the amino group is expected to cause both $\Delta\alpha$ and $\Delta\delta$ to approach zero and even to become positive.⁵⁰ Were the ring-substituent interactions of each of the two amino groups in *p*-diaminobenzene exactly the same as in aniline, there would be additivity of angular distortions and the C2-C1-C6 angle in *p*-diaminobenzene would be $120^\circ - 0.6^\circ - 1.0^\circ = 118.4^\circ$. The observed value of $119.8 \pm 0.2^\circ$ indicates that the conjugation of the amino group with the ring becomes less pronounced when a second amino group is introduced in the para position.

We point out here that any information on ring-substituent interactions in benzene derivatives obtained by comparing ring angles is inherently more accurate than evidence derived by comparing bond distances. The angular distortions are in fact more accurately measured and more easily transferable from one experiment to another than bond length variations.⁴

A less pronounced conjugation of the amino group with the benzene ring should imply an increase in the value of the dihedral angle, ϕ , between the plane of the substituent and that of the ring. Unfortunately, this parameter is rather inaccurately determined both in the microwave study of aniline²⁴ and in the present electron diffraction study of *p*-diaminobenzene. Nevertheless, the values of ϕ obtained for the two molecules, $37.5 \pm 2^\circ$ and $43 \pm 4^\circ$, respectively, are consistent with the preceding observations.

The Crystal Structure. In the crystals of *p*-diaminobenzene the molecules are held together by a complex three-dimensional network of N-H...N hydrogen bonds. The arrangement of the three nonequivalent molecules (A, B, C) and of their closest neighbors is shown in Figure 6. Each of the four crystallographically independent amino groups acts as a proton donor in a hydrogen bond and as a proton acceptor in another. The geometrical parameters obtained here for the four nonequivalent hydrogen bonds are shown in Table VII. Note the unfavorable orientation of the N7_Bⁱ-H71_Bⁱ bond with respect to N7_Aⁱ, resulting

TABLE VII: Geometry of the Hydrogen Bonds in Crystalline *p*-Diaminobenzene^a

hydrogen bond ^b	$r(\text{N}\cdots\text{N})$, Å	$r(\text{H}\cdots\text{N})$, Å	$\angle\text{N-H}\cdots\text{N}$, deg
N7 _A ⁱ -H72 _A ⁱ ...N7 _C ⁱⁱⁱ	3.206 (3)	2.31 (2)	174 (2)
N7 _B ⁱ -H71 _B ⁱ ...N7 _A ⁱ	3.259 (2)	2.63 (2)	127 (2)
N7 _C ⁱ -H71 _C ⁱ ...N8 _A ⁱ	3.292 (3)	2.43 (3)	158 (2)
N8 _A ⁱ -H82 _A ⁱ ...N7 _B ^v	3.281 (3)	2.38 (2)	174 (2)

^a Estimated standard deviations are given in parentheses as units in the last digit. ^b The symmetry operations relating N7_Cⁱⁱⁱ to N7_Cⁱ and N7_B^v to N7_Bⁱ are given in the caption to Figure 6.

in a N-H...N angle of only 127°. The N7_Aⁱ-H72_Aⁱ...N7_Cⁱⁱⁱ hydrogen bond⁵² differs from the others in that the hydrogen atom gets much closer to the ipso carbon of the acceptor molecule. The H72_Aⁱ...C1_Cⁱⁱⁱ separation is indeed only 2.78 Å, while the corresponding separation in the other hydrogen bonds is 3.1-3.4 Å.

An analysis of the nonbonded contacts between adjacent molecules shows that, in addition to hydrogen bonding, other intermolecular interactions are also of importance in determining the crystal structure of *p*-diaminobenzene. As shown in Figure 6, the benzene ring of molecule A is faced from both sides by amino groups of symmetry-related molecules. The N7-H71 bond of molecule Aⁱⁱ and the N8-H81 bond of molecule A^{iv} point toward the middle points of the C1-C2 and C5-C6 bonds of molecule Aⁱ, respectively. The separations H71_Aⁱⁱ...C1_Aⁱ, H71_Aⁱⁱ...C2_Aⁱ, H81_A^{iv}...C5_Aⁱ, and H81_A^{iv}...C6_Aⁱ are 2.76-2.78 Å, somewhat less than the sum of the van der Waals radius of hydrogen, 1.2 Å, and the half-thickness of an aromatic molecule, 1.70 Å.⁵³ Note that the N7-H71 and N8-H81 bonds of molecule A are those not involved in hydrogen bonding.

The B and C molecules are less tightly packed than the A molecules, which explains their more pronounced thermal vibration (see Tables III and IV and Figure 4). The orientation of molecule Cⁱ is such that its amino group does not face a benzene ring (Figure 6) but is involved instead in a short contact with the H2 atom of molecule A (at $x, -1 + y, z$; not shown in Figure 6), with the C2_A-H2_A bond pointing roughly toward the N7_Cⁱ atom. The H...N separation is 2.72 Å, 0.20 Å less than any other C-H...N contact in the crystal. As regards molecule Bⁱ, Figure 6 shows that its amino group faces the benzene ring of molecule Cⁱⁱⁱ, with the N7_Bⁱ-H72_Bⁱ bond pointing toward one of the two central C-C bonds. The H...C separations, however, are now 2.94-2.99 Å,

(50) The expectation is based on experimental evidence from several benzene derivatives studied accurately by low-temperature X-ray crystallography, as discussed in detail in ref 4 and 5. The best example is *N,N*-diphenylaminotriphenylmethane, Ph₂N-CPh₃,⁵¹ where the variation in π -donation from the substituent to the ring is related to conformational changes. This molecule contains a planar nitrogen atom; the two phenyl groups linked to it adopt markedly different conformations in the crystal. One of them makes an angle of only 12.4° with the coordination plane of nitrogen, while the other is almost perpendicular to it (74.6°). The following geometrical changes take place in going from the coplanar to the perpendicular conformation: (i) an increase of the N-C_{ipso} bond distance by 0.033 Å; (ii) a decrease of the C_{ipso}-C_{ortho} bond distances by about 0.013 Å; (iii) an increase of the α angle by 2.4°; and (iv) an increase of the δ angle by 1.5°.

(51) Hoekstra, A.; Vos, A. *Acta Crystallogr., Sect. B* **1975**, *31*, 1716. Hoekstra, A.; Vos, A. *Acta Crystallogr., Sect. B* **1975**, *31*, 1722.

(52) The symmetry operations relating the various molecules (or atoms thereof) to molecules Aⁱ, Bⁱ, or Cⁱ (which are at x, y, z) are given in the caption to Figure 6.

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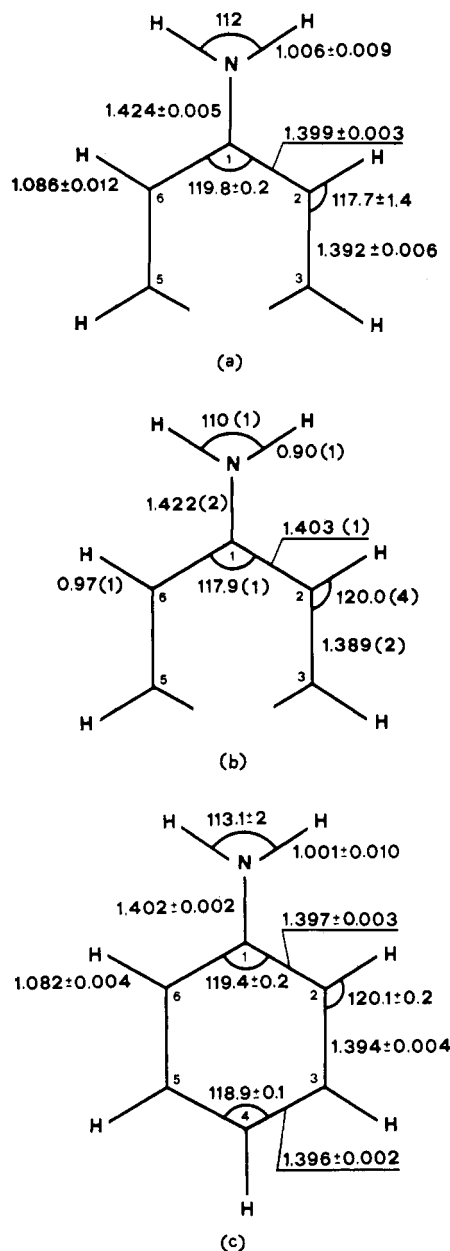


Figure 5. Comparison of the molecular structures of gaseous *p*-diaminobenzene, crystalline *p*-diaminobenzene, and gaseous aniline. Bond distances are given in Å, angles in deg. (a) Geometry of the free molecule of *p*-diaminobenzene, as determined by electron diffraction. Bond distances are r_g values. Total errors (estimated according to Hargittai and Hargittai⁴⁷) are given as error limits. The dihedral angle between the plane of the amino group and that of the ring is $\phi = 43 \pm 4^\circ$. (b) Mean geometry (see text) of the crystal molecule of *p*-diaminobenzene, as determined by X-ray crystallography. Bond distances and angles of the heavy-atom skeleton are corrected for libration. Estimated standard deviations are given in parentheses as units in the last digit. The dihedral angle ϕ has values ranging from 43° to 46° in the four independent amino groups that occur in the crystal. (c) Molecular geometry of aniline in the gas phase, as determined by microwave spectroscopy (after Lister, Tyler, Høg, and Wessel Larsen²⁴). Bond distances are r_g values. The dihedral angle ϕ is $37.5 \pm 2^\circ$.

appreciably larger than with the A molecules.

The Crystal Molecule. Of the three nonequivalent molecules that exist in the crystal, one (A) has no crystallographic symmetry and the others (B and C) are located on crystallographic centers of inversion. Nevertheless, deviations from C_{2h} symmetry are either insignificant (molecule A) or of marginal importance (molecules B and C). In all cases the benzene ring has D_{2h} symmetry within experimental error. The nitrogen atoms, however, are considerably displaced (0.066–0.086 Å) on opposite sides of the ring. The conformation of the amino groups is shown in

1; the dihedral angle between the plane of the substituent and that of the ring has values ranging from 43° to 46° .

Corresponding bond distances, bond angles, and torsion angles in the three molecules are in close agreement, except the C–C bond distances and C–C–C angles of molecule C. This molecule has a large and highly anisotropic motion, which cannot be fitted adequately by the rigid-body model; its geometry should be regarded as less accurately determined than that of the others.

Corresponding geometrical parameters for molecules A and B have been averaged, imposing C_{2h} symmetry, to yield a mean geometry for the crystal molecule of *p*-diaminobenzene. This geometry is shown in Figure 5b.

Comparing bond distances obtained by X-ray crystallography with those obtained by gas electron diffraction is not straightforward, as they have different physical meanings. This may cause apparent variations sometimes as large as those caused by real chemical effects.

The r_g bond distances produced by electron diffraction are thermal-average internuclear separations.⁴⁹ The bond distances obtained by X-ray crystallography are separations between average atomic positions, but unlike r_g distances,⁴⁹ they refer to the centroids of electron density distribution rather than to the nuclei. Moreover, the motion of a molecule in a crystal has substantial contribution from librational rigid-body motions, which may seriously distort the observed geometry.

Thus, comparing bond distances obtained by the two techniques for the same molecule would ideally require (i) changing the r_g values obtained by gas electron diffraction into r_a values; (ii) using only reflections with $\sin \theta/\lambda$ greater than a properly selected value in the refinement of the X-ray diffraction data, so as to eliminate any asphericity in the electron density distribution due to valence electrons and to get essentially the positions of the nuclei; (iii) correcting the X-ray diffraction geometry for the effect of librational motions; and (iv) extrapolating the results to a common temperature.

Even so, it would be necessary to assume that the internal vibrational motions are the same in the two phases.

At first, these problems may appear formidable to overcome. There is increasing evidence, however, that the most serious effects can be treated, at least with relatively rigid molecules. Moreover, the situation is much better when bond angles are compared. In fact, at least with aromatic molecules, bond angles are scarcely sensitive to problems like the exact definition of an atomic position and are less disturbed by the effects of librational motions than are bond distances.⁴

The mean value of the aromatic C–C bond distances in substituted benzene derivatives, $\langle r(C-C) \rangle$, is a parameter that is measured with great precision and is thus particularly well-suited for ascertaining the relative importance of the various corrections. Results from several molecules, mostly studied in our laboratories, are shown in Table VIII. The correction for the effect of libration is seen to be important, about +0.006 Å in most cases. Also important, although somewhat smaller, is the correction for the asphericity of the electron density distribution.

Once these corrections have been applied, the mean value of the aromatic C–C bond distances obtained by X-ray crystallography is seen to agree remarkably well with that obtained by electron diffraction. Note, however, that the r_g values (and not r_a) from electron diffraction are used in the comparison.

Besides *p*-diaminobenzene, there are two molecules in Table VIII where the difference between the $\langle r(C-C) \rangle$ values from the two experiments is larger than 0.002 Å: these are *p*-dicyanobenzene and *p*-diisocyanobenzene. Their geometries have been shown^{16,17} to be affected in opposite ways by the respective crystal fields, as compared with the free molecules. The small, opposite variations of $\langle r(C-C) \rangle$ that occur with these molecules as they go from the gas phase to the crystal are most probably real.^{16,17}

In *p*-diaminobenzene the mean value of the aromatic C–C bond distances obtained by X-ray crystallography is 1.392(1) Å (from molecules A and B). Due to lack of intensity data in the high- θ region, it was not possible to carry out a high- θ refinement and eliminate the effect of the aspherical distribution of valence

TABLE VIII: Mean Values of the Aromatic C-C Bond Distances (Å) in Benzene Derivatives, As Determined by X-ray Crystallography and Gas Electron Diffraction^a

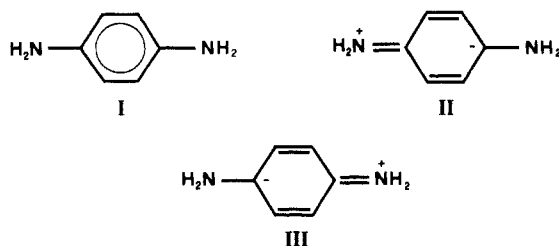
molecules		$\langle r(\text{C-C}) \rangle$ by X-ray crystallography ^b			$\langle r_g(\text{C-C}) \rangle$ by gas electron diffraction ^c
		conventional refinement	high- θ refinement	high- θ refinement, corrected for libration	
3,5-dimethylbenzoic acid ^{d,e}	1,3,5-trimethylbenzene ^f	1.390	1.395	1.401	1.401
3,5-dichlorobenzoic acid ^{e,g}	1,3,5-trichlorobenzene ^h	1.383	1.389	1.394	1.392
3,5-dinitrobenzoic acid ^{e,g}	1,3,5-trinitrobenzene ⁱ	1.381	1.384	1.387	1.388
<i>p</i> -methylsulfonylbenzoic acid ^j	methyl phenyl sulfone ^{j,k}	1.389	1.392	1.398	1.399
<i>p</i> -dicyanobenzene ^l	<i>p</i> -dicyanobenzene ^l	1.388	1.393	1.400	1.397
<i>p</i> -diisocyanobenzene ^m	<i>p</i> -diisocyanobenzene ^m	1.385	1.389	1.396	1.400
<i>p</i> -diaminobenzene ⁿ	<i>p</i> -diaminobenzene ⁿ	1.392		1.402–1.405 ^o	1.397

^a A preliminary account of these results and of their implications has been presented (ref 54). ^b Standard deviations are 0.001–0.002 Å. ^c Total errors are 0.002–0.003 Å. ^d Reference 55. ^e Only the C2–C3, C3–C4, C4–C5, and C5–C6 bond distances have been averaged. This makes the $\langle r(\text{C-C}) \rangle$ value from this molecule more directly comparable with that from the sym-trisubstituted derivative studied in the gas phase. ^f Reference 56. ^g Reference 54. ^h Reference 57. ⁱ Reference 58. ^j Reference 59. ^k Reference 60. ^l Reference 16. ^m Reference 17. ⁿ This work. ^o See text.

electrons. It proved possible, however, to correct the geometry of the molecules for the effect of libration: this caused $\langle r(\text{C-C}) \rangle$ to increase to 1.399 Å. Accounting for the aspherical distribution of valence electrons would most probably have caused an additional increase by some 0.003–0.006 Å, yielding a final value of 1.402–1.405 Å, appreciably larger than that obtained for the free molecule by electron diffraction, $\langle r_g(\text{C-C}) \rangle = 1.397 \pm 0.003$ Å. This suggests that the geometry of the molecule may be severely perturbed by the crystal field.

The difference between the lengths of the C1–C2 and C2–C3 bonds in *p*-diaminobenzene is determined rather accurately by X-ray crystallography. After correcting for libration, we found the C2–C3 bond to be 0.014 Å shorter than the C1–C2 bond (Figure 5b). Although correcting for the aspherical distribution of valence electrons might cause this difference to vary by a few thousandths of an angstrom, there is no doubt that the central C–C bonds of the ring in the crystal molecule are shorter than the other C–C bonds.

In the free molecule the actual value of $\Delta(\text{C-C}) = r(\text{C1-C2}) - r(\text{C2-C3})$ could not be measured accurately, but the analysis of electron diffraction data indicated that the two bonds can be considered as having virtually the same length. If so, one would reach the conclusion that the contribution of canonical forms like II and III is enhanced by the crystal field; in other words, the amino group should be a better π -donor in the crystal than it is in the gaseous phase.



Increasing π -donation from the substituent should cause the N7–C1 bond to become shorter. The values of the bond distance obtained for the crystal molecule, $r(\text{N7-C1}) = 1.422$ (2) Å (corrected for libration), and for the free molecule, $r_g(\text{N7-C1}) = 1.424 \pm 0.005$ Å, are apparently equal within experimental error. However, the value produced by X-ray crystallography is not corrected for the asphericity of the valence electron distribution, a correction that is important for this type of bond. The shift of the centroid of electron distribution with respect to nuclear position is expected to be toward the center of the ring in the case of C1⁵⁵ and toward the lone pair of electrons in the case of N7.⁶¹

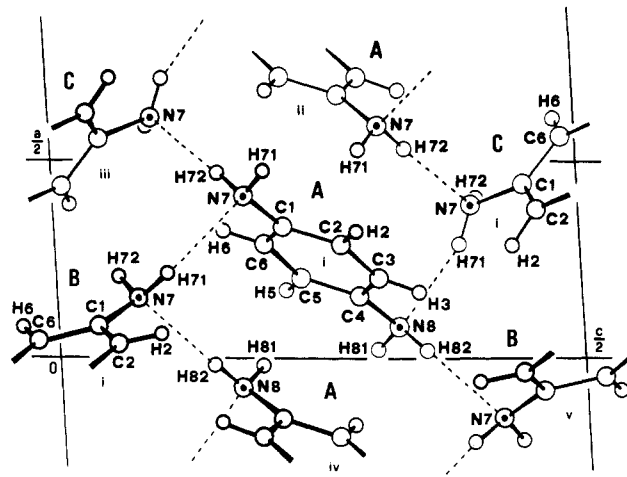


Figure 6. Projection of the crystal structure of *p*-diaminobenzene down *b*, showing the system of intermolecular hydrogen bonds. The symmetry operations relating the various molecules to molecules A', B', or C' (which are at *x*, *y*, *z*) are (ii) $1 - x, -1/2 + y, 1/2 - z$; (iii) $1 - x, 1/2 + y, 1/2 - z$; (iv) $-x, 1/2 + y, 1/2 - z$; (v) $-x, -1/2 + y, 1/2 - z$.

The total effect will be an increase of the value of $r(\text{N7-C1})$ produced by X-ray crystallography with respect to the true internuclear separation. This means that the N7–C1 bond in crystalline *p*-diaminobenzene is likely to be somewhat shorter than in the free molecule.

More persuading evidence for the increased contribution of canonical forms II and III to the electronic structure of crystalline *p*-diaminobenzene as compared with the free molecule comes again from angular changes rather than from variations in bond distances. In the crystal molecule the value of the ipso angle, C2–C1–C6, is 117.9 (1)°; in the free molecule it is $119.8 \pm 0.2^\circ$. The difference is highly significant, as the ipso angle is accurately determined by both experiments.⁶²

The good sensitivity of the ipso angle to variations in the extent of mesomeric interactions between the ring and the amino groups comes as no surprise. In a monosubstituted derivative of benzene increasing conjugation between the substituent and the ring causes the angles at the ipso and para positions, α and δ , to decrease

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(62) As observed earlier in this paper, displacing the N7 atom out of the ring plane by more than 0.30 Å would cause the ipso angle of the free molecule to decrease substantially, approaching the value obtained in the crystal. Such a large displacement of N7 can be ruled out, however, as it causes an unacceptable worsening of the fit. Displacements like those observed in the crystal, 0.066–0.086 Å, are compatible with the experimental data but have virtually no effect on the ipso angle.

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simultaneously by comparable amounts. In a symmetrically para-disubstituted derivative these two changes are superimposed, which obviously enhances the variation of the ipso angle.

The increased π -donation from the amino groups to the ring that occurs in the crystal molecule of *p*-diaminobenzene as compared with the free molecule is induced by intermolecular hydrogen bonding. The strength of a X-H...Y hydrogen bond depends upon both the acidity of the X-H group and the basicity of the Y atom. The amino group is a good base but a very poor acid; hence, the N-H...N hydrogen bond between two amino groups is weak. A stronger bond is apparently formed if a partial positive charge resides on the nitrogen atom. Though depressing the basicity of the amino group, the positive charge substantially increases the polarity of the N-H bonds, making the amino group a much better acid. It is well-known that N-H...O hydrogen bonds become progressively stronger as a partial positive charge is accumulated on the nitrogen atom.⁶³

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Registry No. *p*-Diaminobenzene, 106-50-3.

Supplementary Material Available: Tables of total experimental intensities obtained by electron diffraction, anisotropic thermal parameters, elements of the rigid-body T, L, and S tensors, and geometrical parameters involving hydrogen atoms, as obtained from the X-ray diffraction study (9 pages); tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Multiphoton-Induced Picosecond Photophysics of Chromium(III)-Polypyridyl Complexes

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Transient luminescence studies on a series of $\text{Cr}(\text{NN})_3^{3+}$ complexes (NN = bpy, 4,4'-Me₂bpy, 4,4'-Ph₂bpy, phen, 5-Clphen, 5-Brphen, 5-Mephen, 5-Phphen, 4,7-Me₂phen, 5,6-Me₂phen, 4,7-Ph₂phen, and 3,4,7,8-Me₄phen) have been carried out in aqueous media using picosecond laser excitation at 355 nm with a passively mode-locked Nd:YAG laser (~30-ps-fwhm pulses; 2-3 mJ/pulse). Both transient emission and transient absorption (excite-and-probe technique) were examined in detail for $\text{Cr}(5,6\text{-Me}_2\text{phen})_3^{3+}$; excitation wavelengths were 355 and 266 nm. The complexes show a fast emission component at 500-650 nm that decays with $\tau \sim 50$ ps and, except for NN = 5-Phphen and 4,4'-Ph₂bpy, a slow emission rise (biphasic; $\tau \sim 0.5$ and ~ 10 ns) at $\lambda \geq 665$ nm in the 0-7-ns window of the streak camera. The slow rise is totally quenched by I⁻, a known quencher of $^2\text{T}_1/{}^2\text{E}$ states. Transient absorption (355-nm excitation) reveals a pulse-limited formation of a fast decaying transient ($\tau \sim 50$ ps) at 462 nm and a slower decaying transient ($\tau = 0.5$ ns) at 541 nm. In the 1-10-ns range, a slow rise in absorption (outside of experimental error, $\pm 2\sigma$) is also observed for NN = 5,6-Me₂phen. Transient emission studies (266-nm excitation) show, in addition to the fast emission component and the slow emission rise, a prompt emission centered around 460 nm that shows biphasic decay: $\tau \sim 0.6$ and $\sim 11 \pm 2$ ns. In absorption (266-nm excitation), formation of e_{aq}^- occurs ($\lambda_{\text{max}} = 650$ nm; $\Phi_{\text{e}^-} \sim 0.14$ at 5 ns). For comparison, results of transient emission and absorption studies (266-nm excitation) on the free 5,6-Me₂phen ligand in 1 M HCl ($\Phi_{\text{e}^-} \sim 0.07$ at +50 ps) are also reported. Wavelength-resolved transient luminescence spectra (taken at 0 ps) are given for excitation of $\text{Cr}(5,6\text{-Me}_2\text{phen})_3^{3+}$ at 266 and 355 nm; the two spectra are qualitatively similar, but the intensities of the 460- and 570-nm bands are reversed. A model involving multiphoton excitation into ligand-localized and charge-transfer-to-solvent excited states is suggested to account for the data.

Introduction

The photophysics of chromium(III) complexes, in particular those containing polypyridine (NN) ligands, have been the object of many investigations to understand the behavior of the systems on absorption of light.¹ The four important states are $^4\text{A}_2(\text{F})$ (ground state), the lowest energy spin-allowed quartet state [$^4\text{T}_2(\text{F})$], and the thermally equilibrated lowest energy spin-for-

bidden doublet states [$^2\text{T}_1/{}^2\text{E}(\text{G})$]. These, along with other higher energy excited quartet states [$^4\text{T}_1(\text{F})$ and $^4\text{T}_1(\text{P})$], doublet states ($^2\text{T}_2(\text{G})$), and NN intraligand excited states [$^1\text{B}_1$, $^1\text{A}_1$, and a ligand-centered triplet state] spectroscopically observed and identified by König and Herzog² and by Ohno et al.³ for $\text{Cr}(\text{bpy})_3^{3+}$ are indicated in Figure 1. The figure depicts energy levels (as two-dimensional surfaces) against a distortion coordinate; it is shown only to indicate the complexity of the manifold of states. Also shown are two additional doublet states [$^2\text{A}_1(\text{G})$ and $^2\text{A}_2(\text{F})$] and the energies and labels of the ligand-free Cr^{3+} ion states.⁴ Not

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