

The Molecular Structure of Iodobenzene and *p*-Iodonitrobenzene in the Gaseous State

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The molecular structure of gaseous monoiodobenzene has been determined by a conjoint analysis based on electron diffraction intensities and microwave rotational constants assuming C_{2v} symmetry. The geometrical parameters are: $r_a(\text{C}\cdots\text{C})_{\text{ave}} = 1.3959(6)$, $r_a(\text{C}-\text{I}) = 2.098(4)$ and $r_a(\text{C}-\text{H})_{\text{ave}} = 1.107(5)$ Å, and $\angle_{\alpha}\text{CC}_1\text{C} = 121.2(5)$, $\angle_{\alpha}\text{C}_1\text{C}_2\text{C}_3 = 118.9(5)$, $\angle_{\alpha}\text{C}_1\text{C}_2\text{H}_7 = 122.3(26)$ and $\angle_{\alpha}\text{C}_4\text{C}_3\text{H}_8 = 119.2(34)^\circ$.

The molecular geometry of gaseous *p*-iodonitrobenzene has been determined by electron diffraction where the torsion of the nitro group has been treated as a large-amplitude motion. The geometrical parameters are: $r_a(\text{C}\cdots\text{C})_{\text{ave}} = 1.396(2)$, $r_a(\text{C}-\text{I}) = 2.102(8)$, $r_a(\text{C}-\text{H})_{\text{ave}} = 1.107(16)$, $r_a(\text{C}-\text{N}) = 1.458(15)$ and $r_a(\text{N}=\text{O}) = 1.228(3)$ Å, and $\angle_{\alpha}\text{CC}_1\text{C} = 122.2(5)$, $\angle_{\alpha}\text{CC}_\text{N}\text{C} = 122.2(5)$ and $\angle_{\alpha}\text{CNO} = 117.9(5)^\circ$. The barrier to internal rotation, V_2 , was found to be $8.8(75)$ kcal mol⁻¹.

Values given in parentheses are two standard deviations from the least-squares refinements using a diagonal weight matrix.

A plot of the *ipso* angle for monohalogen-substituted benzenes as a function of Pauling's electronegativity indicates a linear relationship between the *ipso* angle and the electronegativity within the halogens.

Previously we have studied the substitution effects on the molecular geometry for chloro-¹ and bromobenzene,² *o*-, *m*- and *p*-chloro-³⁻⁵ and bromonitrobenzene,^{6,7} and several other nitro-substituted benzene derivatives.^{4,6,8-10} This paper reports an extension of our systematic study of the mutual influence of halogen and nitro groups through the benzene ring and the determination of benzene ring deformations. However, to obtain information about changes in bond lengths and bond angles a high accuracy in the structure determination is required. We have therefore included rotational constants from microwave spectroscopy where such are available.

The aim of the structure determination of iodobenzene is to determine the C–I bond length and the deformation of the benzene ring as accurately as possible for comparison with the C–I bond lengths and ring deformations in other iodobenzene derivatives. It is also of interest to determine the *ipso* CC₁C bond angle. This *ipso* bond angle is found to be larger than 120° for electron-withdrawing substituents and smaller than 120° for electron-donating substituents. This systematic change of the *ipso* angle seems to be linearly dependent on the electronegativity of the substituent within the same period.¹¹ With iodobenzene the gaseous molecular structure of all the mono-halogenated benzenes will be known. It is therefore of interest to see if a similar

relationship between the *ipso* angle and the electronegativity holds within the same group.

Experimental and data reduction

Iodo- and *p*-iodonitrobenzene were prepared by standard procedures and recrystallized several times before use.

The electron diffraction data were recorded with a Balzers Eldigraph KD-G2 instrument¹² using Kodak electron image plates, and the experimental conditions are summarized in Table 1. The optical densities (D) were recorded using a Joyce–Loebl microdensitometer using a blackness correction given by eqn. (1).

$$D_{\text{corr}} = D(1 + 0.03D + 0.09D^2 + 0.03D^3) \quad (1)$$

The data were treated in the usual way¹³ except that an automatic background subtraction program based on the procedure described by Hedberg¹⁴ was used on the individual curves in a modified form. The modified molecular intensities are averaged for each of the two camera distances. The applied modification function was $s(|f_c|/|f_t|)^{-1}$ for both compounds.

The elastic atomic scattering amplitudes and their phases were calculated by using an analytical representation of the atomic potentials¹⁵ by the partial-wave method¹⁶ for C, N, O, I and by the electron density for bonded hydrogen¹⁷ for

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Table 1. Experimental and refinement conditions for iodobenzene and *p*-iodonitrobenzene.

	Iodobenzene		<i>p</i> -Iodonitrobenzene	
	50 cm	25 cm	50 cm	25 cm
Electron wavelength/Å	0.05893	0.05893	0.05893	0.05893
Nozzle temperature/°C	83	82	202/208 ^a	207
Nozzle-to-plate distance/mm	498.05	248.02	497.99/497.85 ^a	247.98
No. of plates	6	6	3/3 ^a	2 ^b
Background polynomial degree	9	9	9	9
Data range/Å ⁻¹				
<i>s</i> _{min}	2.50	6.00	2.50	6.00
<i>s</i> _{max}	14.50	30.0	14.50	26.0
Δ <i>s</i>	0.125	0.25	0.125	0.25
Least-squares weight function ^c				
<i>s</i> ₁ and <i>s</i> ₂	5.0–14.5	6.0–25.0	5.0–14.5	8.0–20.0
<i>w</i> ₁ and <i>w</i> ₂	0.15–0.0	0.0–0.012	0.15–0.0	0.0–0.12
<i>W</i>	1.0	1.0	1.0	1.0

^aTwo different recordings of the experimental data. ^bEach plate has been traced three times using different parts of the photographic plate. ^cSee Ref. 13 for definition.

the H atom. The inelastic scattering factors used were those of Tavard *et al.*¹⁸

Structural analysis and refinements

The following assumptions have been incorporated in the analysis: (a) All *r*_a(C–H) bond distances are equal. (b) Iodobenzene has *C*_{2v} symmetry. (c) The equilibrium geometry of *p*-iodonitrobenzene is planar with *C*_{2v} symmetry, in accordance with nitrobenzene as determined by microwave spectroscopy.¹⁹ (d) For *p*-iodonitrobenzene the C–H bonds bisect the adjacent CCC bond angle. When these assumptions are adopted, the molecular geometry can be described by the independent structural parameters given later in Tables 3 and 5 for iodobenzene and *p*-iodonitrobenzene, respectively.

The asymmetry parameter, κ , in the expression for the electron diffraction intensities is estimated²⁰ from $\kappa = au^4/6$, assuming²¹ $a = 2.0 \text{ \AA}^{-1}$ for all bond distances. The asymmetry parameter is neglected for all non-bonded distances.

Correction for shrinkage is included in the analysis by refining a geometrically consistent *r*_α structure. Definitions of the different bond distances (*r*_a, *r*_g, *r*_α and *r*_α^o) have been given by Kuchitsu and Cyvin.²²

Iodobenzene. The effective rotational constants *B*₀, determined by microwave analysis²³ have been transformed into the *B*_z representation,²² which corresponds to an *r*_z struc-

Table 2. Rotational constants (MHz) for iodobenzene.

	<i>B</i> ₀ (MW) ²³	<i>B</i> _z – <i>B</i> ₀ (calc.)	<i>B</i> _z (MW)	<i>B</i> _z (ED+MW)
A	5671.89(73)	0.031	5671.92(74)	5671.97(79)
B	750.416(2)	–0.215	750.20(7)	750.16(9)
C	662.627(1)	–0.090	662.52(3)	662.54(6)

ture for the conjoint analysis. The correction from *B*₀ to *B*_z is approximately given as *B*_z – *B*₀ ≈ δ_{vib}, and the vibrational correction term was calculated from a harmonic force field. The uncertainty in δ_{vib} is arbitrarily taken to be 30 % of its total value, and is added to the uncertainties in the *B*₀ rotational constants. The *B*₀, *B*_z and δ_{vib} values are given in Table 2. The *B*_z rotational constants are to be compared with the rotational constants calculated from the electron diffraction *r*_α^o structure,²² which is obtained from the *r*_α structure by eqn. (2)

$$r_{\alpha}^o = r_{\alpha} + (K_T - K_0) - 1.5a(u_T^2 - u_0^2) \quad (2)$$

where *T* and 0 refer to the nozzle temperature and 0 K, respectively, and $a = 2.0 \text{ \AA}^{-1}$. The *B*_z rotational constants were given relative weights, σ_z, according to their estimated uncertainties, and the relative weighting of the data from the two methods was such that standard deviations for the *r*_α rotational constants were approximately equal to the values of the σ_z estimate.

***p*-Iodonitrobenzene.** The structural analysis was carried out for both a static and a dynamic model. For the static model the torsional motion of the nitro group is treated conventionally as a small-amplitude motion. The physical interpretation of the dihedral angle determined by this model is an average angle which does not correspond to the minimum of the potential energy distribution of the rotation about the C–N bond. The dynamic model treats the torsional motion of the nitro group as a large-amplitude motion where the potential energy function is explicitly included in the analysis as described elsewhere.²⁴

Nitrobenzene is found to be planar by microwave spectroscopy,¹⁹ and in accordance with this fact the potential energy function was taken as: $V(\Phi) = 0.5V_2(1.0 - \cos 2\Phi)$ for $\Phi \in [0, 90]$. The interval between 0 and 90° was divided into nine sub-intervals, and the population in each sub-interval was calculated as described elsewhere.²⁴

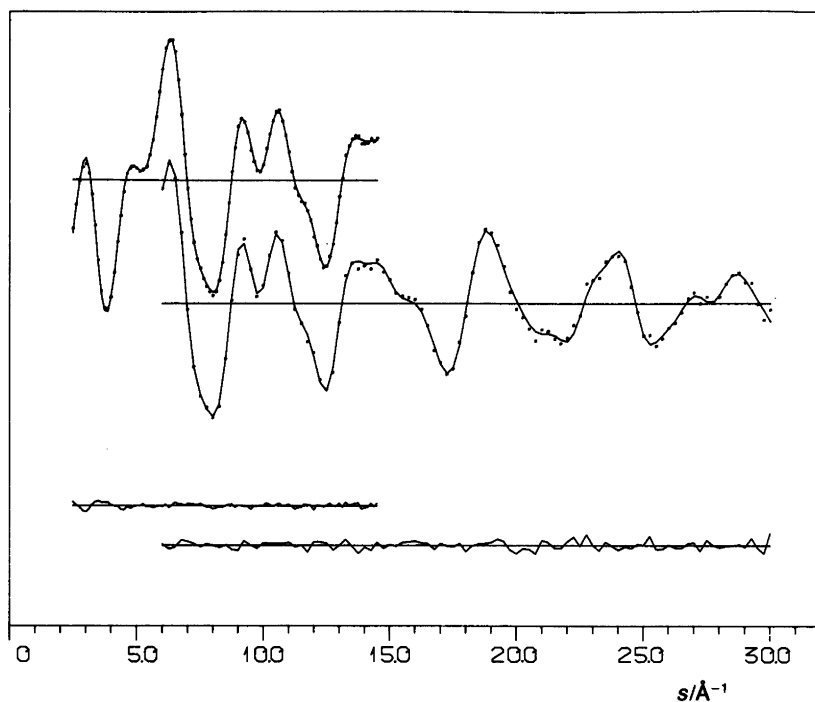
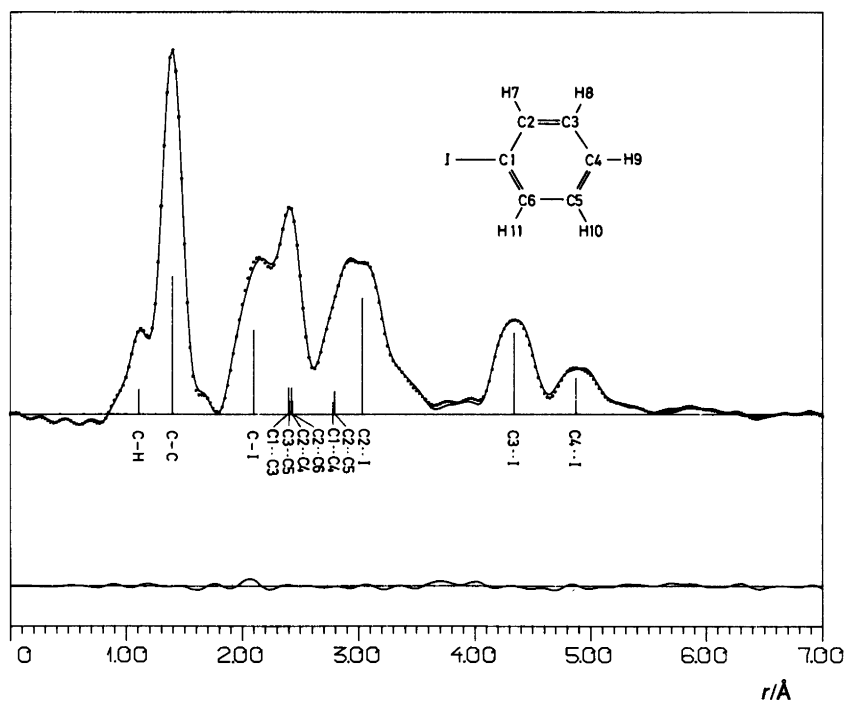


Fig. 1. Experimental (dots) and theoretical (full line) modified intensity curves, $sM(s)$, and difference curves for iodobenzene.

Fig. 2. Experimental (dots) and theoretical (full line) radial distribution curves for iodobenzene with an artificial damping constant $B = 0.0015 \text{ \AA}^2$. Theoretical intensities have been used below $s = 2.50 \text{ \AA}^{-1}$. The position and approximate areas (length of the bar) of the most important distances are indicated. The numbering of the atoms is also given.



Calculation of u - and K -values

The mean-square amplitudes of vibration, u , and perpendicular correction coefficients, K , were calculated by using the force field from bromobenzene²⁵ as a starting force field. The final force field was adjusted to fit the observed frequencies for iodobenzene²⁶ by a "one-step iteration", where the normal coordinate transformation matrix²⁷ was maintained from the starting force field. The same procedure was used for *p*-iodonitrobenzene, starting with the

force constants for stretching and bending given by Rao *et al.*²⁸ and some other constants as used for *p*-bromonitrobenzene.⁷ The final force field was adjusted to fit the frequencies given by Rao *et al.*^{28,29} and a torsional frequency of 55 cm^{-1} as estimated for gaseous nitrobenzene by microwave spectroscopy.¹⁹ For the static model the contribution of the torsional motion of the nitro group is included, while it is excluded for the dynamic model to give framework u - and K -values which were calculated separately for each of the nine sub-intervals from 0 to 90° .

Results and discussion

Iodobenzene. The structural parameters derived from the conjoint analysis of the electron diffraction and microwave spectroscopy data are given in Table 3, and the corresponding modified molecular intensity curves and radial distribution curves are shown in Figs. 1 and 2, respectively.

Attempts to refine the individual C=C bond distances simultaneously when their u -values were kept constant to their calculated values were not successful. These attempts caused convergence problems, large standard deviations and large correlation coefficients. We therefore decided to determine the average value. The correlation coefficients for parameters higher than 0.50 are given in Table 4.

The agreement between the electron diffraction data, Fig. 1, and observed rotational constants, Table 2, is very good. The agreement between the calculated and refined u -values as shown in Table 3 is also satisfactory.

The average r_a (C=C) = 1.3959(6) Å is lightly smaller than $r_a = 1.3975$ Å as used for benzene.³⁰ The average C=C bond distance is generally very little affected by substitution.³¹ However, this small shrinkage of the benzene ring is

also found for bromobenzene² and for other electronegative substituents.³²

The *ipso* angle, $\angle CC_1C = 121.2(5)^\circ$ is larger than 120° , as expected for an electronegative substituent.³³ The *ipso* angles for F,³⁴ Cl,¹ Br² and I are 123.4, 121.7, 121.5 and 121.2° , respectively. The plot of the *ipso* angle as a function of Pauling's electronegativity³⁵ is shown in Fig. 3. This plot indicates that there is a simple relationship between the variation of the *ipso* angle and the electronegativity within the same group similar to that suggested within the same period.

The distortion of the benzene ring caused by the substitution of an iodine atom can be described by the following parameters: $\Delta_1 = C2C1C6 - 120 = 1.2$, $\Delta_2 = C1C2C3 - 120 = -1.1$, $\Delta_3 = C2C3C4 - 120 = 0.7$ and $\Delta_4 = C3C4C5 - 120 = -0.5^\circ$. If the substitution effects are additive, these parameters, together with similar parameters for the nitro group, can be used to estimate the distortion of the benzene ring in *p*-iodonitrobenzene as shown later in Table 7.

The bond distances are transferred to r_a for comparison with the structure derived from NMR spectroscopy.³⁶

Table 3. Structural parameters^a (bond lengths/Å, angles/ $^\circ$ and u /Å) for iodobenzene.

	r_a and \angle_α ED+MW	u -Values		r_a ED+MW	r_a^b and \angle_α NMR ³⁴
		Obs.	Calc.		
Independent distances and angles					
$r(C-I)$	2.098(4)	0.056(5)	0.049	2.095(4)	
$r(C1=C2)$	1.3959	0.046	0.047	1.394	1.404(1)
$r(C2=C3)$	1.3959(6)	0.046(2)	0.047	1.391(6)	1.416(4)
$r(C3=C4)$	1.3959	0.046	0.047	1.393	1.3976 ^c
$r(C2-H7)$	1.107	0.078	0.077	1.094	1.081(1)
$r(C3-H8)$	1.107(5)	0.078(7)	0.077	1.092(5)	1.070(4)
$r(C4-H9)$	1.107	0.078	0.077	1.090	1.0819(3)
$\angle C2C1C6$	121.2(5)				121.2(2)
$\angle C1C2C3$	118.9(5)				119.4(1)
$\angle C1C2H7$	122.3(26)				120.7(1)
$\angle C2C3H8$	120.2(34)				119.31(4)
Refined u -values for dependent distances and dependent angles					
$u(C1=C3)$	2.40	0.057	0.057		
$u(C2=C4)$	2.42	0.057	0.057		
$u(C2=C6)$	2.43	0.059(6)	0.059		
$u(C3=C5)$	2.41	0.057	0.057		
$u(C1=C4)$	2.78	0.073(8)	0.061		
$u(C2=C5)$	2.79	0.074	0.062		
$u(C2=I)$	3.03	0.076(6)	0.072		
$u(C3=I)$	4.34	0.067(6)	0.067		
$u(C4=I)$	4.87	0.076(16)	0.069		
$u(H8=I)$	5.19	0.148(72)	0.112		
$\angle C2C3C4$	120.7(6)				119.0(3)
$\angle C3C4C5$	119.5(7)				122.1(3)
R^d	5.71				

^aUncertainties are two standard deviations from least-squares refinement using diagonal weight matrix. Parameters in braces are refined as one group. ^b r_a bond distances are slightly different owing to differences in the K -values; $r_a = r_a + u^2/r - K$. ^cAssumed.

^d $R = 100[\sum w_i \Delta_i^2 / \sum w_i I_i^2(\text{obs})]^{1/2}$, where $\Delta_i = I_i(\text{obs}) - I_i(\text{calc})$ and w is a weight function as defined in Table 1.

Table 4. Correlation matrix^a for iodobenzene ($\times 100$).

	$r(\text{C}-\text{I})$	$\angle \text{C2C1C6}$	$\angle \text{C1C2C3}$	$u(\text{C}\cdots\text{C})$	$u(\text{C1}\cdots\text{C4})$	$u(\text{C4}\cdots\text{I})$
$\angle \text{C2C1C6}$	82					
$\angle \text{C1C2C3}$	-69	-92				
$u(\text{C1}\cdots\text{C3})$	-52		51			
$u(\text{C2}\cdots\text{I})$					69	
$u(\text{H8}\cdots\text{I})$						55
Scale _{25 cm}				67		

^aOnly elements with values higher than 0.50 are given.

 Table 5. Structural parameters^a (bond lengths/ \AA , angles/ $^\circ$ and $u/\text{\AA}$) for *p*-iodonitrobenzene.

	Static model		Dynamic model		$u(\text{calc})$
	$r_{\text{a}}, \angle_{\alpha}$	$u(\text{obs})$	$r_{\text{a}}, \angle_{\alpha}$	$u(\text{obs})$	
Independent distances and angles					
$r(\text{C}-\text{I})$	2.101(8)	0.052(15)	2.102(8)	0.059(15)	0.053
$r(\text{C}\cdots\text{C})_{\text{ave}}$	1.397(3)	0.044	1.396(2)	0.044	0.048
$r(\text{C}-\text{N})$	1.462(16)	0.045	1.458(15)	0.045	0.049
$r(\text{C}-\text{H})_{\text{ave}}$	1.098	0.0767	1.107(16)	0.0767	0.0767
$r(\text{N}=\text{O})$	1.229(3)	0.037(6)	1.228(3)	0.039(7)	0.041
$\angle \text{CNO}$	118.8(6)		117.9(5)		
$\angle \text{CCN}$	118.6(5)		118.9(5)		
$\angle \text{ICC}$	119.1(5)		118.9(5)		
V_2			8.8(75)		
Φ	15.6(4)				
Refined u -values for dependent distances					
$u(\text{C1}\cdots\text{C3})$	2.40	0.054		0.056	0.060
$u(\text{C2}\cdots\text{C4})$	2.40	0.054		0.056	0.060
$u(\text{C2}\cdots\text{C6})$	2.44	0.055		0.057	0.061
$u(\text{C3}\cdots\text{C5})$	2.44	0.054		0.056	0.060
$u(\text{C3}\cdots\text{N})$	2.46	0.058		0.060	0.064
$u(\text{C4}\cdots\text{O})$	2.30	0.054		0.056	0.060
$u(\text{C1}\cdots\text{C4})$	2.74	0.070		0.074	0.063
$u(\text{C3}\cdots\text{C6})$	2.81	0.075		0.079	0.068
$u(\text{C2}\cdots\text{I})$	3.03	0.070(10)		0.088(10)	0.072
$u(\text{C2}\cdots\text{N})$	3.73	0.100(22)		0.061(16)	0.067
$u(\text{C1}\cdots\text{N})$	4.20	0.076		0.079	0.071
$u(\text{C3}\cdots\text{I})$	4.34	0.076		0.079	0.071
$u(\text{C4}\cdots\text{I})$	4.84	0.081(29)		0.073	0.073
$u(\text{C1}\cdots\text{O})$	4.89	0.104		0.104	0.104
$u(\text{N}\cdots\text{I})$	6.29	0.092(29)		0.093(25)	0.080
$u(\text{O}\cdots\text{I})$	6.94	0.116(13)		0.115(12)	0.115
R	6.90		6.18		

^aSee footnote to Table 3.

 Table 6. Correlation matrix^a for *p*-iodonitrobenzene ($\times 100$).

	$r(\text{C}-\text{N})$	$r(\text{C}-\text{I})$	$r(\text{C}-\text{C})$	$u(\text{C}-\text{N})$	$u(\text{C1}\cdots\text{C4})$
$r(\text{C}\cdots\text{C})$	-82				
$\angle \text{CNO}$	-54	53	50		
$\angle \text{CCN}$	-66				
$\angle \text{CCI}$		-85			
$u(\text{C}-\text{N})$	-60		55		
$u(\text{N}=\text{O})$				63	
$u(\text{C2}\cdots\text{I})$					59

^aOnly elements with values higher than 0.5 are given.

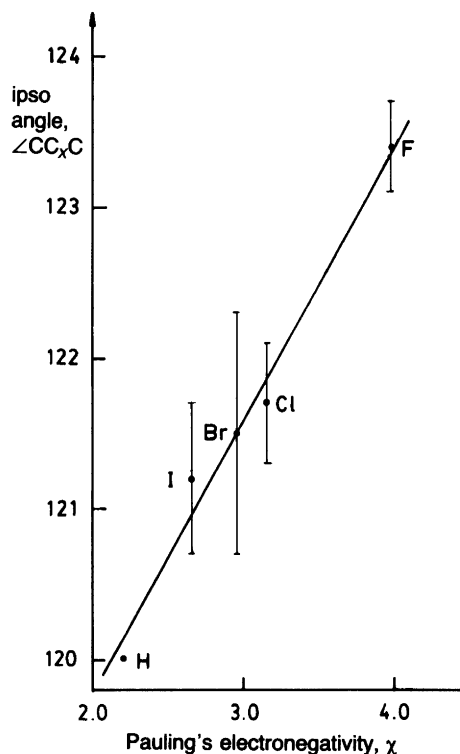


Fig. 3. The ipso angle for monohalogen-substituted benzenes, $\angle CC_xC$, plotted against Pauling's electronegativity, χ . Uncertainties (vertical bars) correspond to two standard deviations. Equation for linear regression: $\angle CC_xC = 1.816\chi + 116.146$; correlation coefficient 0.986.

There is good agreement between bond angles derived from the two different methods, while NMR results indicate differences in the r_a intra-ring bond length of as much as 0.02 Å. The differences in the intra-ring bond distances for substituted benzene derivatives³¹ are usually not as large as found by NMR.

p-Iodonitrobenzene. The structural parameters for *p*-iodonitrobenzene are given in Table 5, and the corresponding molecular intensity curves and radial distribution curves for the dynamic model are shown in Figs. 4 and 5. The correlation coefficients higher than 0.50 for the dynamic model are given in Table 6.

The quality of the data for *p*-iodonitrobenzene is not as good as for iodobenzene. Therefore no attempt was made to refine the individual C::C bond distances. The agreement between the parameters derived from the static and the dynamic models is good. The $r_a(C-I)$ bond distances for *p*-iodonitrobenzene, 2.102(8) Å, and iodobenzene, 2.098(4) Å, are equal within one standard deviation, and this also applies for the $r_a(C::C)$, 1.396(2) and 1.3959(6) Å, and $r_a(C-H)$, 1.107(16) and 1.107(5) Å, bond distances. There is good agreement between the observed and calculated u -values. The average of the absolute value of the torsional angle, Φ , of the nitro group for the static model, 15.6°, can be compared to the calculated value from the dynamic model according to eqn. (3)

$$\Phi_{ave} = \left\{ \int_0^{90} \Phi \exp[V(\Phi)/RT] d\Phi \right\} \left\{ \int_0^{90} \exp[V(\Phi)/RT] d\Phi \right\}^{-1} = 11.2^\circ \quad (3)$$

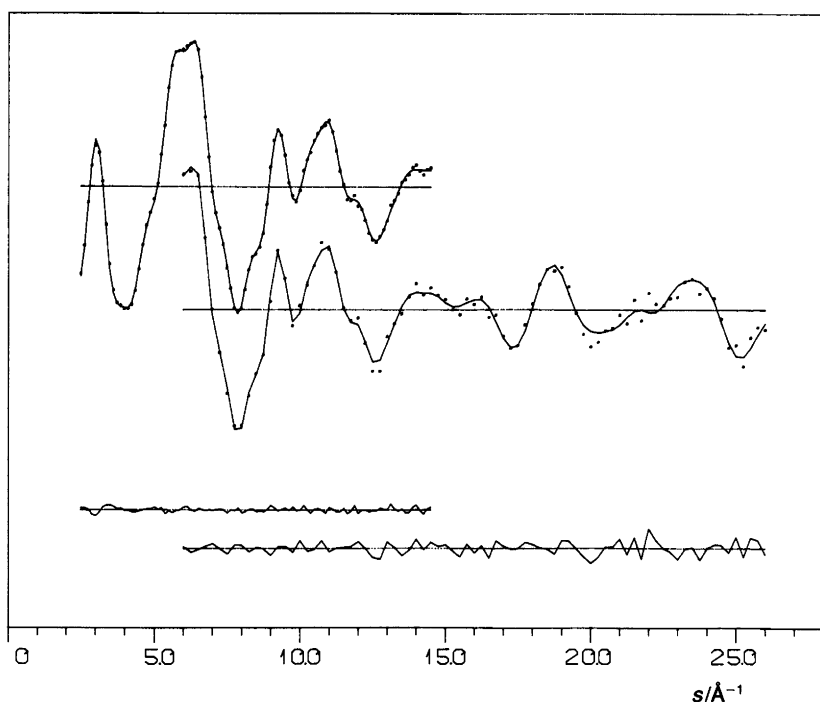


Fig. 4. Experimental (dots) and theoretical (full line) modified intensity curves, $sM(s)$, and difference curves for *p*-iodonitrobenzene.

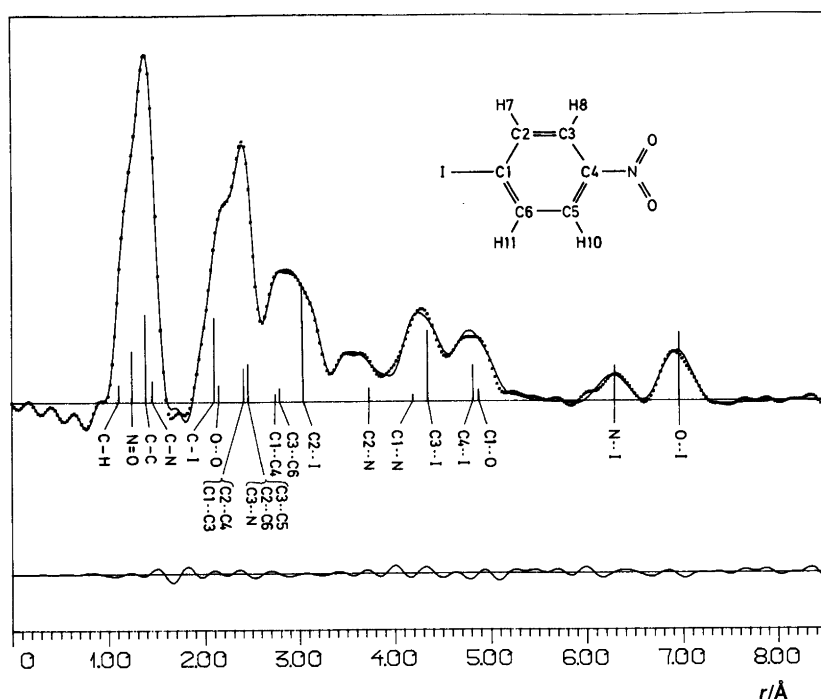


Fig. 5. Experimental (dots) and theoretical (full line) radial distribution curves for *p*-iodonitrobenzene with an artificial damping constant $B = 0.0025 \text{ \AA}^2$. Theoretical intensities have been used below $s = 2.50 \text{ \AA}^{-1}$. The positions and approximate areas (length of the bar) of the most important torsion-independent distances are indicated. The variation of the most important torsion-dependent non-bonded distances from 0 to 90° are: $r(\text{C3}\cdots\text{O})_{\text{syn}} = 2.70\text{--}3.15 \text{ \AA}$; $r(\text{C3}\cdots\text{O})_{\text{anti}} = 3.55\text{--}3.15 \text{ \AA}$; $r(\text{C2}\cdots\text{O})_{\text{syn}} = 4.05\text{--}4.40$ and $r(\text{C2}\cdots\text{O})_{\text{anti}} = 4.70\text{--}4.40 \text{ \AA}$.

Table 7. Estimation of the ring geometry for *p*-iodonitrobenzene from additivity of substitution effects.

	$\angle\text{CC}_i\text{C}$	$\angle\text{C}_i\text{CC}$	$\angle\text{CCC}_N$	$\angle\text{CC}_N\text{C}$
Model 1 ^a	122.0	118.9	118.9	122.4
Model 2 ^b	121.6	119.2	118.8	122.4
Observed	122.2	118.9	118.9	122.2

^aDeformation parameters for the nitro group are from Ref. 31 and for iodine from this work on iodobenzene. ^bDeformation parameters for the nitro group are from Ref. 37 and for iodine from this work on iodobenzene.

where $V(\Phi) = 0.5V_2[1.0 - \cos(2\Phi)]$ with $V_2 = 8.8 \text{ kcal mol}^{-1}$. $V_2 = 5.0 \text{ kcal mol}^{-1}$ gives $\Phi_{\text{ave}} = 15.9^\circ$. The barrier to internal rotation, $8.8(75) \text{ kcal mol}^{-1}$, is about twice as high as for other nitrobenzene derivatives,⁷ but the high uncertainty does not justify any further discussion of the barrier height.

The estimated geometry based on additivity of substitution effects is in very good agreement with the observed benzene ring, as shown in Table 7, and strongly supports the additivity principle as a first estimate of the benzene ring deformation.

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