The Molecular Structure of *ortho*- and *meta*-Iodonitrobenzene in the Gaseous State as Determined by the Electron Diffraction Method. General Trends in the Bond Lengths and STO-3G* *Ab Initio* Calculations on Iodonitrobenzenes

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The molecular structures of gaseous *meta*- and *ortho*-iodonitrobenzene have been studied by the electron diffraction method. The torsion of the nitro group has been treated as a large-amplitude motion, and the potential energy function for internal rotation of the nitro group from electron diffraction data has been determined. The geometrical parameters obtained from the electron diffraction data are for *meta*-iodonitrobenzene: $r_a(\langle C–C\rangle)$ = 1.392(2), $r_a(\langle C–H\rangle)$ = 1.114(13), $r_a(\langle N–O\rangle)$ = 1.226(2), r_a(C–N) = 1.487(11), r_a(C–I) = 2.102(6) Å, $\angle_\alpha$C1C2C3 = 116.4(9), $\angle_\alpha$C2C3C4 = 121.9(7), $\angle_\alpha$CCN = 118.0(5), $\angle_\alpha$CNO = 118.0(5), $\angle_\alpha$C2C3I = 118.4(7)° and for *ortho*-iodonitrobenzene: $r_a(\langle C–C\rangle)$ = 1.398(3), $r_a(\langle C–H\rangle)$ = 1.117(15), $r_a(\langle N–O\rangle)$ = 1.238(3), r_a(C–N) = 1.468(17), r_a(C–I) = 2.101(7) Å, $\angle_\alpha$C1C2C3 = 118.6(11), $\angle_\alpha$C2C2C4 = 120.5(13), $\angle_\alpha$C2C1N = 121.1(14), $\angle_\alpha$C6C1N = 116.1(11), $\angle_\alpha$CNO = 118.8(6)°. Values in parentheses are two standard deviations from least-squares refinement using a diagonal weight matrix. The *ab initio* method has been used for geometry optimalization on *ortho*-, *meta*- and *para*-iodonitrobenzene and iodobenzene using a STO-3G* basis. Compared to the experimentally determined parameters, the bond distances are poorly reproduced by this basis set, while the bond angles are remarkably well reproduced. Bond-distance and bond-angle variations for the halonitrobenzenes are discussed.

Previously we have systematically studied the substitution effects on the molecular geometry for chloro-[1] and bromobenzene[2] and for *ortho*-, *meta*- and *para*-chloro-[3–5] and bromonitrobenzenes.[6,7] Recently we have published the molecular structure of iodobenzene and *p*-iodonitrobenzene,[8] and now we wish to fulfil these series of iodonitrobenzenes by presenting our results for *o*- and *m*-iodonitrobenzene.

The main purposes of this study are to see if there is any systematic change in bond distances and bond angles, and to examine the principle of superposition or additivity[9,10] in order to see if the overall substitution effects can be predicted from the substitution effects of the individual iodo and nitro groups. We also wish to determine the potential energy function for internal rotation of the nitro group from the electron diffraction data.

Experimental and data reduction

The two compounds investigated, *o*- and *m*-iodonitrobenzene, were prepared by standard procedures.

The electron diffraction data were recorded with a Baltzers Eldigraph KD-G2[11] instrument using Kodak electron image plates. The most important experimental data for both *o*- and *m*-iodonitrobenzene are as follows: electron wavelength, 0.058 72 Å; camera distances, 498.33 and 248.53 mm; number of plates, 4. The nozzle temperatures were 110–116 and 129–134 °C for *o*- and *m*-iodonitrobenzene, respectively. The optical densities (D) were recorded by a Snoopy microdensitometer, and a blackness correction[12] as given in eqn. (1) was used. The experimental

$$C_{corr} = -\ln (1.0-0.35\ D)/(0.35\ D) \quad (1)$$

data were processed as described for iodobenzene and *p*-iodonitrobenzene.[8]

Structural analysis and refinements

The following assumptions have been incorporated into the analysis.

m-*Iodonitrobenzene*. (a) All r_a(C–H) bond distances are equal and bisect the adjacent CCC bond angle. (b) All r_a(C–C) bond distances are equal. This assumption is based

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on the experience that it was not possible to refine the individual C–C bond distances in iodobenzene even if rotational constants from microwave spectroscopy were included. (c) The equilibrium geometry is planar and has C_s symmetry. (d) The two r_a(N–O) bond distances, the two $\angle_\alpha$CNO bond angles and the two $\angle_\alpha$CCN bond angles are equal owing to the fact that the environments for the NO_2 group are quite similar. The following eleven independent geometrical parameters were selected to describe the molecular geometry: r(C–I), r(C–C), r(C–N), r(N–O) $r(\langle$C–H$\rangle)$, ∠CCN, ∠CNO, ∠C1C2C3, ∠C2C3C4, ∠ICC2 and the dihedral angle φ, defined as 0° for a planar arrangement of the atoms. For the atom numbering see Fig. 2 later.

o-*Iodonitrobenzene.* (a) and (b) as above. (c) The equilibrium geometry is allowed to be non-planar, but the phenyl and the CNO_2 group are assumed planar. (d) The two r(N–O) bond distances and the two $\angle_\alpha$CNO bond angles are assumed equal, but the two $\angle_\alpha$CCN bond angles can be different. The molecular geometry is described by twelve independent parameters as given above for *m*-iodonitrobenzene, but ∠CCN is replaced by ∠C2C1N and ∠C6C1N. For the atom numbering see Fig. 4 later.

The asymmetry parameter, $\varkappa$, in the expression for the electron diffraction intensities was estimated from the formula[13] $\varkappa = au^4/6$ assuming $a = 2.0$ Å^{-1} for all bond distances.[14] The asymmetry parameter is neglected for all non-bonded distances.

Ab initio calculations have been carried out using the Gaussian 88 package[15] and STO-3G* basis. The molecular structure of iodobenzene and *o*-, *m*- and *p*-iodonitrobenzene have been completely optimised applying the constraints that the phenyl ring and the CNO_2 group are planar. The rotational barriers have been deduced from the calculations with dihedral angles of 0 and 90° as mentioned above, while for *o*-iodonitrobenzene the dihedral angle has also been optimised.

Rotational barrier

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 method is an average angle which does not correspond to the minimum of the potential energy distribution for rotation about the C–N bond. An average dihedral angle different from 0° does therefore not necessarily mean that the equilibrium dihedral angle is different from zero.

The dynamic model treats the torsional motion of the nitro group as a large-amplitude motion for which the potential energy function is explicitly included in the analysis as described elsewhere.[16]

The potential energy function for *m*-iodonitrobenzene was taken as eqn. (2). This function gives a planar equilibrium structure as found for nitrobenzene[17] and also used previously for non-*ortho*-substituted nitrobenzenes.[7,8]

$$V(\varphi) = 0.5V_2(1.0 - \cos 2\varphi)\ 0 \leq \varphi \leq 90° \quad (2)$$

The potential energy function for *o*-iodonitrobenzene was taken as eqn. (3). This function can give a barrier

$$V(\varphi) = 0.5V_2(1.0 + \cos 2\varphi)$$

$$+0.5V_4(1.0 + \cos 4\varphi)\ 0° \leq \varphi \leq 90° \quad (3)$$

at 0° and 90° and a minmum between 0 and 90° if $V_4 \neq 0$. $V_4 = 0$ gives a planar equilibrium geometry.

For both functions the interval between 0 and 90° was divided into nine sub-intervals, and the population for each sub-interval was calculated as described elsewhere.[16] The framework values where the contribution from the torsional motion is excluded for the root mean-square amplitude of vibration, u, and the perpendicular correction coefficients, K, were calculated for each sub-interval.

Calculation of *u*- and *K*-values

The root mean-square amplitudes of vibration,[18] u, and the perpendicular correction coefficients,[18] K, were calculated by adjusting the force field we have used for iodobenzene and *p*-iodonitrobenzene to fit the frequencies given by Rao *et al.*[19] A program written by Hilderbrandt *et al.*[20] was used for these calculations. The K-values are used to correct for the shrinkage effect.

The torsional frequency for the nitro group is estimated to be 55 cm^{-1} for gaseous nitrobenzene by microwave spectroscopy.[16] We have used a torsional force constant of 0.10 mdyn Å rad^{-2} for both *o*- and *m*-iodonitrobenzene, which gives calculated torsional frequencies of 68.8 and 67.8 cm^{-1}, respectively. The corresponding observed frequencies[19] are 92 and 68 cm^{-1}. The experimentally determined u-values for the non-bonded O13···I and O14···I distances using the static model are 0.169 and 0.114 Å for *m*-iodobenzene and 0.544 and 0.826 Å for *o*-iodonitrobenzene. These experimentally determined u-values should be compared to the calculated values of 0.153 and 0.093 Å for *m*-iodonitrobenzene and 0.251 and 0.202 Å for *o*-iodonitrobenzene. This indicates that the torsional force constant should be less than 0.10 mdyn Å rad^{-2} in the gaseous state, and (in particular) this is the case for *o*-iodonitrobenzene. Lowering the torsional force constant to 0.05 mdyn Å rad^{-2} gives calculated torsional frequencies of 51.3 and 49.3 cm^{-1} for *o*- and *m*-iodonitrobenzene, respectively, which is closer to the value of 55 cm^{-1} reported for gaseous nitrobenzene.[16] However, the calculated K-values for some of the bond distances were unreasonably large, which we believe is due to the use of rectilinear coordinates in the normal coordinate calculations. This problem is avoided by using a large-amplitude approach for the torsional motion of the nitro group. We want to emphasize that the calculated

Table 1. *u*-Values (in Å) for *o*- and *m*-iodonitrobenzene.

ortho dynamic model				*meta* dynamic model			
Type[a]	*r*	Obs.[b]	Calc.	Type[a]	*r*	Obs.[b]	Calc.
⟨C–H⟩	1.117		0.077		1.114		0.077
O–N	1.238	0.051(6)[c]	0.040		1.226	0.042(5)	0.040
⟨C–C⟩	1.398	0.053 } (4)	0.047		1.392	0.044 } (4)	0.047
C–N	1.468	0.057 }	0.051		1.487	0.049 }	0.052
C–I	2.101	0.051(9)	0.055		2.102	0.055(8)	0.055
C2···H7	2.17		0.101	C1···H7	2.19		0.101
C1···H10	2.19		0.100		2.18		0.099
C4···H7	2.17		0.101	C3···H7	2.19		0.101
C3···H8	2.18		0.100		2.17		0.100
C4···H9	2.17		0.102		2.16		0.102
C5···H8	2.19		0.100		2.17		0.100
C5···H10	2.19		0.100		2.18		0.099
C6···H9	2.16		0.102		2.16		0.102
O···O	2.16		0.049		2.17		0.050
C1···C3	2.40	0.067 }	0.055		2.36	0.061 }	0.056
C1···C5	2.38	0.068	0.056		2.37	0.062	0.057
C1···O13	2.33	0.078	0.066		2.33	0.072	0.067
C1···O14	2.33	0.078	0.066		2.33	0.072	0.067
C2···C4	2.42	0.068 } (4)	0.056		2.43	0.061 } (4)	0.056
C2···C6	2.45	0.067 }	0.055		2.46	0.061 }	0.056
C2···N	2.49	0.073	0.061		2.47	0.066	0.061
C3···C5	2.41	0.068	0.056		2.40	0.062	0.057
C4···C6	2.45	0.068	0.056		2.42	0.061	0.056
C6···N	2.43	0.073 }	0.061		2.46	0.066 }	0.061
C1···C4	2.77		0.062		2.74		0.063
C2···C5	2.78		0.064		2.81		0.065
C3···C6	2.82		0.063		2.79		0.064
C1···I	3.10		0.068	C2···I	3.02	0.085 } (6)	0.070
C3···I	3.01		0.070	C4···I	3.04	0.085 }	0.070
C3···N	3.75		0.063		3.72	0.075 } (13)	0.064
C5···N	3.70		0.064		3.72	0.075 }	0.064
C4···N	4.23		0.066		4.22		0.066
C4···I	4.33	0.095 } (18)	0.069	C1···I	4.31	0.074 } (9)	0.069
C6···I	4.42	0.093 }	0.067	C5···I	4.34	0.074 }	0.069
C5···I	4.87	0.050(16)	0.069	C6···I	4.88	0.077(17)	0.069
C4···O13	4.97		0.102		4.91		0.096
C4···O14	4.92		0.102		4.90		0.096
N···I	3.36	0.118(22)	0.109		5.47	0.075(24)	0.089
I···O13[d]	2.76		0.164		5.49	0.160 } (28)	0.149
	3.57		0.148		6.01	0.133 }	0.123
I···O14[d]	4.58		0.116		6.56	0.116 } (19)	0.086
	3.99		0.137		6.10	0.147 }	0.118

[a]Type for *m*-iodonitrobenzene is the same as for *o*-iodonitrobenzene if not explicitly given. The numbering is given in Figs. 2 and 4. [b]The calculated *u*-values are framework values, i.e. the contribution from the torsion is excluded. For torsion-independent distances this contribution is essentially zero. The observed *u*-values are fixed at the calculated ones if not refined. [c]Uncertainties are two standard deviations from least-squares refinement using a diagonal weight matrix. Parameters in braces are refined as one group. [d]The interval of variation of the non-bonded distance and *u*-values for $\varphi \approx 5$ and 85°.

framework *u*- and *K*-values are independent of the torsional force constant and show the advantage of using a dynamic model for such large-amplitude motions. We have used the same torsional force constant for both *o*- and *m*-iodonitrobenzene even if the assigned torsional frequency is considerably larger for *o*-iodonitrobenzene. This has been done because our determination of the rotational barrier from electron diffraction and the STO-3G* *ab initio* calculations gives a lower rotational barrier for *o*-iodonitrobenzene than for non-*ortho*-iodonitrobenzenes, which indicates a lower torsional frequency for *o*- than for *m*-iodonitrobenzene. The assigned torsional frequency of 92 cm^{-1} for the nitro group in *o*-iodobenzene[19] is therefore not in agreement with the *ab initio* results or our experimentally determined potential for internal rotation. Both the *ab initio* calculations and the electron diffraction results indicate that the torsional frequency for the nitro group is smaller in *o*-iodonitrobenzene than in *m*-iodonitrobenzene.

The most important *u*-values, together with the corresponding distances, are given in Table 1.

Results

m-*Iodonitrobenzene.* The structural parameters derived from electron diffraction, together with *ab initio* STO-3G* calculations, are given in Table 2. The corresponding mod-

Table 2. Structural parameters[a] (bond lengths in Å, angles in °) for *m-* and *o*-iodonitrobenzene.

	meta r_a and $\angle_\alpha$			*ortho* r_a and $\angle_\alpha$		
	Static	Dynamic	STO-3G*	Static	Dynamic	STO-3G*
r(C1–C2)	1.391(2)	1.392(2)	1.3867	1.399(3)	1.398(3)	1.3969
r(C2–C3)			1.3919			1.3965
r(C3–C4)			1.3965			1.3863
r(C4–C5)			1.3882			1.3878
r(C5–C6)			1.3862			1.3839
r(C6–C1)			1.3860			1.3894
r(C2–H7)/ r(C3–H7)	1.102(13)	1.114(13)	1.0836	1.129(17)	1.117(15)	1.0824
r(C4–H8)			1.0833			1.0833
r(C5–H9)			1.0828			1.0826
r(C6–H10)			1.0836			1.0836
r(N–O13)	1.225(2)	1.226(2)	1.2780	1.237(3)	1.238(3)	1.2761
r(N–O14)			1.2782			1.2796
r(C–N)	1.494(10)	1.487(11)	1.5083	1.463(16)	1.468(17)	1.5119
r(C–I)	2.102(6)	2.102(6)	2.0717	2.092(7)	2.101(7)	2.0694
∠C1C2C3	116.6(8)	116.4(9)	118.51	119.9(15)	118.6(11)	117.65
∠C2C3C4	121.7(7)	121.9(7)	119.74	119.3(15)	120.5(13)	120.92
∠C3C4C5	119.5	119.4	120.48	119.3	118.9	120.54
∠C4C5C6	120.9	121.1	120.36	122.8	122.4	119.49
∠C5C6C1	117.4	117.2	118.38	116.5	116.8	119.81
∠C6C1C2	123.9	124.0	122.53	122.2	122.8	121.59
∠C1C2H7/ ∠C2C3H7	121.7	121.8	119.26	120.4	119.8	119.34
∠C3C4H8	120.3	120.3	119.85	120.4	120.6	119.37
∠C4C5H9	119.6	119.5	119.66	118.6	118.8	120.48
∠C5C6H10	121.3	121.4	122.11	121.8	121.6	121.49
∠C2C1N	118.1(5)	118.0(5)	118.52	122.6(14)	121.1(14)	122.78
∠C6C1N	118.1(5)	118.0(5)	118.95	115.1(11)	116.1(11)	115.63
∠C1NO13	118.2(4)	118.0(5)	117.91	119.3(6)	118.8(6)	119.01
∠C1NO14			117.76			116.69
∠C2C3I/ ∠C1C2I	118.2(7)	118.4(7)	120.08	123.8(9)	124.1(11)	123.93
φ	14.0(38)	0.0	0.0	69.5(43)	60.0	40.97
R^b	4.62	4.59		5.64	5.53	

[a]Uncertainties are two standard deviations from least-squares refinement using a diagonal weight matrix. Parameters in braces are refined as one group. Elements in the correlation matrix larger than 0.6 for *m*-iodonitrobenzene are: C–N/⟨C–C⟩ = −0.73; C–N/CCN = −0.66; C1C2C3/CCN = 0.70; C2C3C4/C–I = 0.80; C2C3C4/C1C2C3 = −0.64; C2C3I/C–I = −0.75; C2C3I/C2C3C4 = −0.60; *u*(N–O)/*u*(⟨C–C⟩ = 0.74 and for *o*-iodonitrobenzene are: V_2/V_4 = 0.73; C–N/⟨C–C⟩ = −0.86; C–I/C1C2C3 = 0.70; C1C2C3/C2C3C4 = −0.64; C1C2I/C1C2N = −0.91; ⟨C–C⟩/*u*(⟨C–C⟩) = 0.67; C–N/*u*(⟨C–C⟩) = −0.73; *u*(O–N)/*u*(⟨C–C⟩) = 0.70; C2C3C4/*u*(C4···I) = 0.64; V_2/u(N···I) = 0.65; V_4/u(N···I) = 0.74. [b]Goodness of fit factor; $R = [\Sigma w_i \Delta_i^2 \Sigma w_i I_i(\text{obs})]^{1/2}$, where $\Delta_i = I_i(\text{obs}) - I_i(\text{calc})$ and *w* is a weight function.

ified molecular intensity curves and the radial distribution curves for the dynamic model are shown in Figs. 1 and 2, respectively. The correlation coefficients for parameters larger than 0.60 are given as a footnote in Table 2. The numbering of the atoms is shown in Fig. 2.

The agreement between the observed r_a bond distances and the calculated r_e bond distances using the STO-3G* basis set is rather poor. The differences between calculated and observed bond distances of N–O, C–N and C–I are about 0.05, 0.02 and −0.03 Å, respectively. However, the agreement between the observed $\angle_\alpha$ bond angles is much better, with deviations of usually less than 1.5°, and in particular the agreement between the observed $\angle_\alpha$ bond angles and the assumption that the molecular deformation is additive is quite good. Our assumptions about the geometry, i.e. that the *r*(C–C), *r*(C–H) and *r*(N–O) bond distances are assumed equal and that the bond angles ∠CCN and ∠CNO are also assumed equal, are in good agreement with the *ab initio* calculations.

The structural parameters derived from the static and the dynamic model are essentially the same, giving an insignificantly better fit to the experimental data for the dynamic model. The refined and calculated *u*-values are also satisfactory.

o-*Iodonitrobenzene.* The structural parameters from electron diffraction, together with the *ab initio* STO-3G* calculations, are given in Table 2. The corresponding modified molecular intensity curves and radial distribution curves for the dynamic model are shown in Figs. 3 and 4, respectively.

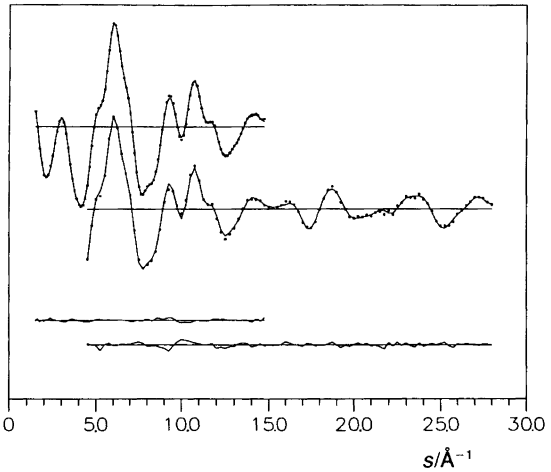


Fig. 1. Experimental (dots) and theoretical (full line) modified intensity curves, *s*M(*s*), and difference curves for *m*-iodonitrobenzene.

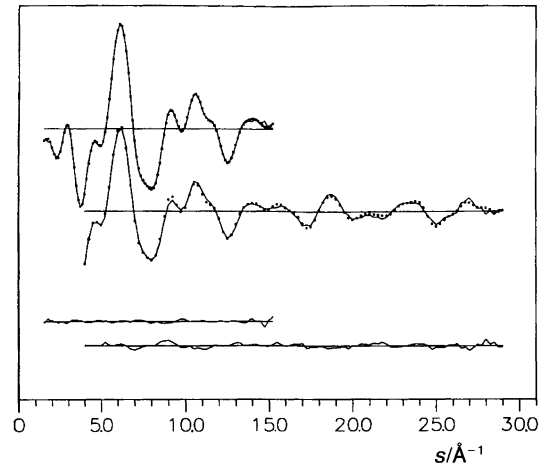


Fig. 3. Experimental (dots) and theoretical (full line) modified intensity curves, *s*M(*s*), and difference curves for *o*-iodonitrobenzene.

The correlation coefficients for parameters larger than 0.60 are given as a footnote in Table 2. The numbering of the atoms is given in Fig. 4.

The agreement between the observed bond distances r_a and r_e, bond distances calculated using the STO-3G* basis set, is as for *m*-iodonitrobenzene. The differences between calculated and observed values for the N–O, C–N and C–I bond distances are about 0.04, 0.04 and −0.03 Å, respectively. The agreement between the observed $\angle_\alpha$ bond angles and the STO-3G* calculations, and the assumption that the molecular deformation is additive, is not as good as for *m*- and *p*-iodonitrobenzene. The reason for this might be the fact that the nitro group is not coplanar with the benzene ring, but is twisted by 60° owing to steric interaction between the iodine and oxygen atoms. The sum of the van der Waals radii[21] for iodine and oxygen is 3.55 Å, compared to the value of 3.49 Å observed for the static model. The assumptions about the geometry we have made are mostly justified by the results from the *ab initio* calculations. The only minor disagreement is that the difference in $\angle_\alpha$CNO is calculated to be 2.3°, while we have assumed these two angles equal. However, we are pleased that the significant difference between $\angle_\alpha$C2C1N = 121.1(14)° and $\angle_\alpha$C6C1N = 116.1(11)° is reproduced by the *ab initio* calculations, which give the values 122.78 and 115.63°, respectively.

The structural parameters derived from the static and dynamic model are essentially the same, giving a slightly better fit to the experimental data for the dynamic model.

Iodobenzene and p-*iodonitrobenzene.* The calculated structural parameters for iodo- and *p*-iodonitrobenzene using a

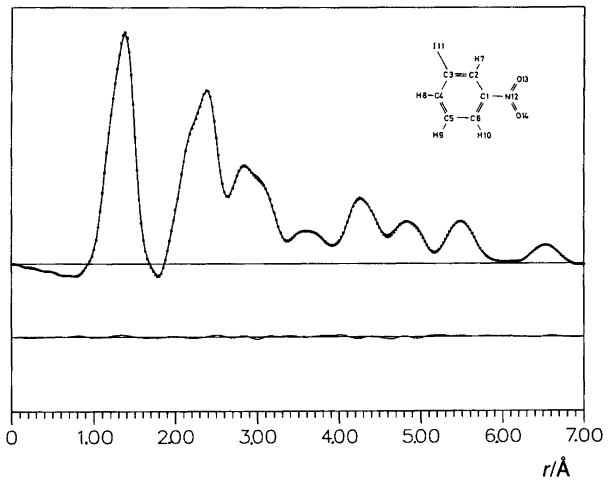


Fig. 2. Experimental (dots) and theoretical (full line) radial distribution curves for *m*-iodonitrobenzene with an artificial damping constant B = 0.0025 Å^2. Theoretical intensities have been used below s = 2.50 Å^{-1}. The most important distances, the peaks in the radial distribution and their *u*-values are given in Table 2.

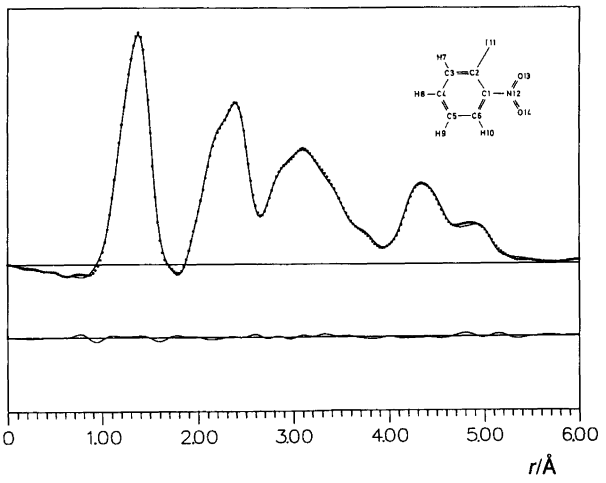


Fig. 4. Experimental (dots) and theoretical (full line) radial distribution curves for *o*-iodonitrobenzene with an artificial damping constant B = 0.0025 Å^2. Theoretical intensities have been used below s = 2.50 Å^{-1}. The most important distances, the peaks in the radial distribution and their *u*-values are given in Table 2.

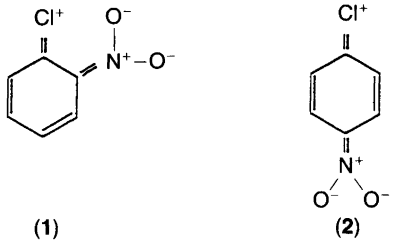
Table 3. Structural parameters[a] (r_a/Å and $\angle_\alpha$/°) for iodobenzene and *p*-iodonitrobenzene from electron diffraction[8] and STO-3G* *ab initio* calculations.

	Iodobenzene		*p*-Iodonitrobenzene	
	ED	STO-3G*	ED	STO-3G*
r(C2–H)		1.0827		1.0836
r(C3–H)	1.107(5)	1.0824	1.107(16)	1.0824
r(C1–X)[b]		1.0827	1.458(15)	1.5070
r(N–O)			1.228(3)	1.2783
r(C1–C2)		1.3867		1.3866
r(C2–C3)	1.3959(6)	1.3866	1.396(2)	1.3858
r(C3–C4)		1.3931		1.3961
r(C4–I)	2.098(4)	2.0769	2.102(8)	2.0721
$\angle_\alpha$C1C2C3	120.7(6)	120.33	118.9	118.94
$\angle_\alpha$C2C3C4	118.9(5)	119.74	118.9	119.93
$\angle_\alpha$C3C4C5	121.2(5)	120.00	122.2(5)	120.26
$\angle_\alpha$C6C1C2	119.5(7)	119.97	122.2(5)	120.26
$\angle_\alpha$C1C2H7	119.1	120.16	120.6	120.51
$\angle_\alpha$C2C3H8	118.2	120.04	120.6	120.04
$\angle_\alpha$C1NO			117.9(5)	117.84

[a]See Fig. 2 for numbering of the carbon atoms. [b]X = H (iodobenzene); X = N (*p*-iodonitrobenzene).

STO-3G* basis set, together with previous r_a structure parameters from electron diffraction,[8] are given in Table 3. The C–I bond distance is calculated to be 0.02 and 0.03 Å too short for iodobenzene and *p*-iodonitrobenzene, while the C–N and N–O bond distances are calculated to be 0.05 Å too long in *p*-iodonitrobenzene. This is the same trend as found for *o*- and *m*-iodonitrobenzene. The assumption that the molecular deformation of the benzene ring is additive is quite good.

Structural trends. Even if the agreement between some of the observed and calculated structure parameters is rather poor for the bond distances, the *ab initio* values can be very useful in predicting changes due to substitution at different positions. The structural changes for the halonitrobenzenes can be rationalized from the resonance picture between (**1**) and (**2**). From this resonance picture we would



(**1**) (**2**)

predict a shorter C–X (X=F,Cl,Br,I) bond distance for substitution in the *ortho* and *para* positions as compared with *meta*. The experimental results and bond distances computed by the *ab initio* method are shown in Fig. 5. The observed trends for the C–Cl bond distances of *o*-, *m*- and *p*-chloronitrobenzenes[3–5] seem to fit the predictions from this resonance picture, but the variations of the experimentally determined bond distances are much larger than calculated. For the corresponding bromonitrobenzenes[6,7] it is quite clear that *m*-bromonitrobenzene does not follow the predicted trend found for the other molecules and by the *ab initio* calculations. It seems as if the C–Br bond distance is about 0.03 Å too short. New data will be recorded to reinvestigate this molecule. It is therefore of interest to compare the structural changes for the iodonitrobenzenes with the expected trends, and also to see if these trends are reproduced by our *ab initio* calculations. For the iodonitrobenzenes the variation in the C–I bond distance is very small, as shown in Fig. 5 and also predicted from the *ab initio* calculations.

It might be a more general effect for all halonitrobenzenes that the substitution effects decrease with the electronegativity of the substituent. This is the case for the *ipso* angle of monosubstituted halobenzenes, where the deviation from 120° decreases with the electronegativity.[8] As shown in Fig. 5, the variations in the C–X bond distances as calculated by the *ab initio* method are largest for X=F and smallest for X=I, the same trend as found for the *ipso* angle for monosubstituted halobenzens.[8] However, different basis sets have been used, owing to the storage capacity of our computer, so therefore it cannot be ruled out that this is a basis set effect.

The C–N bond distances are shorter for *p*- and *o*-iodonitrobenzene [1.458(15) and 1.468(17) Å] than for *m*-iodo-

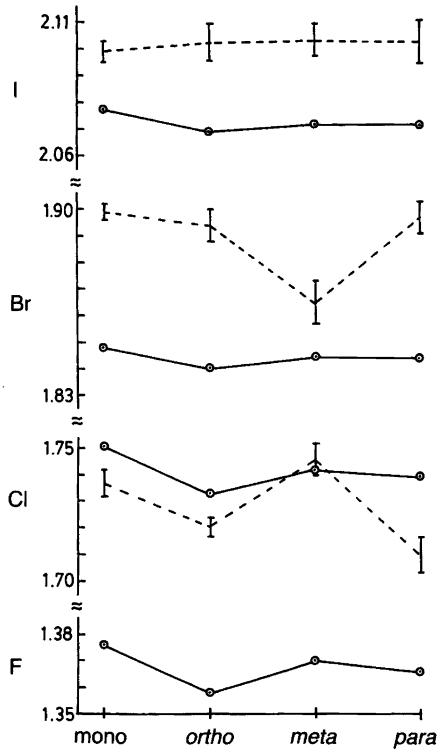


Fig. 5. r_g(C–X) bond distances (broken line) for various positions of the X substituent on nitrobenzene and the corresponding r_e(C–X) bond distances (full line) from *ab initio* calculations. The basis sets used in the calculations were 6-31G for X = F, 3-21G* for X = Cl and STO-3G* for X = Br and I, respectively (mono indicates halobenzene and *ortho*, *meta* and *para* denote the position of substitution of the halogen atom in nitrobenzene).

Table 4. The additivity principle[a] applied to *p*-, *m*- and *o*-iodonitrobenzene.

	p-Iodonitrobenzene		*m*-Iodonitrobenzene		*o*-Iodonitrobenzene	
	ED	STO-3G*	ED	STO-3G*	ED	STO-3G*
$\angle_\alpha$C1C2C3	119.2	119.76	117.0	118.29	119.3	118.55
$\angle_\alpha$C2C3C4	118.8	118.88	121.5	120.02	119.2	119.76
$\angle_\alpha$C3C4C5	122.4	122.12	119.3	120.34	121.1	120.93
$\angle_\alpha$C4C5C6	118.8	118.88	121.0	120.35	119.8	119.88
$\angle_\alpha$C5C6C1	119.2	119.76	117.6	118.41	118.8	118.88
$\angle_\alpha$C6C1C2	121.6	120.60	123.6	122.59	121.8	122.00

[a]The additivity in column ED is obtained by using the deformation parameters on the benzene ring caused by the nitro group given in Ref. 10 and from Ref. 8 for the iodo atom. In column STO-3G* the deformation parameters are obtained from STO-3G* calculations on iodo- and nitrobenzene.

nitrobenzene [1.487(11) Å] as expected from the resonance structure. The C–N bond distance for *o*-iodonitrobenzene is 0.01 Å longer than for *p*-iodonitrobenzene. This elongation is partially due to the fact that all *ortho* halonitrobenzenes have non-planar equilibrium structures while *p*- and *m*-iodonitrobenzene have planar equilibrium structures. *Ab initio* calculations show that the C–N bond distance increases when the nitro group is perpendicular to the phenyl ring. This is also found experimentally by comparing the average of the C–N bond distances for several *p*- and *m*-halonitrobenzenes with average C–N bond distances from several *o*-halonitrobenzenes.[22]

The additivity or superposition of substitution effects is simply to add the deformation of benzene caused by the iodo atom alone and by the nitro group alone. The bond angles within the benzene ring, assuming additivity of the substitution effects, are given in Table 4 for *o, m*- and *p*-iodonitrobenzene. Compared to the results given in Tables 2 and 3, this principle works very well for *para* and *meta* substitution but not quite as well for *ortho* substitution. The same conclusion can be drawn if only *ab initio* calculations are applied.

Rotational barrier. The barriers to internal rotation for the nitro group are given in Table 5. *o*-Iodonitrobenzene has a non-planar equilibrium structure while the equilibrium structure of *m*-iodonitrobenzene is planar. The dihedral angle corresponding to the minimum of the potential energy function is found to be 60.0° for *o*-iodonitrobenzene using the dynamic model, and an average angle of 69.5(43)° using the static model. We also found that the barrier height at φ=0° is much larger than at φ=90°. This indicates that the steric repulsion between the iodine and oxygen atoms is larger than the π-stabilization, favouring a planar structure. A lower barrier height at φ=90° than at φ=0° will give an average dihedral angle larger than the equilibrium angle, as was also found using a static model. The minimal STO-3G* basis set gives a rotational barrier for nitrobenzene which is in much better agreement with the experiment than larger basis sets.[23] This is also the case for our calculations, in which the agreement between experiment and the *ab initio* calculations is fairly good for *o*-iodonitrobenzene and very good for *m*-iodonitrobenzene.

However, from the very simple conceptual resonance picture given above, we would expect the rotational barrier for nitrobenzene and *meta*-substituted nitrobenzenes to be approximately equal, with a higher barrier for *para*-substituted nitrobenzenes. As seen from Table 5 the STO-3G* *ab initio* calculations fail to reproduce this trend, whereby the barrier for *m*-iodonitrobenzene is larger than the barrier for nitrobenzene. This is also found experimentally[24] for *m*-fluoronitrobenzene, where the barrier is even higher than for *p*-fluoronitrobenzene.

Simple conceptual pictures are important in chemistry, but care should be taken not to try to explain all chemical properties from such oversimplifications. It is quite clear that such conceptual pictures should be applied with caution. However, they still serve to stimulate research and critical analysis of such ideas and hypotheses.

Table 5. Parameters[a] related to the rotation of the nitro group.

	Nitrobenzene		*o*-Iodonitrobenzene		*m*-Iodonitrobenzene		*p*-Iodonitrobenzene	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
V_0	0.0	0.0	1.55	0.87	0.0	0.0	0.0	0.0
V_{90}	2.8–3.3[b]	5.02	0.17	1.06	4.5(1.3)	5.01	8.8(75)	5.02
φ_{min}	0.0	0.0	60.0[c]	40.97	0.0	0.0	0.0	0.0

[a]V_2 and V_4 in eqn. (2) are 1.38(40) and 0.69(44) kcal mol^{-1}, respectively. Uncertainties are as described in footnote (*a*) to Table 3. Barrier heights; $V_0 = V(\varphi=0) - V(\varphi=\varphi_{min})$ and $V_{90} = V(\varphi=90) - V(\varphi=\varphi_{min})$ in kcal mol^{-1} and $\varphi_{min} = 0.5 \arccos(-V_2/4V_4)$ in degrees. Calc. means 3-21G* basis. [b]Refs. 17, 24 and 25. [c]For the static model φ_{min} is refined to 69.5(43)°.

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