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# Molecular structure and conformation of nitrobenzene reinvestigated by combined analysis of gas-phase electron diffraction, rotational constants, and theoretical calculations

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**Abstract** The molecular structure and conformation of nitrobenzene has been reinvestigated by gas-phase electron diffraction (GED), combined analysis of GED and microwave (MW) spectroscopic data, and quantum chemical calculations. The equilibrium  $r_e$  structure of nitrobenzene was determined by a joint analysis of the GED data and rotational constants taken from the literature. The necessary anharmonic vibrational corrections to the internuclear distances ( $r_e - r_a$ ) and to rotational constants ( $B_e^{(i)} - B_0^{(i)}$ ) were calculated from the B3LYP/cc-pVTZ quadratic and cubic force fields. A combined analysis of GED and MW data led to following structural parameters ( $r_e$ ) of planar nitrobenzene (the total estimated uncertainties are in parentheses):  $r(\text{C}-\text{C})_{\text{av}} = 1.391(3) \text{ \AA}$ ,  $r(\text{C}-\text{N}) = 1.468(4) \text{ \AA}$ ,  $r(\text{N}-\text{O}) = 1.223(2) \text{ \AA}$ ,  $r(\text{C}-\text{H})_{\text{av}} = 1.071(3) \text{ \AA}$ ,  $\angle \text{C2}-\text{C1}-\text{C6} = 123.5(6)^\circ$ ,  $\angle \text{C1}-\text{C2}-\text{C3} = 117.8(3)^\circ$ ,  $\angle \text{C2}-\text{C3}-\text{C4} = 120.3(3)^\circ$ ,  $\angle \text{C3}-\text{C4}-\text{C5} = 120.5(6)^\circ$ ,  $\angle \text{C}-\text{C}-\text{N} = 118.2(3)^\circ$ ,  $\angle \text{C}-\text{N}-\text{O} = 117.9(2)^\circ$ ,  $\angle \text{O}-\text{N}-\text{O} = 124.2(4)^\circ$ ,  $\angle (\text{C}-\text{C}-\text{H})_{\text{av}} = 120.6(20)^\circ$ . These structural parameters reproduce the experimental  $B_0^{(i)}$  values within 0.05 MHz. The

experimental results are in good agreement with the theoretical calculations. The barrier height to internal rotation of nitro group,  $4.1 \pm 1.0 \text{ kcal/mol}$ , was estimated from the GED analysis using a dynamic model. The equilibrium structure was also calculated using the experimental rotational constants for nitrobenzene isotopomers and theoretical rotation–vibration interaction constants.

**Keywords** Nitrobenzene · Gas-phase electron diffraction · Microwave spectroscopy · Ab initio and DFT calculations · Molecular structure · Internal rotation

## Introduction

Although the molecular structure of gaseous nitrobenzene was investigated by microwave spectroscopy (MW) [1, 2], gas-phase electron diffraction (GED) [3–5], IR and Raman spectroscopy (see Refs. [6, 7] and references within), we found it desirable to acquire more accurate data on the structure of this important molecule, especially concerning its form of torsion and the values of its bond length C–N and angle  $\angle \text{CC}_{\text{NO}_2}\text{C}$ . According to MW spectra, the nitrobenzene has the planar structure of  $C_{2v}$  symmetry. Vibrational spectra of nitrobenzene were also interpreted for planar structure. However, average non-planar structures ( $r_a$ ) of  $C_2$  symmetry with the torsional angles of the nitro group  $\phi(\text{C}-\text{N}) = 22.7(41)^\circ$  and  $\phi(\text{C}-\text{N}) = 13.3(14)^\circ$  were determined from GED by Shishkov et al. [3] and Domenicano et al. [4], respectively. The non-planarity of nitrobenzene was attributed to large-amplitude torsional motion of the nitro group, which causes the average molecular structure obtained by GED to deviate appreciably from planar. The equilibrium  $r_e$  structure or  $r_{\text{h1}}$  structure, corrected for dynamic and nonlinear kinematic

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effects, was not determined from GED data. Borisenko and Hargittai [5] have applied a dynamic model to GED data. Initially assuming a planar equilibrium structure of nitrobenzene and using Monte Carlo optimization, the barrier height to internal rotation was estimated to be  $4.5 \pm 0.7$  kcal/mol. Their discussion came out strongly in favor of the planar equilibrium structure.

From the MW [2] and GED [4] studies, the value of  $r(\text{C-N})$  was determined to be 1.492(2) and 1.486(4) Å, respectively. These values are appreciably larger than the average value (1.467 Å) for aromatic nitro compounds [8]. The value of  $r(\text{C-N}) = 1.478(13)$  Å determined from GED study [3] is somewhat less compared to above-mentioned experimental data; however, its uncertainty is rather large. Thus, the determination of the equilibrium value of C–N bond length from GED data and high-level theoretical calculations is of great importance. Moreover, there is a substantial disagreement in the experimental values of  $\angle \text{CCNO}_2\text{C}$ . In the GED study [4] the value of this angle was determined to be  $123.4(3)^\circ$ , which was smaller than those from MW [2] and the earlier GED [3] studies, respectively.

To get a confirmation and greater confidence about the non-planarity and structural parameters of nitrobenzene, we decided to reinvestigate the molecular structure, conformation, and torsional potential of nitrobenzene by GED, this time assisted by the combined analysis of GED data, rotational constants, and ab initio and density functional theory calculations. Using results of theoretical calculations, it is possible to reanalyze the static GED model with fewer restrictions on geometry than in the previous GED studies. A previous investigation of dynamic model [5] was restricted to estimation of barrier to internal rotation. In this work it is proposed to examine the GED dynamic model more fully. And what is more important, we for the first time determined the equilibrium geometry of nitrobenzene by calculating the anharmonic vibrational corrections to the internuclear distances ( $r_e - r_a$ ). These corrections together with anharmonic corrections to rotational constants ( $B_e^{(i)} - B_0^{(i)}$ ) allow us to carry out a joint analysis of GED data and experimental rotational constants taken from the literature.

Of particular value is the reanalysis of the experimental MW spectra [1, 2] carried out in this work using the method for determination of the equilibrium geometry of a molecule from experimental rotational constants and theoretical rotational–vibrational interaction constants [9].

## Theoretical calculations

### Computational details

Ab initio MP2 and density functional B3LYP calculations with different basis sets were carried out to obtain the

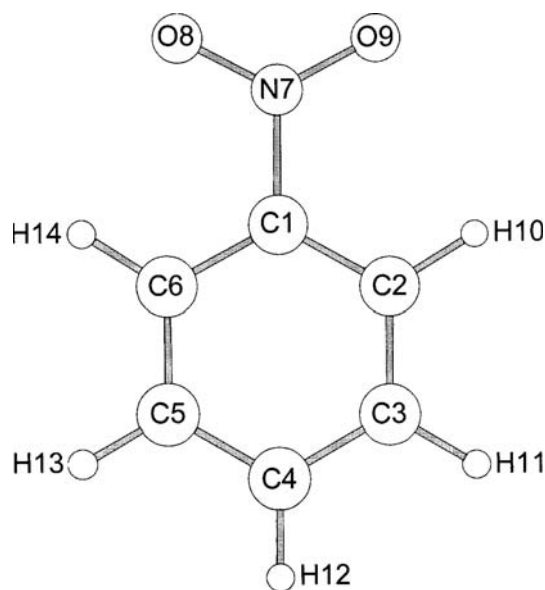
initial predictions for geometric, vibrational, and torsional parameters and estimate the vibrational corrections to rotational constants and internuclear distances. Larger basis sets and higher levels of theory than have been previously reported for nitrobenzene [4, 6, 7, 10–12] were employed in this study. All calculations were carried out using the Gaussian 03 program package [13].

Geometry optimization was performed at the hybrid density functional B3LYP level with 6-31G(d,p), 6-31G(2df,p), 6-311++G(3df,2p), and cc-pVTZ basis sets and at the ab initio MP2 level with 6-31G(d,p), 6-311++G(d,p), cc-pVTZ and aug-cc-pVTZ basis sets. Potential functions for internal rotation around the C–N bond were obtained at the same levels of theory by calculating the molecular energies for the torsional angle from  $0^\circ$  to  $90^\circ$  with  $10^\circ$  increments, while all other structural parameters were optimized. Besides, the torsional potential was also determined from the G3X calculations. The G3X method [14] is one of compound methods developed in an attempt to achieve high accuracy in energy calculations. The G3X prediction of the barrier height to internal rotation in nitrobenzene would thus be expected to be of high reliability. The B3LYP/cc-pVTZ vibrational amplitudes were used as initial values in the GED analysis of static models. For geometrical parameters, the starting values were taken both from planar B3LYP/cc-pVTZ structure and from non-planar MP2/6-311++G(d,p) structure.

A dynamic model was based on the concept that large-amplitude motion due to torsion of the nitro group may be represented by a mixture of pseudo-conformers. The initial values of structural parameters and amplitudes of vibration for all pseudo-conformers were obtained from B3LYP/6-31G(2df,p) calculations. From B3LYP/6-31G(2df,p) quadratic force field, the root-mean-square amplitudes of vibration and perpendicular amplitude corrections were calculated for all pseudo-conformers using SHRINK program [15].

### Geometry and torsional potential

Computed bond lengths and angles, rotational constants, and potential barrier heights for nitrobenzene (Fig. 1) together with experimental MW data are given in Table 1. The torsional potentials for nitrobenzene obtained from theoretical calculations are shown in Fig. 2. The twisted structure with torsional angle  $\phi(\text{C-N}) = 21.1^\circ$  is predicted for nitrobenzene only by MP2/6-311G++(d,p) method; however, the value of the barrier height toward planar configuration, 0.17 kcal/mol can be considered to be within the accuracy of theoretical calculation. Therefore, more likely this result points to large-amplitude torsional motion of  $\text{NO}_2$  group about the planar position. By other



**Fig. 1** Molecular structure of nitrobenzene with atom numbering

theoretical methods, the equilibrium structure of nitrobenzene is predicted to be planar.

In general, the calculated geometric parameters are not very sensitive to changes in theoretical treatments: the bond lengths agree within 0.02 Å and the differences between bond angles do not exceed 0.7°. As to comparison with MW data, there is rather appreciable difference in the C–N and C1–C2 bond lengths and the C2–C1–C6 bond angle. The calculated values of the C–N bond length are 0.014–0.022 Å smaller than the one, 1.4916(17) Å, obtained from MW data [2]. The average theoretical value of  $r(\text{C1–C2})$  is 0.02 Å larger than the value determined from MW spectra [2], while the theoretical values of C2–C1–C6 angle are from 2.2 to 2.8° lower than experimental one.

The calculations at all levels of theory employed in this study, except for MP2/6-311G++(d,p) method, result in torsional potential function with a minimum for planar conformation and sufficiently high barrier to orthogonal conformation (4.7–7.5 kcal/mol). A very flat potential in the vicinity of the equilibrium position with a shallow minimum at  $\phi(\text{C–N}) = 21.1^\circ$  was obtained at the MP2/6-311G++(d,p) level (Fig. 2). For this theoretical model, the barrier height to orthogonal conformation (3.5 kcal/mol) is very close to the experimental value of  $3.0 \pm 1.5$  kcal/mol determined from MW study [1]. The values of the barrier, 4.7 and 4.8 kcal/mol, predicted by G3X and MP2/aug-cc-pVTZ methods, respectively, are consistent with the experimental one if considering the inherent uncertainties of the techniques involved. Following the results of theoretical calculations, it was decided to test different torsional potentials in a dynamic GED model.

## Force field calculations

In this study a joint analysis of GED and MW data was carried out to obtain the equilibrium structure  $r_e$  by calculating anharmonic vibrational corrections based on the cubic force field. The equilibrium structure, quadratic, and cubic force constants in Cartesian representation, and vibrational frequencies of nitrobenzene were calculated at the B3LYP/cc-pVTZ level. The harmonic force constants were calculated from analytical expressions for the second energy derivatives and the cubic force constants were obtained by numerical differentiation of second derivatives. The quadratic Cartesian force constants obtained from this calculation were transformed to those described by a set of internal vibrational coordinates of local symmetry [16]. This force field was scaled to correct it for systematic overestimation of force constants by the DFT methods. The scaling procedure was carried out using the program of Krasnoshchiokov et al. [17] and experimental frequencies from Refs. [7, 10]. The optimized scale factors are given in Table 2. Vibrational frequencies calculated from the scaled force field are listed in Table 3 together with experimental values. The average difference between experimental and calculated frequencies is  $5 \text{ cm}^{-1}$ . From the scaled force field and complete set of cubic force constants, the values of vibrational amplitudes, anharmonic corrections to the internuclear distances ( $r_e - r_a$ ), and anharmonic vibrational corrections to the rotational constants ( $B_e^{(i)} - B_0^{(i)}$ ) were calculated using the SHRINK program [15, 18].

## Calculation of equilibrium geometry from experimental rotational constants and theoretical rotation–vibration interaction constants

The equilibrium geometrical structure ( $r_e$ ) of a polyatomic molecule can be found if the equilibrium rotational constants  $B_e$  for a sufficient number of its isotopomers are known. This problem is complicated by the fact that the experimentally observed rotational constants  $B$  are effective and depend on the vibrational quantum number  $v$ . Usually observed constants are related to the ground vibrational state ( $v = 0$ ) and in this case they are designated as  $B_0$ . Using an approximate Hamiltonian, one can obtain the following expression for effective rotational constants  $B_v$  as a series

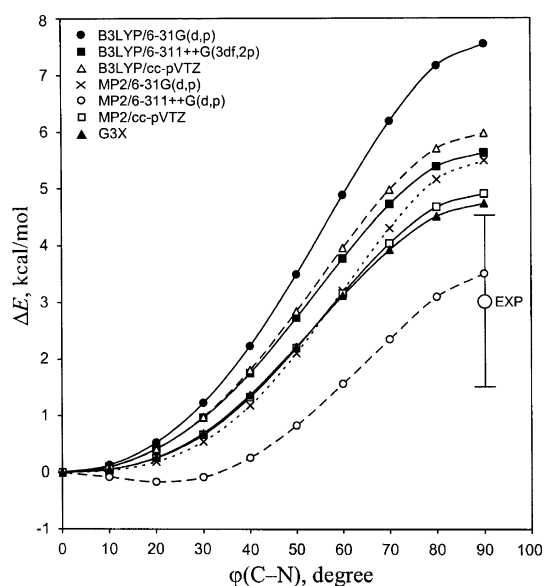
$$B_v = B_e - \sum_r \alpha_r^B \left( v_r + \frac{1}{2} \right) + \sum_{r \geq s} \gamma_{rs}^B \left( v_r + \frac{1}{2} \right) \left( v_s + \frac{1}{2} \right) + \dots \quad (1)$$

where  $r$  are the normal coordinates,  $\alpha_r^B$  and  $\gamma_{rs}^B$  are the vibration–rotation interaction constants, and the summation is carried out over all normal modes. Since quantities  $\gamma_{rs}^B$  are

**Table 1** Comparison of molecular parameters of nitrobenzene obtained from theoretical calculations and microwave study

Parameter <sup>a</sup>	MW <sup>b</sup>	Calculations <sup>c</sup>							
		B3LYP				MP2			
		/6-31G(d,p)	/6-31G(2df,p)	/6-311++ G(3df,2p)	/cc-pVTZ	/6-31G(d,p)	/6-311++G(d,p)	/cc-pVTZ	/aug-cc-pVTZ
C1–C2	1.3748(9)	1.394	1.390	1.388	1.388	1.392	1.395	1.388	1.389
C2–C3	1.4026(5)	1.393	1.390	1.388	1.388	1.394	1.398	1.392	1.392
C3–C4	1.3958(2)	1.397	1.394	1.392	1.391	1.397	1.401	1.394	1.394
C–N	1.4916(17)	1.473	1.473	1.477	1.478	1.472	1.476	1.472	1.470
N–O	1.2272(2)	1.231	1.224	1.221	1.222	1.242	1.232	1.228	1.230
C2–H	1.080(5)	1.083	1.081	1.079	1.079	1.080	1.084	1.079	1.080
C3–H	1.0829(2)	1.085	1.084	1.081	1.081	1.082	1.086	1.081	1.082
C4–H	1.0803(2)	1.086	1.085	1.082	1.082	1.082	1.086	1.081	1.082
C2–C1–C6	124.99(13)	122.4	122.3	122.3	122.2	122.8	122.8	122.6	122.7
C1–C2–C3	117.11(7)	118.5	118.5	118.5	118.6	118.1	118.1	118.3	118.2
C2–C3–C4	120.30(2)	120.2	120.2	120.2	120.2	120.5	120.5	120.4	120.4
C3–C4–C5	120.18(1)	120.4	120.4	120.3	120.3	120.0	120.0	120.0	120.1
C2–C1–N	117.51(7)	118.8	118.9	118.8	118.9	118.6	118.6	118.7	118.6
C–N–O	117.82(1)	117.7	117.6	117.7	117.7	117.6	117.4	117.4	117.5
O–N–O	124.35(1)	124.6	124.8	124.7	124.7	124.8	125.3	125.1	124.9
C1–C2–H	120.7(5)	119.4	119.3	119.6	119.5	119.8	120.0	119.6	119.7
C4–C3–H	120.05(1)	120.2	120.2	120.2	120.2	120.1	120.1	120.1	120.1
C3–C4–H	119.91(1)	119.8	119.8	119.9	119.8	120.0	120.0	120.0	120.0
$\varphi(\text{C–N})$	0	0	0	0	0	0	21.1	0	0
V	3.0(15)	7.5	4.7 <sup>d</sup>	5.6	6.0	5.5	3.5	4.9	4.8

<sup>a</sup> Bond lengths in Å, angles in degrees, barrier for internal rotation (V) in kcal/mol; uncertainties for experimental values are given in parentheses<sup>b</sup>  $r_s$  Structure from Ref. [2]<sup>c</sup> Equilibrium structure  $r_e$ <sup>d</sup> Value calculated at the G3X level



**Fig. 2** Potential functions for internal rotation around the C–N bond in nitrobenzene calculated at the different levels of theory. Large open circle with the uncertainty bars is the barrier hindering internal rotation obtained from microwave data (Ref. [1])

approximately two orders smaller than  $\alpha_r^B$ , the constants  $B_e$  for the ground vibrational state ( $v = 0$ ) could be written as

$$B_e = B_0 + \frac{1}{2} \sum_r \alpha_r^B \quad (2)$$

Thus, for determination of the equilibrium rotational constants one needs to know the constants of vibration–rotation interaction  $\alpha_r^B$  summed up over all normal modes  $r$ . Generally speaking, the complete sets of constants for small molecules can be found out from experimental data if the vibrational bands for all normal modes have the resolved rotational structure.

The vibration–rotation interaction constants  $\alpha_r^B$  may also be theoretically calculated by the use of second order perturbation theory [19–21]. In the case of asymmetrical tops  $\alpha_r^{(i)}$  ( $i = A, B, C$ ) the perturbation theory leads to a formula [21]:

$$\begin{aligned} \alpha_r^{(i)} = & -2 \frac{(B_e^{(i)})^2}{\omega_r} \left[ \frac{3}{4} \sum_j \left( \frac{\partial I^{(ij)}}{\partial Q_r} \right)^2 (I_{jj})^{-1} \right. \\ & + \sum_{s \neq r} (\zeta_{rs}^{(i)})^2 \frac{3\omega_r^2 + \omega_s^2}{\omega_r^2 - \omega_s^2} \\ & \left. + \pi \left( \frac{cu}{h} \right)^{\frac{1}{2}} \sum_s \varphi_{rrs} \frac{\partial I^{(ii)}}{\partial Q_s} \left( \frac{\omega_r}{\omega_s^{\frac{3}{2}}} \right) \right] \quad (3) \end{aligned}$$

where  $\omega_r$  is a harmonic frequency ( $\text{cm}^{-1}$ ),  $I^{(ii)}$  is the  $i$ -th principal inertia moment for the equilibrium geometry,

$\partial I^{(ij)} / \partial Q_r$  is a partial derivative from inertia tensor matrix element by normal coordinate  $Q_r$ ,  $\zeta_{rs}^{(i)}$  is the Coriolis interaction constant,  $u$  is the atomic mass unit, and  $\phi_{rrs}$  is the cubic force constant for the expansion of the potential by a series of the dimensionless normal coordinates [21].

Thus, although for many medium size molecules the sets of the vibrational constants  $B_0$  are known for several isotopomers that are sufficient for the exact determination of  $r_0$  structure, as a rule, it is impossible to determine experimentally all necessary constants of vibration–rotation interaction. Due to this reason a combined method had been developed (see for example Refs. [22, 23]), where the experimental sets  $B_0$  and the theoretical constants  $\alpha_r^B$  are used. This method was successful for a rather large number of molecules. Among the recently published works, for

**Table 2** Scale factors employed for harmonic B3LYP/cc-pVTZ force field of nitrobenzene<sup>a</sup>

No.	Scale factor	Internal coordinate
1	0.962	C1–C2 str., C1–C6 str.
2	0.953	C2–C3 str., C3–C4 str., C4–C5 str., C5–C6 str.
3	0.973	C–N str.
4	0.970	NO <sub>2</sub> s. str.
5	0.955	NO <sub>2</sub> as. str.
6	0.926	C4–H str.
7	0.928	C2–H str., C6–H str.
8	0.929	C3–H str., C5–H str.
9	0.981	C–N rock.
10	0.953	C2–H rock., C3–H rock., C4–H rock., C5–H rock., C6–H rock.
11	0.961	NO <sub>2</sub> def.
12	1.004	NO <sub>2</sub> rock.
13	0.963	Ring trigonal def.
14	0.958	CCC as. def.
15	0.947	CCC as. def.
16	0.969	Ring puck.
17	1.041	Ring as. tors.
18	0.979	Ring as. tors.
19	0.995	CN wag.
20	0.968	C4–H wag.
21	0.985	C2–H wag., C6–H wag.
22	0.956	C3–H wag., C5–H wag.
23	0.952	NO <sub>2</sub> wag.
24	0.910	C–N tors.

Notation (see Ref. [16] for the definition of internal coordinates): stretching (str.), deformation (def.), rocking (rock.), wagging (wag.), puckering (puck.), and torsion (tors.); symmetric (s.) and asymmetric (as.)

<sup>a</sup> Atom numbering as in Fig. 1



example, the Ref. [24] may be mentioned, where the equilibrium structure of 1,3-butadiene was determined.

When trying to use the specified combined method for such large molecules as nitrobenzene, a substantial difficulty is the fact that with the increase of the number of independent geometrical parameters the solution becomes ill-conditioned. In other words, a solution becomes strongly dependent on accidental errors in initial data. In a number of cases this problem can be successfully solved by using the additional information about a geometrical structure that is contained, for example, in the equilibrium quantum mechanical geometry. Direct minimization of Tikhonov's functional is a suitable numerical method for the implementation of this idea [25]:

$$F(r_e, \lambda) = \sum_i \sum_k w_k^i \left( I_k^{i(\text{obs})} - I_k^{i(\text{calc})}(r_e) \right)^2 + \lambda \sum_j \left( (g_j^{(0)} - g_j(r_e)) / g_j^{(0)} \right)^2 = \min, \quad (4)$$

where  $k$  is the isotopomer index,  $\lambda$  is a scalar parameter, called regularization parameter,  $g_j^{(0)}$  and  $g_j(r_e)$  is the initial approximation for geometrical parameters and their current value, respectively. If a problem is ill-conditioned or has an infinite number of solutions, an addition of the second item in Eq. 4 means that among the all variety of solutions those are being found which minimize the functional (4) under condition of their proximity to a set ( $g^{(0)}$ ). A detailed description of this method is given in Ref. [9].

Experimental rotational constants  $B_0$  for nine nitrobenzene isotopomers  $k$  were taken from MW study [2]. Theoretical equilibrium geometry and the vibration–rotation interaction constants were calculated at the B3LYP/cc-pVTZ level of theory. The choice of this method was caused by the fact that the expected quality of theoretical geometry and harmonic force field in such a case better agrees with the experimental. Calculations, carried out for simpler molecules [9], showed that the constants  $\alpha_r^B$  change insignificantly with isotopic substitution. Since in doing so the absolute value of the constants  $\alpha_r^B$  for the basic nitrobenzene isotopomer were not large (approximately one order smaller in comparison with other molecules), and because of the complexity of the constants calculations for each isotopomer separately, an approximation was used in which equal values  $\frac{1}{2} \sum \alpha_r^B$  were accepted for all isotopomers. A criteria of the correctness of such a procedure is the degree of consistency between the experimental rotational constants, reduced to an equilibrium structure, and the calculated values of  $B_e$  that were obtained with an optimized geometry. The result of the rotational constants calculation is presented in Table 4. The calculated

**Table 3** Experimental and calculated fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of nitrobenzene

Mode	Symmetry	Experiment <sup>a</sup>	Calculation	
			Unscaled <sup>b</sup>	Scaled <sup>c</sup>
1	$A_1$	3107	3227	3104
2		3082	3197	3076
3		3049	3175	3055
4		1588	1632	1594
5		1479	1517	1482
6		1356 <sup>d</sup>	1376	1356
7		1174	1198	1170
8		1108	1119	1098
9		1021	1046	1022
10		1004	1025	1003
11	$A_2$	852	869	853
12		676	698	685
13		392	396	389
14		990	1005	990
15		840	863	848
16		417	421	416
17		51	54	51
18	$B_1$	1004	1025	1009
19		975	972	965
20		793	819	805
21		701 <sup>d</sup>	726	711
22		681	698	687
23		436	449	450
24		182	170	170
25	$B_2$	3107	3226	3104
26		3076	3188	3067
27		1620	1656	1621
28		1549 <sup>d</sup>	1591	1555
29		1455	1494	1459
30		1316	1353	1323
31		1308	1343	1312
32		1162	1187	1159
33		1070	1102	1076
34		611	629	613
35		532	526	524
36		255	258	255

<sup>a</sup> From the liquid IR and Raman spectra [7] (except where marked; see d)

<sup>b</sup> Calculated at the B3LYP/cc-pVTZ level

<sup>c</sup> Calculated using the theoretical force field after scaling (see text and Table 2)

<sup>d</sup> From the gaseous FT-IR spectrum [10]

geometrical parameters are given in Table 5 together with parameters obtained from previous interpretation of MW data [2].

**Electron diffraction structural analysis****Experimental data**

The experimental intensity data of nitrobenzene recorded earlier at the Budapest laboratory and analyzed in previous GED study [4] were used in this work. The nozzle temperature was about 353 K. Nozzle to plate distances of about 50 and 19 cm were used. The final molecular

intensities (the experimental ones corresponding to revised background lines) and radial distributions are shown in Figs. 3 and 4, respectively.

**Static model**

The analysis of GED data was carried out by applying the least squares method to the molecular intensities using UNEX program [26]. In this program the molecular

**Table 4** Experimental, corrected, and calculated rotational constants (MHz) for nine nitrobenzene isotopomers

	Experiment, $B_0$	Corrected, $B_e^{\text{exp a}}$	Calculated, $B_e^{\text{calc b}}$	Error <sup>c</sup>
Nitrobenzene				
A	3968.0780	3995.6019	3995.9618	−0.3599
B	1286.9203	1296.9334	1297.1252	−0.1918
C	972.6605	979.2050	979.2514	−0.0464
Nitrobenzene- <sup>18</sup> O				
A	3899.4900	3927.0139	3926.7529	0.2610
B	1255.5697	1265.5828	1265.5376	0.0452
C	950.6344	957.1789	957.0831	0.0958
Nitrobenzene- <sup>15</sup> N				
A	3968.2030	3995.7269	3995.9618	−0.2349
B	1278.1820	1288.1951	1288.2089	−0.0138
C	967.6692	974.2137	974.1611	0.0526
Nitrobenzene-2-D				
A	3830.7900	3858.3139	3858.0909	0.2230
B	1286.9856	1296.9987	1297.1032	−0.1045
C	964.2345	970.7790	970.7378	0.0412
Nitrobenzene-3-D				
A	3832.6320	3860.1559	3860.0750	0.0809
B	1267.6672	1277.6803	1277.6430	0.0373
C	953.4692	960.0137	959.9199	0.0938
Nitrobenzene-4-D				
A	3967.9970	3995.5209	3995.9618	−0.4409
B	1244.5958	1254.6089	1254.5372	0.0717
C	948.2951	954.8396	954.7821	0.0575
Nitrobenzene-2- <sup>13</sup> C				
A	3922.5400	3950.0639	3950.0278	0.0361
B	1286.1686	1296.1817	1296.3301	−0.1484
C	969.4745	976.0190	976.0180	0.0010
Nitrobenzene-3- <sup>13</sup> C				
A	3923.7900	3951.3139	3951.0178	0.2961
B	1275.4149	1285.4280	1285.4767	−0.0487
C	963.4234	969.9679	969.9125	0.0554
Nitrobenzene-4- <sup>13</sup> C				
A	3968.1800	3995.7039	3995.9618	−0.2579
B	1265.6106	1275.6237	1275.6521	−0.0284
C	960.4448	966.9893	966.9633	0.0260

<sup>a</sup> Calculated in accordance with Eq. 2

<sup>b</sup> Calculated in accordance with Eq. 4

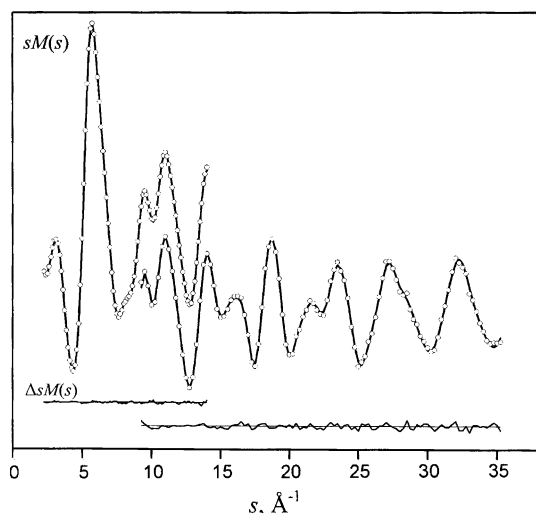
<sup>c</sup>  $B_e^{\text{exp}} - B_e^{\text{calc}}$



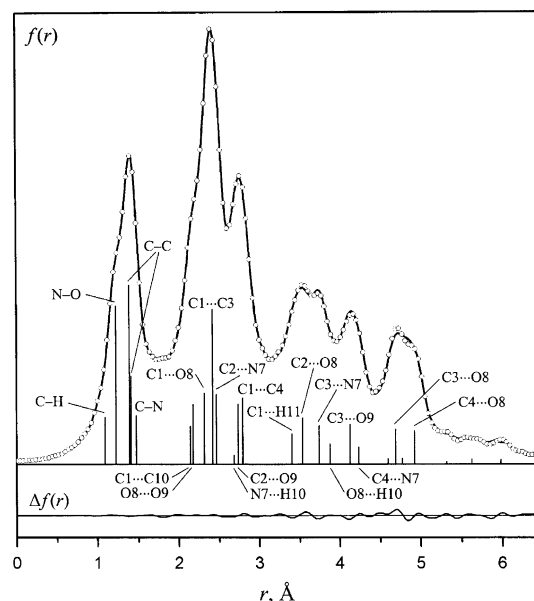
**Table 5** Comparison of nitrobenzene structural parameters determined from MW data

Parameter <sup>a</sup>	MW [1, 2]	Reanalysis of MW data [1, 2], this work
	$r_s$ ( $\angle_s$ )	$r_e$ ( $\angle_e$ )
C1–C2	1.3748(9)	1.3896(46)
C2–C3	1.4026(5)	1.3897(71)
C3–C4	1.3958(2)	1.3926
C–N	1.4916(17)	1.4733(65)
N–O	1.2272(2)	1.2189(42)
C2–H	1.080(5)	1.0750(65)
C3–H	1.0829(2)	1.0718(58)
C4–H	1.0803(2)	1.0738(64)
C2–C1–C6	124.99(13)	122.54
C1–C2–C3	117.11(7)	118.49(35)
C2–C3–C4	120.30(2)	119.88
C3–C4–C5	120.18(1)	120.72
C2–C1–N	117.51(7)	118.73(25)
C1–N–O	117.82(1)	117.35(31)
O–N–O	124.35(1)	125.30
C1–C2–H	120.7(5)	119.29(45)
C4–C3–H	120.05(1)	120.06(41)
C3–C4–H	119.91(1)	119.64
$\phi(\text{C–N})$	0	0

<sup>a</sup> Bond lengths in Å, angles in degrees

**Fig. 3** Experimental (open circles) and theoretical (solid line) molecular intensities for nitrobenzene. The difference curves are experimental minus theoretical for the GED static model shown in Table 9

geometry is specified in a format of Z-matrix. We found it convenient to choose the non-bonded interatomic distance C1...C4 as one of the independent parameters together with bond lengths and angles (Table 6). The C–H bonds and C–C–H angles were described by only one variable each (C2–H10 and  $\angle\text{C1–C2–H10}$ , respectively). The differences between their respective values were constrained at the values obtained from theoretical calculation.

**Fig. 4** Experimental (open circles) and theoretical (solid line) radial distribution curves of nitrobenzene with difference curve for the GED static model. Distances distribution is indicated by vertical bars

The vibrational amplitudes were refined in 10 groups. The groups were selected according to the magnitude of the interatomic distances. The first three groups contain the amplitudes of the bonded atom pairs from the first peak of the radial distribution curve. The amplitudes in the remaining groups belong to the non-bonded atom pairs

**Table 6** Independent geometrical parameters used in structural analysis of nitrobenzene

No.	Parameter	$r_a(\angle_{hl})^a$
1	C1...C4	2.761 (9)
2	C1–C2	1.387 (4)
3	C3–C4	1.394 (4)
4	C1–N7	1.478 (6)
5	N7–O8	1.228 (2)
6	C2–H10	1.096 (6)
7	$\alpha = \frac{1}{2}\angle C2-C1-C6$	61.6 (3)
8	$\beta = \frac{1}{2}\angle C3-C4-C5$	60.3 (3)
9	$\angle C1-N7-O8$	117.7 (2)
10	$\angle C1-C2-H10$	122.3 (22)
11	$\varphi = \angle C2-C1-N7-O9$	1.0 (2)

<sup>a</sup> Distances ( $r_a$ ) are in Å and angles ( $\angle_{hl}$ ) in degrees. Parameters of final refinement of GED static model are given; values in parentheses are three times the standard deviations

from the second to the sixth peak of the radial distribution curve. In all GED static models the initial values of vibrational amplitudes were taken from B3LYP/cc-pVTZ calculations.

Two starting models for geometrical parameters, the B3LYP/cc-pVTZ with  $\phi(C-N) = 0^\circ$  and MP2/6-311++G(d,p) with  $\phi(C-N) = 21.1^\circ$ , were used in the GED analysis. Three types of refinements were performed for each model: without vibrational corrections, with harmonic vibrational corrections ( $r_{hl} - r_a$ ), and with anharmonic vibrational corrections ( $r_e - r_a$ ). In the final refinement 10 geometrical parameters (Table 6) and 10 amplitudes of vibration (Table 7) were refined simultaneously. The correlation matrix for the refined parameters is presented in Table 8. As one might expect, there is strong correlation between the C1–C2 and C3–C4 bond lengths. Nevertheless, these parameters were varied independently in the preliminary refinements. We tried to keep the constraints in our GED

models to a feasible minimum. In the final refinement (Table 9) these bonds were refined together in a group. In the combined analysis of GED data and rotational constants (see below), the difference between C1–C2 and C3–C4 bond lengths was constrained at the computed value. The results of the refinement *without* vibrational corrections are given in Table 9 (static model,  $r_g$  and  $\angle_a$ ). There are some differences as compared with the results of the previous GED study [4]. The torsional angle  $\phi(C-N)$  is slightly larger than that from previous study, whereas the C–N bond length is somewhat smaller. The origin of the differences may be in the revised background lines, the differences in the vibrational amplitudes, and in the choice of the constraints used in the present study as compared with those of Ref. [4].

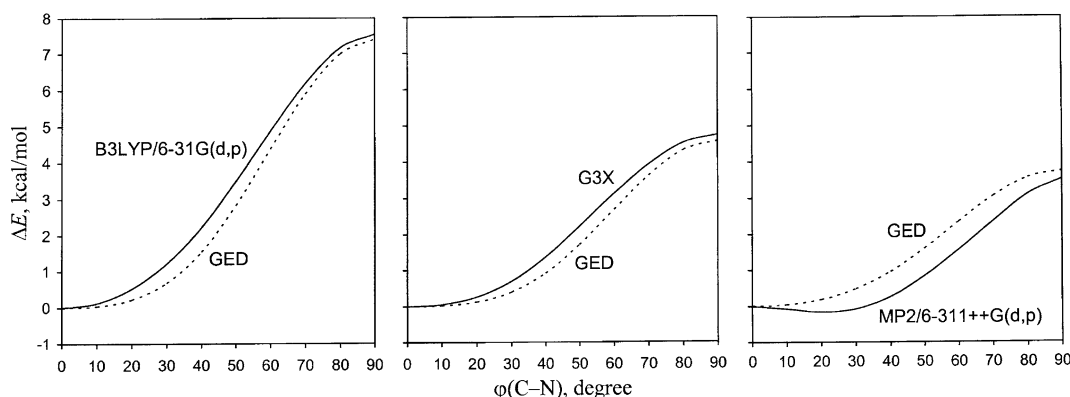
Essentially planar structure of nitrobenzene was obtained in all refinements where vibrational corrections, both harmonic and anharmonic, were used in the GED analysis. The results obtained for the refinement *with* harmonic corrections are given in Table 9 (static model,  $r_g$  and  $\angle_{hl}$ ). Thus, it may be concluded that even harmonic vibrational corrections, calculated from quadratic force constants, lead to a planar conformation of nitrobenzene.

#### Dynamic model

To investigate a large-amplitude motion in nitrobenzene, a dynamic model was tested in the present GED study. The GED data were refined by fitting a torsional potential:

$$V(\varphi) = \frac{1}{2}V_2(1 - \cos 2\varphi) + \frac{1}{2}V_4(1 - \cos 4\varphi) \quad (5)$$

to the experimental data. The internal rotation was modeled by 10 pseudo-conformers with dihedral angle  $\phi(C-N)$  ranging from  $0^\circ$  to  $90^\circ$  at  $10^\circ$  intervals. The statistical weight of each pseudo-conformer was determined on the



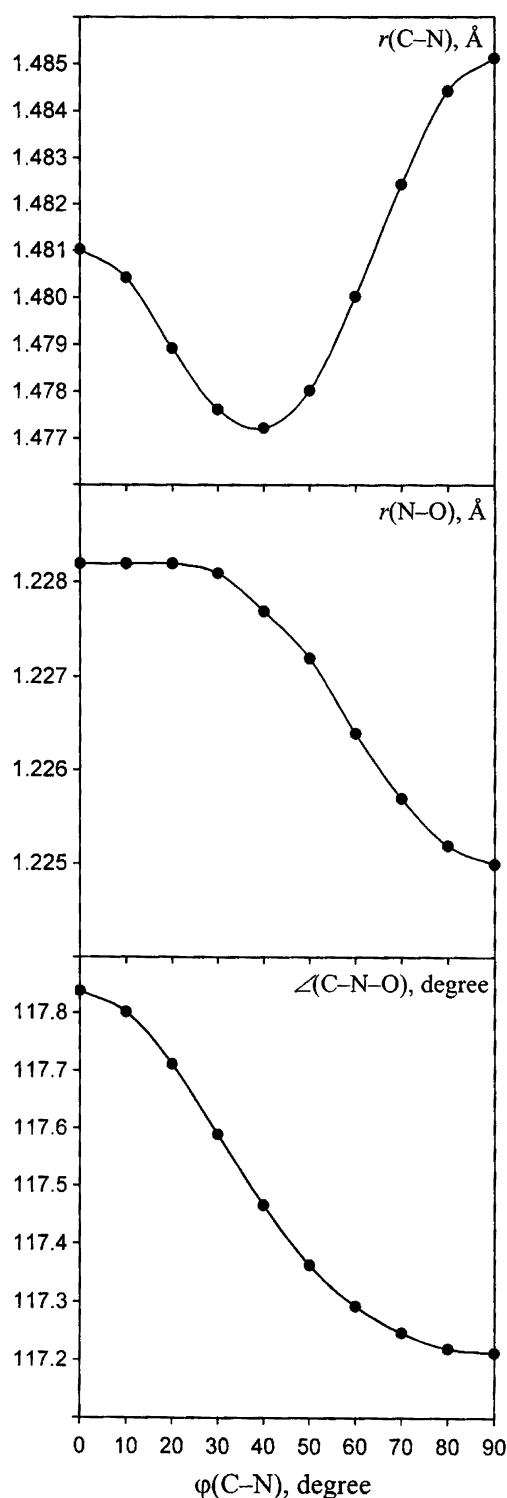
**Fig. 5** Comparison between potential functions for internal rotation of nitrobenzene calculated at three different levels of theory with those obtained from GED dynamic models where the corresponding theoretical functions were used as the initial potential

basis of their symmetry: the statistical weights of 1 and 2 were used for the  $C_{2v}$  ( $\phi = 0^\circ$  and  $\phi = 90^\circ$ ) and  $C_2$  ( $\phi = 10\text{--}80^\circ$ ) forms, respectively. The pseudo-conformers were treated as distinct molecules undergoing the usual framework vibrations, except for torsional motion about the C–N bond. The initial values of structural parameters and vibrational amplitudes for each pseudo-conformer were obtained from B3LYP/6-31G(2df,p) calculations. This level of theory is used in the G3X method for geometry optimization. The vibrational amplitudes were calculated by including the contributions from all normal modes except the torsion about the C–N bond. The differences of bond distances, bond angles, and vibrational amplitudes between the planar conformer with  $\phi(\text{C–N}) = 0^\circ$  and other pseudo-conformers were taken from theoretical calculations. The molecular parameters of the planar conformer were refined in structural analysis, but the values of other pseudo-conformers were deduced by adding the differences to the refined values of the planar conformer.

Three theoretical potential functions, B3LYP/6-31G(d,p), MP2/6-311++G(d,p), and G3X, were used to obtain the initial values of potential coefficients in Eq. 5. As can be seen from Fig. 2, among theoretical potentials calculated in this work, these three have the highest, the lowest, and the medium-high value of torsional barrier, respectively. The results obtained from the refinements of three potential functions are shown in Fig. 5. As is seen, the derived GED potentials depend on the initial potential. The most appreciable discrepancy between the starting and final potential is observed for the MP2 model: the GED potential function is not so much flat as the MP2 indicates and does not have a shallow minimum in the region of the torsional angle of about  $20^\circ$ . Therefore, the dynamic GED model does not support the twisted equilibrium structure of nitrobenzene.

Table 9 shows the result of dynamic model refinement, where the G3X potential was used as an initial approximation. This model was preferred by analyzing the tendency in the GED potentials depending on the initial model. As is seen from Fig. 5, the most plausible GED potential lies in the range between the G3X and MP2 potentials. In the final refinement eight independent geometrical parameters (the differences between C–C bond lengths were constrained at the theoretical values), 10 vibrational amplitudes, and two potential energy coefficients were refined simultaneously. The results of the group refinement of amplitudes are given in Table 7.

The change in geometric parameters of nitro group during internal rotation is shown in Fig. 6. The most substantial change is found for the C–N bond length, whose value at first decreases by  $0.003 \text{ \AA}$  and starting with  $\phi(\text{C–N}) = 40^\circ$  increases by  $0.007 \text{ \AA}$ . The value of the N–O bond



**Fig. 6** Change in geometrical parameters of C–NO<sub>2</sub> group during internal rotation according to calculations at the B3LYP/6-31G(2df,p) level of theory

length does not change up to  $\phi(\text{C–N}) = 30^\circ$ , then slightly decreases. The C–N–O angle decreases continuously with increasing torsional angle. The changes in geometrical

**Table 7** Interatomic distances ( $r_a$ ), experimental and calculated vibrational amplitudes at 353 K ( $l$ )<sup>a</sup>

	$r_a$ , Å	$l_{\text{calc}}$ , Å		$l_{\text{exp}}$ , Å	
		B3LYP /cc-pVTZ <sup>b</sup>	B3LYP /6-31G(2df,p) <sup>c</sup>	Static model	Dynamic model
C2–H10	1.089	0.076	0.075	0.076(7) <sup>1</sup>	0.079(8) <sup>1</sup>
C4–H12	1.092	0.077	0.075	0.076 <sup>1</sup>	0.079 <sup>1</sup>
C3–H11	1.092	0.077	0.075	0.076 <sup>1</sup>	0.079 <sup>1</sup>
N7–O8	1.229	0.040	0.039	0.040(1) <sup>2</sup>	0.040(2) <sup>2</sup>
C1–C2	1.388	0.046	0.045	0.046(2) <sup>3</sup>	0.046(2) <sup>3</sup>
C2–C3	1.397	0.046	0.045	0.046 <sup>3</sup>	0.046 <sup>3</sup>
C3–C4	1.406	0.046	0.046	0.046 <sup>3</sup>	0.046 <sup>3</sup>
C1–N7	1.476	0.053	0.051	0.053 <sup>3</sup>	0.052 <sup>3</sup>
C2...H11	2.147	0.099	0.098	0.103(9) <sup>4</sup>	0.098(9) <sup>4</sup>
C1...H10	2.150	0.100	0.098	0.103 <sup>4</sup>	0.098 <sup>4</sup>
C3...H10	2.160	0.099	0.098	0.103 <sup>4</sup>	0.098 <sup>4</sup>
C3...H12	2.160	0.099	0.098	0.103 <sup>4</sup>	0.098 <sup>4</sup>
O8...O9	2.174	0.049	0.048	0.047(4) <sup>5</sup>	0.046(3) <sup>5</sup>
C4...H11	2.175	0.099	0.098	0.103 <sup>5</sup>	0.098 <sup>5</sup>
C1...O8	2.317	0.059	0.058	0.057 <sup>5</sup>	0.056 <sup>5</sup>
C1...C3	2.395	0.056	0.055	0.054 <sup>5</sup>	0.053 <sup>5</sup>
C2...C4	2.420	0.056	0.055	0.054 <sup>5</sup>	0.053 <sup>5</sup>
C2...C6	2.434	0.056	0.055	0.053 <sup>5</sup>	0.053 <sup>5</sup>
C3...C5	2.440	0.056	0.055	0.053 <sup>5</sup>	0.053 <sup>5</sup>
O8...H14	2.455	0.170	0.161	0.166 <sup>5</sup>	0.159 <sup>5</sup>
C2...N7	2.462	0.063	0.062	0.061 <sup>5</sup>	0.060 <sup>5</sup>
N7...H10	2.666	0.137	0.136	0.133(4) <sup>6</sup>	0.131(5) <sup>6</sup>
C2...O9	2.740	0.091	0.086	0.088 <sup>6</sup>	0.081 <sup>6</sup>
C1...C4	2.756	0.062	0.062	0.059 <sup>6</sup>	0.057 <sup>6</sup>
C2...C5	2.807	0.063	0.063	0.060 <sup>6</sup>	0.058 <sup>6</sup>
C1...H11	3.375	0.096	0.094	0.114(18) <sup>7</sup>	0.116(19) <sup>7</sup>
C2...H12	3.400	0.096	0.094	0.114 <sup>7</sup>	0.116 <sup>7</sup>
C4...H10	3.405	0.095	0.094	0.114 <sup>7</sup>	0.116 <sup>7</sup>
C2...H14	3.406	0.096	0.095	0.114 <sup>7</sup>	0.116 <sup>7</sup>
C3...H13	3.427	0.096	0.095	0.114 <sup>7</sup>	0.116 <sup>7</sup>
C2...O8	3.535	0.066	0.062	0.076(7) <sup>8</sup>	0.067(8) <sup>8</sup>
C3...N7	3.737	0.065	0.064	0.076 <sup>8</sup>	0.069 <sup>8</sup>
C1...H12	3.839	0.095	0.094	0.105 <sup>8</sup>	0.099 <sup>8</sup>
O8...H10	3.849	0.139	0.134	0.148 <sup>8</sup>	0.139 <sup>8</sup>
C3...H14	3.887	0.095	0.094	0.105 <sup>8</sup>	0.099 <sup>8</sup>
C2...H13	3.890	0.096	0.094	0.106 <sup>8</sup>	0.099 <sup>8</sup>
C3...O9	4.122	0.094	0.089	0.089(9) <sup>9</sup>	0.086(10) <sup>9</sup>
C4...N7	4.227	0.068	0.067	0.064 <sup>9</sup>	0.064 <sup>9</sup>
N7...H11	4.599	0.110	0.108	0.107(7) <sup>10</sup>	0.109(10) <sup>10</sup>
C3...O8	4.687	0.072	0.067	0.070 <sup>10</sup>	0.069 <sup>10</sup>
O8...H13	4.779	0.144	0.138	0.141 <sup>10</sup>	0.140 <sup>10</sup>
C4...O8	4.916	0.085	0.080	0.082 <sup>10</sup>	0.082 <sup>10</sup>
N7...H12	5.308	0.099	0.097	0.097 <sup>10</sup>	0.099 <sup>10</sup>
O8...H11	5.628	0.109	0.104	0.107 <sup>10</sup>	0.105 <sup>10</sup>
O8...H12	5.974	0.115	0.110	0.112 <sup>10</sup>	0.111 <sup>10</sup>

Equal superscripts indicate that these amplitudes were refined as a group

<sup>a</sup> Values in parentheses are three times the standard deviations

<sup>b</sup> Theoretical amplitudes calculated from B3LYP/cc-pVTZ force field were used in the refinement of static GED models

<sup>c</sup> Theoretical amplitudes calculated from B3LYP/6-31G(2df,p) force field were calculated excluding the low-frequency torsion mode and were used as initial values in the refinement of dynamic model; the corresponding amplitudes were calculated for all pseudo-conformers

**Table 8** Correlation matrix ( $\times 100$ ) for refined parameters of GED static model

Parameter <sup>a</sup>	$\sigma_{LS}^b$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
1 $k_1$	0.003	100																					
2 $k_2$	0.008	46	100																				
3 C1...C4	0.003	4	0	100																			
4 C1–C2	0.004	–17	–10	–16	100																		
5 C3–C4	0.007	22	12	12	–87	100																	
6 C1–N7	0.002	26	29	–28	–43	42	100																
7 N7–O8	0.000	–32	–7	–26	–12	9	22	100															
8 C2–H10	0.002	–59	–31	–7	5	–15	–14	26	100														
9 $\alpha$	0.068	–34	–35	–3	–1	–6	–55	21	41	100													
10 $\beta$	0.761	16	5	–14	4	–25	11	7	1	–10	100												
11 C1–N7–O8	0.133	21	10	44	–50	72	–2	–21	–23	–12	–36	100											
12 C1–C2–H10	0.107	7	6	79	–5	8	4	–10	–13	–14	–11	10	100										
13 $l(1)$	0.002	6	0	10	1	0	–2	–47	0	–8	–5	4	5	100									
14 $l(2)$	0.000	8	31	5	0	–2	–6	–19	17	2	–1	–3	2	46	100								
15 $l(3)$	0.001	43	49	19	–17	49	–8	–31	–38	–10	–31	65	11	12	18	100							
16 $l(4)$	0.003	–2	–6	20	19	–13	–53	–42	–4	13	–24	17	–1	13	8	26	100						
17 $l(5)$	0.001	24	31	6	–89	81	36	15	–6	6	–11	52	–9	–5	8	32	–9	100					
18 $l(6)$	0.001	29	43	43	–7	9	8	–15	–27	–30	15	35	34	1	5	30	–9	13	100				
19 $l(7)$	0.006	12	0	14	–68	51	9	–5	2	9	5	29	–6	6	7	6	3	58	–5	100			
20 $l(8)$	0.002	5	10	8	–21	16	7	–2	6	1	–8	11	1	3	7	5	0	21	4	32	100		
21 $l(9)$	0.003	–10	–5	–38	29	–30	–26	8	13	27	4	–29	–39	–5	4	–11	9	–19	–27	–4	3	100	
22 $l(10)$	0.002	8	12	–8	0	5	3	–3	–6	–5	–12	6	–8	1	4	12	3	5	–1	–1	1	–7	100

<sup>a</sup> The values of scale factors ( $k_1$  and  $k_2$ ) for two intensity curves are 0.9453 and 0.7920, respectively; see Table 7 and 9 for amplitude groups,  $l(1)$ – $l(10)$ , and geometrical parameters, respectively

<sup>b</sup> Standard deviations from least squares refinements. Distances and amplitudes in Å, angles in degrees

parameters as a whole are moderate, and do not exceed 0.01 Å for  $r(\text{C–N})$ , 0.003 Å for  $r(\text{N–O})$ , and 0.6° for  $\angle\text{C–N–O}$ .

#### Combined analysis of GED data and rotational constants

The structural analysis based on the GED data alone (Table 9), shows that the static model is well suited for description of the equilibrium structure of nitrobenzene. Due to this, the static model was used in the joint analysis of GED and MW data. The rotational constants  $A_0$ ,  $B_0$ , and  $C_0$  determined by MW spectroscopy [1] were corrected to  $A_e$ ,  $B_e$ , and  $C_e$  values using corrections ( $B_e^{(i)} - B_0^{(i)}$ ) calculated from the B3LYP/cc-pVTZ quadratic and cubic force constants as described above. The values of corrections and corrected experimental rotational constants are given in Table 10 together with the rotational constants calculated from the  $r_e$  structure by combined analysis of GED and MW data. The corrections to internuclear distances ( $r_e - r_a$ ) were calculated at the same level of theory. Refinements were done by the method of least squares adjusting the theoretical intensity data and rotational constants to

experimental ones by varying simultaneously nine independent geometrical parameters, eight vibrational amplitude groups, and two scale factors. According to results from static and dynamic models, the value of  $\varphi(\text{C–N})$  was fixed at zero value. The C1–C2 bond was used as an independent parameter, and  $r(\text{C3–C4})$  was constrained by assuming the difference between them at the B3LYP/cc-pVTZ value. The C...H amplitudes from groups (1) and (7) were also kept at their computed values; when they were not constrained, unreasonable values were obtained for  $\angle\text{C–C–H}$ .

The  $r_e$  geometrical parameters resulting from the joint refinement of the GED and MW data are given in Table 9 together with previous GED results. Table 10 compares the experimental rotational constants with those obtained from the combined analysis of GED and MW data. The weights of the rotational constants relative to the GED intensities were empirically adjusted so that to obey a balance between sufficiently accurate reproducing rotational constants and reliability of GED structural analysis. As is seen from Table 10, the rotational constants calculated from the joint analysis of GED and MW data are very close to the corrected experimental ones.

**Table 9** Molecular structure of nitrobenzene obtained by gas-phase electron diffraction studies

Parameter <sup>a</sup>	Ref. [3]	Ref. [4]	This work			
			Static model		Dynamic model <sup>b</sup>	GED + MW static model
			Structure			
			$r_a$	$r_{h1}$		$r_e$
			$r_g(\angle_a)$	$r_g(\angle_{h1})$	$r_g(\angle_{h1})$	$r_e(\angle_e)$
C–C <sub>av</sub>	1.391(2)	1.399(3)	1.399(7)	1.399(7)	1.399(4)	1.391(3)
C1–C2			1.387(3) <sup>c</sup>	1.389(4) <sup>c</sup>	1.394(4) <sup>d</sup>	1.385(3) <sup>c</sup>
C2–C3			1.415(15)	1.414(13)	1.406(4)	1.401(11)
C3–C4			1.393(3) <sup>c</sup>	1.395(4) <sup>c</sup>	1.398(4) <sup>d</sup>	1.389(11) <sup>c</sup>
C–N	1.478(13)	1.486(4)	1.474(6)	1.479(6)	1.483(6)	1.468(5)
N–O	1.218(4)	1.223(3)	1.228(2)	1.229(2)	1.229(2)	1.223(2)
C2–H	1.114(12)	1.093(4)	1.097(6) <sup>e</sup>	1.101(6) <sup>e</sup>	1.104(6) <sup>e</sup>	1.069(5) <sup>e</sup>
C3–H			1.099(6) <sup>e</sup>	1.103(6) <sup>e</sup>	1.107(6) <sup>e</sup>	1.072(5) <sup>e</sup>
C4–H			1.099(6) <sup>e</sup>	1.103(6) <sup>e</sup>	1.108(6) <sup>e</sup>	1.073(5) <sup>e</sup>
C2–C1–C6	125.1(14)	123.4(3)	123.5(6)	123.1(6)	123.1(7)	123.5(6)
C1–C2–C3	115.7(11)	117.7(3)	117.8(5)	118.0(5)	118.0(5)	117.8(5)
C2–C3–C4	122.5	120.5(2)	120.2(6)	120.1(5)	120.1(4)	120.3(5)
C3–C4–C5	118.3	120.2(4)	120.6(7)	120.6(7)	120.1(4)	120.5(6)
C2–C1–N			118.2(3)	118.4(3)	118.5(4)	118.2(3)
C1–N–O	118.3(8)	117.3(1)	117.8(2)	117.7(2)	117.8(2)	117.9(2)
O–N–O	123.4(16)	125.3(2)	124.4(4)	124.7(4)	124.3(4)	124.2(4)
C1–C2–H			122.7(26) <sup>e</sup>	122.3(24) <sup>e</sup>	121.2(26) <sup>e</sup>	120.7(20) <sup>e</sup>
C4–C3–H			122.8(26) <sup>e</sup>	122.4(24) <sup>e</sup>	122.0(26) <sup>e</sup>	121.3(20) <sup>e</sup>
C3–C4–H			119.7(4) <sup>e</sup>	119.7(3) <sup>e</sup>	119.6(3) <sup>e</sup>	119.7(3) <sup>e</sup>
$\varphi(\text{C–N})$	22.7(41)	13.3(14)	17.7(30)	1.0(2)	0	0
$V_2$					4.6(2)	
$V_4$					–1.0(3)	
$R_L$		1.6	1.2	1.1	1.3	1.3
$R_S$		6.7	6.2	6.1	6.6	6.4
$R_{\text{tot}}$	8.2	2.9	2.5	2.5	2.7	2.6

<sup>a</sup> Bond lengths in Å, angles in degrees, potential coefficients ( $V_2$ ,  $V_4$ ) in kcal/mol; values in parentheses are three times the standard deviations; together with total value of agreement factor ( $R_{\text{tot}}$ ), the  $R$ -factors are given for long ( $R_L$ ) and short ( $R_S$ ) camera distance

<sup>b</sup> The G3X potential was used as starting

<sup>c</sup> The C1–C2 and C3–C4 bond lengths were refined in the group together with each other, whereas the C1...C4 distance was refined independently (see Table 6 for adjustable parameters)

<sup>d</sup> Three independent parameters, C1–C2, C3–C4, and C1...C4 (Table 6) were refined in the group

<sup>e</sup> All C–H bond lengths and C–C–H angles were refined in appropriate groups

## Results and discussion

The average molecular structure ( $r_a$ ) of nitrobenzene obtained in this work is in general agreement with that determined in previous study [4]. Some differences concerning  $r_g(\text{C–N})$  and  $\varphi_a(\text{C–N})$  and their possible origins have already been pointed out. The torsional angle is especially difficult to determine with high accuracy from GED data alone. Besides, some constraints used in the structural analysis in Ref. [4] were removed in the present re-investigation, such as the equality of  $r(\text{C2–C3})$  and

$r(\text{C3–C4})$ ; that of the five C–H bond lengths, and that the C–H bonds bisect the C–C–C angles.

In distinction to previous GED studies [3, 4], nonlinear kinematic and harmonic or anharmonic vibrational effects were taken into account in this work ( $r_{h1}$  or  $r_e$  structure, respectively). Both structures show planar conformation for nitrobenzene. The parameters of  $r_{h1}$  structures for static and dynamic GED models are given in Table 9. As is seen, the structural parameters are very close to each other.

The dynamic model allows the estimation of the torsional barrier for this molecule. Although the uncertainty of



**Table 10** Comparison between experimental rotational constants (MW) and those calculated from joint analysis of GED and MW data

	MW			GED + MW		Differences <sup>a</sup>
	$B_0^{(i)}$ (exp) <sup>b</sup>	$(B_e^{(i)} - B_0^{(i)})^c$	$B_e^{(i)}$ (exp)	$B_e^{(i)}$ (calc)	$B_0^{(i)}$ (calc)	
A, MHz	3968.078 ± 0.009	28.0127	3996.0907	3996.1349	3968.1222	−0.0442
B	1286.9204 ± 0.0006	9.6176	1296.5380	1296.5875	1286.9699	−0.0495
C	972.6605 ± 0.0005	6.3349	978.9954	978.9553	972.6204	0.0401

<sup>a</sup> Refer to the difference between  $B^{(i)}$ (exp) and  $B^{(i)}$ (calc)<sup>b</sup> Ref. [1]<sup>c</sup> Anharmonic corrections calculated from B3LYP/cc-pVTZ quadratic and cubic force fields

$V_2$  and  $V_4$  coefficients determined by least squares method is rather small (Table 9), the derived value of barrier height to orthogonal conformation, as is seen from Fig. 5, depends strongly on the initial approximation for potential function. The B3LYP/6-31G(d,p) and G3X potentials, probably, have too high barriers, and their refinement results in slightly decreased barriers compared to the starting values. In contrast, the refinement of low MP2 barrier leads to increased barrier value. The potential coefficients are difficult to determine from GED. Nevertheless, the fitted values of G3X and MP2 torsional barriers converge, and their average value,  $4.1 \pm 1.0$  kcal/mol, lends justification to the estimation of the barrier to rotation from the GED data. This result is exactly the same (both for its magnitude and its estimated error) as obtained using the static model in Ref. 4 and is also in good agreement with the experimental MW value ( $3.0 \pm 1.5$  kcal/mol) [1] and the result of theoretical G3X method (4.7 kcal/mol), which gives reasonable predictions of energies. Furthermore, the present results are in excellent agreement with the value of 4.5 kcal/mol determined from the dynamic model by Monte Carlo optimization [5].

The joint analysis of GED and MW data yielded good agreement with the results of structural analysis of GED alone (Table 9). The equilibrium  $r_e$  geometry of nitrobenzene agrees well with the geometries calculated by high-level quantum chemical methods (Table 1). The agreement between the experimental rotational constants and those calculated from the combined analysis of GED and MW data is within 0.05 MHz or 0.004% (Table 10). This result shows that anharmonic corrections lead to substantially better reproduction of experimental rotational constants than harmonic corrections.

The  $r_e(\text{C}–\text{N})$  value obtained in this work ( $1.468 \pm 0.005$  Å) agrees reasonably well with the results of theoretical calculations (1.472–1.478 Å, Table 1) and with the value from the reanalysis of MW data ( $1.473 \pm 0.006$  Å, Table 5). Thus, this bond length shows no distinct peculiarity as compared with similar systems (see Ref. [8]).

In the previous GED study [4] special attention was given to the angle  $\angle \text{C2}–\text{C1}–\text{C6} = 123.4 \pm 0.3^\circ$  due to its importance in understanding substituent effects in benzene derivatives. The present re-investigation fully confirms the findings of Ref. [4] in this respect.

### Notes added in proofs

The paper by Zewail's group [27] about ultrafast electron diffraction study of nitrobenzene was published shortly after the present work was finished. Since the molecular structure in [27] was corrected for vibrational effects according to Sipachev's method developed in 1985 [15] (i.e. using nonlinear relation between Cartesian and internal vibrational coordinates at the level of the first-order perturbation theory) it could be identified as  $r_{h1}$  structure similar to that from the literature (see Refs. from [28], for example [29]). The  $\angle_{h1}$  angles listed in the present paper are in agreement with those from [27]. In comparison to [27] a more precise determination of molecular structure was carried out in the present study taking into account also anharmonic vibrational corrections calculated from quantum-chemical force constants (equilibrium  $r_e$  structure).

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