

Vibrational spectra and structure of 1,4-dinitrobenzene and its ^{15}N labelled derivatives: an ab initio and experimental study

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Abstract

Infrared and Raman spectra in solid state and solution of 1,4-dinitrobenzene, 1,4-dinitrobenzene- ^{15}N , ^{15}N and 1,4-dinitrobenzene- ^{14}N , ^{15}N have been studied and their fundamental frequencies have been assigned using isotopic frequency shifts and Raman depolarization ratios. Ab initio quantum chemical calculations have been carried out for the three 1,4-dinitrobenzene isotopomers at the 3-21G, 6-31G and 6-31G** basis set levels and the computed vibrational frequencies have been compared with the experimental ones. Best coincidence was achieved with the frequencies calculated at the 6-31G level: the mean deviation is 26.5 cm^{-1} . The calculated isotopic frequency shifts, induced by the ^{15}N labelling, are in very good accordance with the measured ones. Except the C–H bond lengths, all the geometry parameters, calculated for the isolated molecule, are in good agreement with the X-ray data, obtained for the 1,4-dinitrobenzene monocrystal. The nitro groups in the molecule hold charges of 0.390 e^- each; there is practically no nitro group/phenylene ring conjugation. © 1997 Elsevier Science B.V.

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1. Introduction

The first overall assignment of the infrared and Raman spectra of the isomeric dinitrobenzenes—*ortho*, *meta* and *para* [1] pointed out that the nitro groups are vibrationally coupled in the three molecules. The frequency difference between the IR active nitro stretching bands of 1,4-dinitrobenzene (220 cm^{-1}) is considerably larger than these between the highest and the lowest nitro group stretching frequencies in 1,3-dinitrobenzene (195

cm^{-1}) and 1,2-dinitrobenzene (188 cm^{-1}) [1]. The larger frequency difference in the 1,4-dinitrobenzene case, i.e. the stronger vibrational coupling, is the reason for the drastic deviation of the point for this compound from the correlations between the nitro group band frequencies in series of aromatic nitro compounds and their physical and chemical characteristics, e.g. Hammett σ -constants, $\text{p}K$ values, solvent effects, etc. [2–4] (and references cited therein).

Except the first interpretation of 1,4-dinitrobenzene [1] and the partial assignment of some of its bands by studying the differential infrared linear

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dichroic spectra [5] no reports on the vibrational spectra and assignment of 1,4-dinitrobenzene isotopic labelled derivatives seem to have appeared up to now. The normal coordinate analysis data for the corresponding 1,3-isomer were published quite a long time ago [6].

On the other hand, ab initio MO calculations for various classes of organic molecules [7–15] and ions [7,11–15] have been used successfully to study their force field and structure. However, except a short communication [16], ab initio MO data for 1,4-dinitrobenzene have not been published up to now.

The purpose of the present study is to assign the fundamental vibration frequencies and to elucidate both the force field and structure of 1,4-dinitrobenzene molecule on the basis of IR and Raman spectra, isotope labelling, and ab initio force field calculations.

2. Experimental

1,4-dinitrobenzene and its mono- ^{15}N labelled isotopomer 1,4-dinitrobenzene- $^{14}\text{N},^{15}\text{N}$ were prepared from the corresponding 4-nitroaniline and 4-nitroaniline- ^{15}N (labelled in the nitro group, 98 at.% enrichment, Isokommerz) and NaNO_2 , according to ref. [17]. The synthesis of the di- ^{15}N labelled 1,4-dinitrobenzene- $^{15}\text{N},^{15}\text{N}$ was carried out using 4-nitroaniline- ^{15}N (a sample as above) and $\text{Na}^{15}\text{NO}_2$ (52.8 at.% enrichment, Isokommerz). Hence, three mixtures of 1,4-dinitrobenzenes with the following contents were prepared:

1. 52.8% of $\text{O}_2^{15}\text{NC}_6\text{H}_4\text{NO}_2$ and 47.2% of $\text{O}_2\text{NC}_6\text{H}_4\text{NO}_2$
2. 47.32% of $\text{O}_2^{15}\text{NC}_6\text{H}_4\text{NO}_2$, 51.74% of $\text{O}_2^{15}\text{NC}_6\text{H}_4^{15}\text{NO}_2$, and 0.94% $\text{O}_2\text{NC}_6\text{H}_4\text{NO}_2$
3. 98% of $\text{O}_2^{15}\text{NC}_6\text{H}_4\text{NO}_2$ and 2% of $\text{O}_2\text{NC}_6\text{H}_4\text{NO}_2$

The IR spectra of the 1,4-dinitrobenzenes studied were recorded in the solid state in CsI pellets, and in CCl_4 and CS_2 solutions on a Bruker IFS-113v spectrometer in the 4000 to 160 cm^{-1} region

with a resolution of 1 cm^{-1} , as well as in polyethylene on a Grubb-Parsons interferometer in the far IR range (down to 50 cm^{-1}). The Raman spectra were measured in the solid state, and in CCl_4 , toluene and CH_3OH solutions on a Bruker Raman module FTR 106 with 1 cm^{-1} resolution. A diode-pumped Nd:YAG laser with wavelength 1064 nm was used for excitation with a 180° arrangement [18]. In the $120\text{--}20\text{ cm}^{-1}$ range the spectra were recorded on Jobin-Yvon Ramanor; the 514.5 nm line of a Spectra Physics Ar^+ laser with a power of about 120 mW was used for excitation. The data are given in Table 1.

3. Computations

The ab initio quantum chemical computations were performed using the GAMESS software [19] at the HF 3-21G, 6-31G and 6-31G** basis set levels.

It is well known that the neat (native, unscaled) frequencies, obtained by ab initio force field calculations, are always higher than the experimental ones. Thus, for a better comparison between these values, the theoretical results have usually been modified by using empirical scaling factors for either the force constants [10] or resulting frequencies [8], or by applying empirical correlation equations [11–15]. The latter method of scaling has been used in this work (Table 2).

The comparison between theoretical and experimental frequencies of 1,4-dinitrobenzene has shown that the agreement between them is improved when the 6-31G basis set is used instead of the 3-21G one. The implementation of polarization functions in the basis set, however, does not lead to a further improvement of the results. The mean deviations, found by comparison between the calculated and measured frequency values are, as follows: 44.4 cm^{-1} for 3-21G, 26.5 cm^{-1} for 6-31G, and 34.4 cm^{-1} for 6-31G**. Thus the polarization basis sets not only prolonged the processing time but also deteriorated the predicted frequencies of 1,4-dinitrobenzene.

4. Results and discussion

4.1. Vibrational assignment

The molecular symmetry in 1,4-dinitrobenzene

Table 1
Vibrational frequencies (cm^{-1}) of 1,4-Dinitrobenzene and its ^{15}N -labelled derivatives

| No. | $^{14}\text{N}, ^{14}\text{N}$ | | $^{15}\text{N}, ^{15}\text{N}$ | | $^{14}\text{N}, ^{15}\text{N}$ | |
|-----|--------------------------------|-------------------|--------------------------------|-------------------|--------------------------------|-------------------|
| | IR | Raman | IR | Raman | IR | Raman |
| 1. | 3110 | — | 3111 | — | 3111 | 3111 ^s |
| 2. | — | 3105 ^s | — | 3105 ^s | — | 3105 ^s |
| 3. | — | 3092 ^s | — | 3093 ^s | — | 3093 ^s |
| 4. | 3088 | — | 3088 | — | 3088 | — |
| 5. | — | 1590 | — | 1591 | — | 1589 |
| 6. | — | 1590 | — | 1591 | — | 1589 |
| 7. | 1556 | — | 1524 | — | 1549 | 1551 |
| 8. | — | 1535 | — | 1505 | 1513 | 1511 |
| 9. | 1480 | — | 1480 | — | 1480 | 1478 |
| 10. | 1378 | — | 1378 | — | 1379 | 1384 |
| 11. | — | 1358 | — | 1326 | 1340 | 1342 |
| 12. | 1339 | — | 1315 | — | 1321 | 1322 |
| 13. | — | 1287 | — | 1287 | — | 1284 |
| 14. | 1216 | — | 1216 | — | 1216 | — |
| 15. | — | 1165 | — | 1165 | — | 1164 |
| 16. | — | 1108 | — | 1108 | — | 1108 |
| 17. | 1106 | — | 1106 | — | 1106 | — |
| 18. | 1101 | — | 1101 | — | 1101 | — |
| 19. | 1012 | — | 1012 | — | 1012 | — |
| 20. | — | 973 | — | 974 | — | 974 |
| 21. | 970 | — | 970 | — | 970 | — |
| 22. | 871 | — | 868 | — | 869 | — |
| 23. | — | 867 | — | 864 | — | 865 |
| 24. | — | 837 | — | 831 | — | 831 |
| 25. | 835 | — | 828 | — | 831 | — |
| 26. | — | 771 ^s | — | 760 ^s | — | 764 ^s |
| 27. | — | 714 ^s | — | 713 ^s | — | 713 ^s |
| 28. | 711 | — | 696 | — | 703 | — |
| 29. | — | 663 ^s | — | — | — | — |
| 30. | — | 622 ^s | — | 622 | — | 623 ^s |
| 31. | — | 550 ^s | — | 548 | — | — |
| 32. | 514 | — | 514 | — | 514 | — |
| 33. | 506 ^s | — | 506 ^s | — | — | — |
| 34. | 444 ^s | — | 443 ^s | — | 443 ^s | — |
| 35. | 417 | — | 417 | — | 417 | — |
| 36. | — | 303 ^s | — | 301 ^s | — | 302 ^s |

crystal is C_{2h} [20,21]. Since the nitro groups in the free molecule are expected to be coplanar with the benzene ring, the selection rules must be derived from the D_{2h} symmetry and the distribution of the 42 fundamentals in 1,4-dinitrobenzene and 1,4-dinitrobenzene- ^{15}N , ^{15}N are classified into $8A_g + 7B_{1g} + 2B_{2g} + 4B_{3g} + 3A_u + 3B_{1u} + 7B_{2u} + 8B_{3u}$. The 'mutual exclusion principle' holds that makes the assignment of some bands difficult because the corresponding counterparts in the IR or Raman spectrum can not be correlated with them. Part of these problems have been solved by comparing the spectra of 1,4-dinitrobenzene and 1,4-dinitrobenzene- ^{15}N , ^{15}N as well as by the assignment of the spectrum of 1,4-dinitrobenzene- ^{14}N , ^{15}N , where the symmetry descends from D_{2h} to C_{2v} .

The assignments given by Green and Lowers for 1,4-dinitrobenzene [1] were adopted with a few revisions based on the comparison between the vibrational spectra of the 1,4-dinitrobenzene isotopic derivatives (Table 1). The experimental IR and Raman data are compared with the calculated ones in Table 2. A good agreement between the scaled theoretical and the experimental vibrational frequencies is seen there. The frequency isotopic shifts are also well reproduced (Table 3).

4.1.1. Ring vibrations

The 1234 cm^{-1} band in the IR spectrum of 1,4-dinitrobenzene has been assigned [1] to the B_{2u} normal mode. We did not observe any band near this wavenumber in the IR spectrum of 1,4-dinitrobenzene- ^{15}N , ^{15}N . On the other hand, a 1216 cm^{-1} band appears in the IR spectra of all the 1,4-dinitrobenzene isotopomers studied, so we assigned it to this normal vibration.

The 622 cm^{-1} band in the Raman spectrum of 1,4-dinitrobenzene was assigned [1] tentatively to the normal mode A_g and B_{3g} . To our opinion the polarised 622 cm^{-1} band is really an A_g mode (calculated 646 cm^{-1}), whereas the 714 cm^{-1}

Table 2

Theoretical vibrational frequencies and IR intensities, and experimental (solid state) IR and Raman data for 1,4-dinitrobenzene

| No. | Ab initio scaled ^a force field | | | | Approximate description ^b | Experimental | |
|-----|---|-----------------------------------|---------------------------------|---------------------------|--|---------------------------|-----------------------------------|
| | 3–21G ν (cm ⁻¹) | 6–31G** ν (cm ⁻¹) | 6–31G ν (cm ⁻¹) | A (km mol ⁻¹) | | ν (cm ⁻¹) | Assignment ^c |
| 1. | 3089 | 3075 | 3088 | 0.0 | 99 ν_{CH} | 3110 | 20a |
| 2. | 3088 | 3074 | 3086 | 18.0 | 99 ν_{CH} | 3105 | 2 |
| 3. | 3078 | 3064 | 3075 | 0.0 | 99 ν_{CH} | 3092 | 7b |
| 4. | 3077 | 3063 | 3074 | 7.5 | 99 ν_{CH} | 3088 | 20b |
| 5. | 1606 | 1698 | 1638 | 0.0 | 70 ν_{CC} , 17 δ_{CCC} | 1590 | 8a |
| 6. | 1602 | 1681 | 1633 | 0.0 | 67 ν_{CC} , 21 δ_{CCH} | 1590 | 8b |
| 7. | 1496 | 1628 | 1507 | 9.1 | 64 δ_{CCH} , 18 δ_{CN} | 1480 | 19a |
| 8. | 1430 | 1602 | 1493 | 586.2 | 48 $\nu(\text{NO}_2)$, 43 δ_{CCN} | 1556 | $\nu(\text{NO}_2)$ |
| 9. | 1316 | 1498 | 1439 | 0.0 | 86 $\nu(\text{NO}_2)$, 14 δ_{CCN} | 1535 | $\nu(\text{NO}_2)$ |
| 10. | 1290 | 1488 | 1401 | 198.3 | 39 ν_{NO_2} , 30 δ_{CCH} , 26 ν_{CC} | 1378 | 19b |
| 11. | 1275 | 1471 | 1351 | 0.0 | 66 $\nu(\text{NO}_2)$, 18 ν_{CN} | 1358 | $\nu(\text{NO}_2)$ |
| 12. | 1234 | 1417 | 1336 | 434.7 | 70 $\nu(\text{NO}_2)$, 14 ν_{CN} , 14 δ_{CNO} | 1339 | $\nu(\text{NO}_2)$ |
| 13. | 1213 | 1294 | 1330 | 0.0 | 89 δ_{CCH} | 1287 | 3 |
| 14. | 1203 | 1206 | 1255 | 185.3 | 75 ν_{CC} , 12 δ_{CCN} | 1216 | 14 |
| 15. | 1186 | 1169 | 1195 | 0.0 | 69 δ_{CCH} , 27 ν_{CC} | 1165 | 7a |
| 16. | 1123 | 1119 | 1122 | 6.3 | 42 δ_{CCC} , 20 δ_{CCN} , 20 ν_{CN} | 1106 | 18b |
| 17. | 1109 | 1118 | 1117 | 0.0 | 50 ν_{CC} , 24 ν_{CN} , 13 ν_{NO} | 1108 | 9a |
| 18. | 1100 | 1074 | 1114 | 4.5 | 43 ν_{CC} , 49 δ_{CCH} | 1101 | 13 |
| 19. | 1084 | 1022 | 1076 | 0.0 | 83 τ_{CCCH} , 13 τ_{CCCC} | 1012 | 12 |
| 20. | 1080 | 1015 | 1075 | 0.0 | 83 τ_{CCCH} , 15 τ_{CCCN} | 973 | |
| 21. | 1014 | 1002 | 1024 | 10.8 | 83 δ_{CCC} , 12 δ_{CCN} | 970 | |
| 22. | 980 | 909 | 942 | 87.4 | 90 τ_{CCCH} , 10 τ_{CCCN} | 871 | 11 |
| 23. | 963 | 885 | 903 | 0.0 | 100 τ_{CCCH} | 837 | 10a |
| 24. | 799 | 863 | 846 | 0.0 | 36 δ_{CNO} , 28 δ_{CCN} , 16 ν_{NO} , 13 ν_{CN} | 867 | $\delta^{\text{ip}}(\text{NO}_2)$ |
| 25. | 788 | 858 | 818 | 77.8 | 58 δ_{CNO} , 19 ν_{NO} , 11 δ_{CCN} | 835 | $\delta^{\text{op}}(\text{NO}_2)$ |
| 26. | 762 | 796 | 770 | 0.0 | 43 τ_{CCCC} , 43 τ_{CCNO} | 771 | $\omega^{\text{ip}}(\text{NO}_2)$ |
| 27. | 683 | 747 | 714 | 0.0 | 54 δ_{CCN} , 40 δ_{CNO} | 714 | 4 |
| 28. | 680 | 717 | 704 | 82.2 | 76 τ_{CCNO} | 711 | $\omega^{\text{op}}(\text{NO}_2)$ |
| 29. | 664 | 667 | 678 | 0.0 | 47 τ_{CCCC} , 30 τ_{CCNO} | 663 | |
| 30. | 653 | 625 | 646 | 0.0 | 80 δ_{CCC} | 622 | 6b |
| 31. | 515 | 547 | 545 | 0.0 | 51 δ_{CNO} , 40 δ_{CCN} | 550 | $\rho^{\text{ip}}(\text{NO}_2)$ |
| 32. | 514 | 526 | 524 | 35.9 | 52 ν_{CN} , 28 δ_{CNO} | 514 | $\rho^{\text{op}}(\text{NO}_2)$ |
| 33. | 489 | 471 | 495 | 3.8 | 73 δ_{CNO} , 25 δ_{CCN} | 506 | 16b |
| 34. | 469 | 465 | 478 | 0.8 | 78 τ_{CCCC} , 19 τ_{CCNO} | 444 | |
| 35. | 456 | 422 | 434 | 0.0 | 89 τ_{CCCN} | 417 | 16a |
| 36. | 309 | 306 | 310 | 0.0 | 40 δ_{CCC} , 35 ν_{CN} , 10 δ_{CNO} | 303 | 6a |
| 37. | 230 | 304 | 298 | 0.0 | 54 δ_{CCN} , 36 δ_{CNO} | 303 | |
| 38. | 288 | 270 | 276 | 0.0 | 84 τ_{CCCN} | 257 | 9b |
| 39. | 182 | 185 | 182 | 14.8 | 99 δ_{CCN} | 185 | 15 |
| 40. | 102 | 96 | 99 | 14.3 | 100 τ_{CCCN} | 107 | |
| 41. | 85 | 60 | 67 | 0.0 | 100 τ_{CCNO} | 68 | $\tau(\text{NO}_2)$ |
| 42. | 60 | 46 | 50 | 0.0 | 100 τ_{CCNO} | 68 | |

^a Scaled, according to the correlation equation $\nu(\text{exp}) = 0.8952 \cdot \nu(6-31\text{G}) + 10.2$ [12].^b Vibrational modes: ν , stretching; δ , deformation (all kinds of); τ , torsion: superscript *s*, symmetric; superscript *as*, antisymmetric; superscript *ip*, in-phase; superscript *op*, out-of-phase. The numbers before the mode symbols indicate percent contribution (10 or more) of a given mode to the corresponding normal vibration, according to the energy distribution matrix [19].^c Based on Green and Lauwers's one and on the isotopic shifts (see text). Wilson's notation is used for the phenylene modes; others symbols are as follows: ν , δ , ω , ρ and τ -stretching, bending, wagging, rocking and torsional vibrations, respectively.

Table 3
 ^{15}N isotopic shifts of the nitro group vibrations of 1,4-dinitrobenzene

| No. | Vibrational modes | $\text{N}^{15}, \text{N}^{15}$ | | $\text{N}^{14}, \text{N}^{15}$ | |
|-----|--|--------------------------------|----------|--------------------------------|----------|
| | | Calculated | Observed | Calculated | Observed |
| 8. | $\nu_{\text{as}}^{\text{op}}(\text{NO}_2)$ | 19 | 32 | 10 | 7 |
| 9. | $\nu_{\text{s}}^{\text{ip}}(\text{NO}_2)$ | 31 | 30 | 17 | 24 |
| 11. | $\nu_{\text{as}}^{\text{ip}}(\text{NO}_2)$ | 26 | 32 | 7 | 16 |
| 12. | $\nu_{\text{s}}^{\text{op}}(\text{NO}_2)$ | 25 | 24 | 13 | 18 |
| 24. | $\delta^{\text{ip}}(\text{NO}_2)$ | 4 | 3 | 2 | 2 |
| 25. | $\delta^{\text{op}}(\text{NO}_2)$ | 7 | 7 | 4 | 4 |
| 26. | $\omega^{\text{ip}}(\text{NO}_2)$ | 7 | 11 | 3 | 7 |
| 28. | $\omega^{\text{op}}(\text{NO}_2)$ | 16 | 15 | 6 | 8 |
| 31. | $\rho^{\text{ip}}(\text{NO}_2)$ | 2 | 2 | 1 | 0 |
| 32. | $\rho^{\text{op}}(\text{NO}_2)$ | 0 | 0 | 0 | 0 |
| 41. | $\tau(\text{NO}_2)$ | 0 | 3 | 0 | 1 |

The 1587 cm^{-1} band in the Raman spectrum of 1,4-dinitrobenzene was assigned [1] to the C–C vibrations (8a in Wilson's notation), and the other C–C normal mode (8b) were correlated with a shoulder at 1582 cm^{-1} in the spectra of the labelled 1,4-dinitrobenzenes. There is only one band in the solution spectra of the three 1,4-dinitrobenzenes studied in this region (1590 cm^{-1}), so we assigned it to both vibrations (8ab). Calculated normal vibrations in the theoretical spectrum at 1637 and 1633 cm^{-1} correspond to these skeletal vibrations.

Two bands at 1480 and 1378 cm^{-1} in the experimental IR spectrum correspond to the 19a and 19b vibrations. The theory predicts only one IR active purely skeletal vibration in this frequency region, viz. ν_7 (Table 2). According to the theoretical predictions the other IR active skeletal vibration in this region should be mixed with the ν_{NO} mode (39% participation, Table 2, ν_{10}). The corresponding IR band should be quite stronger than ν_7 and it should show a 15 cm^{-1} ^{15}N isotopic shift. In fact according to the experiment there is no such a strong mixing, and the 19a and 19b bands are practically equiintense, and their frequencies do not depend on the ^{15}N labelling (Table 1).

4.1.2. Nitro group vibrations

The analysis of the normal vibrations shows that the ab initio force field calculations reproduce well the vibrational interaction between the two nitro group, which results in the appearance of two IR

active vibrations: out-of-phase symmetrical (ν_{12}) and out-of-phase antisymmetrical (ν_8), and two Raman active ones: in-phase symmetrical (ν_9) and in-phase antisymmetrical (ν_1) (Table 2).

According to the theory the out-of-phase antisymmetrical vibration should be coupled with the skeletal deformation (43% participation of the latter). Probably for this reason the corresponding calculated frequency is quite lower than the measured one, lower even than the frequency of the skeletal deformation 19a. The largest deviation between the calculated and measured isotopic shifts corresponds just to the $\nu_{\text{as}}^{\text{op}}$ band (Table 3, ν_8). The theory reproduces well the strong $\nu(\text{NO}_2)$ splitting in the IR spectra, caused by the nitro group vibrational interaction: calculated 175 cm^{-1} .

In a full agreement between theory and experiment, the highest intensities among all the IR bands correspond to the $\nu(\text{NO}_2)$ vibrations.

All four bands become active in both IR and Raman spectra of 1,4-dinitrobenzene- $^{14}\text{N}, ^{15}\text{N}$, because of mass-assymetrization. The $\nu_{\text{s}}(\text{NO}_2)$ appears practically at the same position, like those of nitrobenzene and nitrobenzene- ^{15}N respectively [22], whereas both $\nu_{\text{as}}(\text{NO}_2)$ of 1,4-dinitrobenzene- $^{14}\text{N}, ^{15}\text{N}$ show slightly higher frequencies than those of nitrobenzene and nitrobenzene- ^{15}N .

We mentioned in the Experimental that we have prepared three different mixtures of 1,4-dinitrobenzenes- $^{14}\text{N}, ^{15}\text{N}$. In the infrared spectrum of the first isotopic mixture (52.8% of

$\text{O}_2^{15}\text{NC}_6\text{H}_4\text{NO}_2$ and 47.2% of $\text{O}_2\text{NC}_6\text{H}_4\text{NO}_2$) two bands for the scissoring $\delta(\text{NO}_2)$ with almost equal intensity appear at 835 and 831 cm^{-1} , i.e. 4 cm^{-1} downward shift is observed due to ^{15}N substitution. The IR spectrum of the third isotopic mixture (practically 100% 1,4-dinitrobenzene- $^{14}\text{N},^{15}\text{N}$) shows one IR $\delta(\text{NO}_2)$ band at 831 cm^{-1} . There are two bands in the IR spectrum of the second isotopomeric mixture as well, again equiintense, at 831 and 828 cm^{-1} : the latter band corresponds obviously to $\delta(\text{NO}_2)$ of 1,4-dinitrobenzene- $^{15}\text{N},^{15}\text{N}$, therefore this band undergoes a 7 cm^{-1} downward ^{15}N isotopic shift. This vibration is calculated as mixed but dominated by $\delta^{\text{op}}(\text{NO}_2)$ (Table 2, ν_{25}). The theoretical isotopic shifts of these vibrations agree with the experimental ones (Table 3).

The 867 cm^{-1} Raman band corresponds to the scissoring deformation $\delta^{\text{ip}}(\text{NO}_2)$ predicted at 847 cm^{-1} (Table 3). The $\delta^{\text{ip}}(\text{NO}_2)$ and the out-of-plane C–H deformation bands have alternative position in the theoretical and in the experimental spectra.

The wagging vibration of the nitro groups $\omega(\text{NO}_2)$ demonstrates the following behaviour with respect to the ^{15}N labelling:

(i) The IR spectrum of the isotopic mixture 1 (see Section 2) shows two equiintense bands at 703 and 711 cm^{-1} . The corresponding bands of the isotopic mixture 2 appear at 703 and 696 cm^{-1} .

(ii) The IR spectrum of the mixture 3 (98% mono-labelling) shows one $\omega(\text{NO}_2)$ band at 703 cm^{-1} .

Thus the ^{15}N di-labelling of 1,4-dinitrobenzene results in a 15 cm^{-1} downward shift of this vibrational frequency and it is well reproduced by the calculations (Table 3, ν_{28}).

The other $\omega(\text{NO}_2)$ at 771 cm^{-1} in the 1,4-dinitrobenzene Raman spectrum shifts to 760 cm^{-1} in the 1,4-dinitrobenzene- $^{15}\text{N},^{15}\text{N}$ one, i.e. a 11 cm^{-1} $^{14}\text{N}-^{15}\text{N}$ isotopic shift is observed in this case (Table 1). This vibration is predicted to be mixed with the out-of-plane skeletal deformation (Table 2, ν_{26}); the calculated isotopic shifts are less than the measured ones (Table 3). The downward shifts upon $^{14}\text{N}-^{15}\text{N}$ substitution of both $\omega(\text{NO}_2)$ are the largest among the shifts of all bending

vibrations of the nitro groups in 1,4-dinitrobenzene- $^{15}\text{N},^{15}\text{N}$.

The rocking vibrations of the nitro groups $\rho(\text{NO}_2)$ of 1,4-dinitrobenzene at 550 cm^{-1} (Raman) and 514 cm^{-1} (IR) undergo considerably less ^{15}N isotopic shifts (the second frequency remains unchanged), than those of other bending vibrations. Both frequencies and isotopic shifts of $\rho(\text{NO}_2)$ are well reproduced by the calculations (Table 3).

The 68 cm^{-1} band in the Raman spectrum of 1,4-dinitrobenzene was assigned to the torsional mode of the nitro groups. This band undergoes 3 cm^{-1} upward isotopic shift by $^{15}\text{N},^{15}\text{N}$ -labelling (Table 1).

4.2. Structure of 1,4-dinitrobenzene molecule

According to X-ray studies [20,21] the benzene ring in 1,4-dinitrobenzene crystal is planar and both nitro groups are twisted about the C–N bonds, so that the NO_2 planes form angles of approximately 10.2° with the benzene ring plane. For the description of the structure of 1,4-dinitrobenzene molecule we performed ab initio optimization of the molecular geometry on the 3-21G, 6-31G, and 6-31G** basis set levels. The optimized geometry parameters are compared with the measured [21] on the basis of X-ray diffraction in Table 4. It is seen there that the phenylene ring bonds of the isolated molecule should be a bit longer than that in the monocystal of 1,4-dinitrobenzene.

The largest deviation between the experimental and calculated bond angles for the free molecule is observed for ONO and $\text{C}_7\text{C}_3\text{C}_6$. It is known [21] that when the nitro group is bonded in *para* position to a strong π -acceptor the internal angle of the phenylene ring increases. The X-ray study pointed out [21] that the $\text{C}_7\text{C}_3\text{C}_6$ angle in 1,4-dinitrobenzene crystal is 123.44°. The theoretically predicted at the 3-21G basis set value for the free molecule is with 1.14° smaller. Just the opposite variation is predicted for the ONO bond angle: the 3-21G calculations gave a 1.32° larger angle. The theoretical results for both these angles become considerably closer to the experimental ones when 6-31G basis set is used. The data in Table 4

Table 4
Experimental and calculated bond lengths (Å) and angles (°) at different bases sets for the 1,4-Dinitrobenzene molecule

| Geometry parameters ^a | Experimental ^b | Calc. 3-21G | $\Delta = \text{exp.-calc.}$ | Calc. 6-31G | $\Delta = \text{exp.-calc.}$ | Calc. 6-31G** | $\Delta = \text{exp.-calc.}$ |
|--|---------------------------|-------------|------------------------------|-------------|------------------------------|---------------|------------------------------|
| R(N–C ₁) | 1.4705 | 1.454 | 0.0165 | 1.454 | 0.0165 | 1.464 | 0.0065 |
| R(C ₁ –C ₂) | 1.3894 | 1.377 | 0.0124 | 1.383 | 0.0064 | 1.382 | 0.0074 |
| R(C ₁ –C ₃) | 1.3901 | 1.377 | 0.0131 | 1.383 | 0.0071 | 1.382 | 0.0081 |
| R(C ₂ –C ₄) | 1.3912 | 1.378 | 0.0132 | 1.384 | 0.0072 | 1.382 | 0.0092 |
| R(N–O ₁) | 1.2283 | 1.242 | –0.0137 | 1.224 | 0.0043 | 1.192 | 0.0363 |
| R(N–O ₂) | 1.2281 | 1.242 | –0.0139 | 1.224 | 0.0041 | 1.192 | 0.0361 |
| R(C–H) | 0.95 | 1.067 | –0.117 | 1.069 | –0.119 | 1.071 | –0.121 |
| <(NC ₁ C ₂) | 118.23 | 118.8 | –0.57 | 118.7 | –0.47 | 118.6 | –0.37 |
| <(NC ₁ C ₃) | 118.32 | 118.8 | –0.48 | 118.7 | –0.38 | 118.6 | –0.28 |
| <(C ₂ C ₁ C ₃) | 123.44 | 122.3 | –1.14 | 122.7 | 0.74 | 122.8 | 0.64 |
| <(O ₁ NO ₂) | 124.28 | 125.6 | –1.32 | 124.0 | 0.28 | 125.2 | –0.92 |
| <(O ₁ NC ₁) | 117.76 | 117.2 | 0.56 | 118.0 | –0.24 | 117.4 | 0.36 |
| <(O ₂ NC ₁) | 117.96 | 117.2 | 0.76 | 118.0 | –0.04 | 117.4 | 0.56 |
| <(C ₁ C ₂ C ₄) | 118.39 | 118.8 | –0.41 | 118.7 | –0.31 | 118.6 | –0.21 |
| <(C ₁ C ₂ H) | | 119.5 | | 120.2 | | 120.2 | |
| <(C ₄ C ₂ H) | | 121.6 | | 121.1 | | 121.1 | |

^a Numbering of atoms as in Fig. 1.

^b Ref. [21].

pointed out that the introduction of polarization functions in the basis set does not alter practically the results for the CCN and C₇C₃C₆ bond angles but gives opposite changes for ONO and CNO angles. The calculations with all the methods predict increased C₃C₆C₈ angle in the free molecule.

According to the 6-31 calculations, the nitro groups in the 1,4-dinitrobenzene molecule hold a 0.390 e[−] net charge each. This value is close to the 0.419 e[−] one, calculated [9] for the nitro group in the nitrobenzene molecule. The value of 0.791, calculated for the C–N bond order of 1,4-dinitrobenzene (Fig. 1) is smaller, but close to that of nitrobenzene, 0.83 [23], and away from the

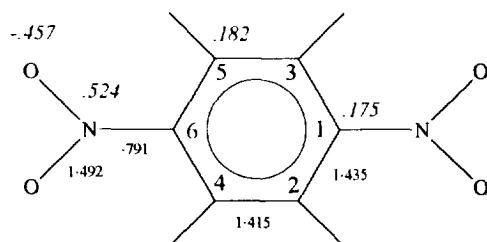


Fig. 1. Mulliken net charges (in italics) and bond orders in the 1,4-dinitrobenzene molecule.

value of 0.88, calculated [23] for lithium p-nitrophenolate. These results agree with the statement [23] about the weak mesomeric interactions between the benzene ring and the nitro group; these interactions become enhanced by strong electron releasing substituents at the p-position [23].

5. Conclusions

The calculated normal frequencies of 1,4-dinitrobenzene and its ¹⁵N-labelled isotopomers as well as the ¹⁵N-frequency shifts are in good agreement with the experimental ones. According to ab initio calculations there is no conjugation between the nitro group and phenylene ring of 1,4-dinitrobenzene free molecule.

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