Characterization of the structure, electronic conjugation and vibrational spectra of the radical anions of p- and m-dinitrobenzene: a quantum chemical study

D. Y. Yancheva

Department of Structural Organic Analysis, Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 9, 1113 Sofia, Bulgaria

The structure, charge distribution and electronic coupling between the functional groups, caused by the conversion of two main nitrobenzenes (p- and m-dinitrobenzene) into radical anions was studied at B3LYP/6-311++G** level. The vibrational spectra of the neutral compounds and the radical anions, which are closely related to the structural and electronic changes, were also studied and discussed. The enhanced vibrational coupling between the nitro groups in the radical anion species was described on the basis of force field analysis and frequency reduction upon radicalization. The electronic density analysis showed that in both cases the nitro groups bear equal parts of the additional electron: 0.36 e^- for the p-compound and 0.29 e^- for the m-isomer. The radical anion species are characterized by quinoid-like structures as well as a larger and stronger conjugated system than the corresponding neutral forms.

INTRODUCTION

The radical anions of nitro compounds currently receive much attention as important intermediates in the metabolic pathways of antibacterial, antiprotozoal and anticancer agents [1–5]. Several nitro compounds and some of their metal complexes [6–9] are used in the medicine as radio-sensitizers in the anti-tumor therapy, and the efficiency of the drugs is also related to the one-electron reduction potential of these compounds [6]. Some radical anions of nitroaromatic compounds present an environmental concern as metabolites of synthetic intermediates, dyes, pesticides, and explosives [10–12]. The nitro radical anions are extensively studied in view of the intramolecular electron-transfer dynamics as well [13–15].

Therefore, an understanding of the structure, the electronic charge distribution and the changes related to the chemical transformation of the nitro compounds into radical anions is very important from both fundamental and practical points of view. On the other hand, radical anion species are difficult to isolate and study due to their high reactivity. So far, the properties and reactivity of the nitro radical anions have been explored mainly by pulse radiolysis [16] and cyclic voltammetry [17,18]. The IR spectral studies also provide valuable information on the structure and formation of organic aromatic anions (radical-anions, carbanions, dianions, etc.) [19–21], and particularly on the formation of nitro radical anions [22]. Optical spectra measurements combined with computational methods present another relevant investigation approach [23]. Hence, the experimental spectral techniques complemented with computational methods are a reasonable choice of analytical tools to monitor the changes occurring when neutral molecules are converted into radical anions and to explain the observed effects from a theoretical point of view.

The present contribution is focused on p- and m-dinitrobenzene as simple model compounds describing the interaction of two nitro groups through an aromatic spacer. The effect of the relative positions of the nitro groups (para *vs*. meta) during conversion of the dinitrobenzenes into radical anions was analysed by DFT calculations. The essential changes in the structure, charge distribution and electronic coupling between the functional groups, caused by the conversion, are reported. Since the electronic structure and the nature of the aromatic substitution have a profound effect on the bioactivity, toxicity and redox properties of the nitroaromatic compounds, special emphasis is put on the discussion of the different electronic interactions characterizing the radical anion species. The vibrational spectra of the neutral compounds and the radical anions, which are

* To whom all correspondence should be sent:
E-mail: deni@orgchm.bas.bg

closely related to the structural and electronic changes, are also studied and discussed.

COMPUTATIONAL DETAILS

All theoretical calculations were performed using the Gaussian 09 package [24] of programs. The molecular geometry of the neutral compounds and the radical anions was optimized at B3LYP/6–311++G** level. The optimized structures were confirmed to be the local minima by frequency calculation (no imaginary frequency). Spin densities were computed using the Mulliken population analysis. For a better correspondence between experimental and calculated IR frequencies, the results were modified using the empirical scaling factor of 0.9688, reported by Merrick and Radom [25]. The theoretical vibrational spectra were analyzed in terms of potential energy distributions (PEDs) by using the VEDA 4 program [26]. For the plots of simulated IR spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}.

RESULTS AND DISCUSSION

The conversion of p-dinitrobenzene (**1a**) and m-dinitrobenzene (**2a**) into radical anions (**1b** and **2b**, Scheme 1) could be done electrochemically in DMSO solution [22]. The negative radical formation is accompanied by color change and new spectral behavior reflecting the structure, electronic coupling and interactions established in the anionic species. The changes are related to those observed for monosubstituted nitrobenzene, but due to the interactions between the two electron acceptor groups attached to the phenyl ring their nature is more complex and subtle.
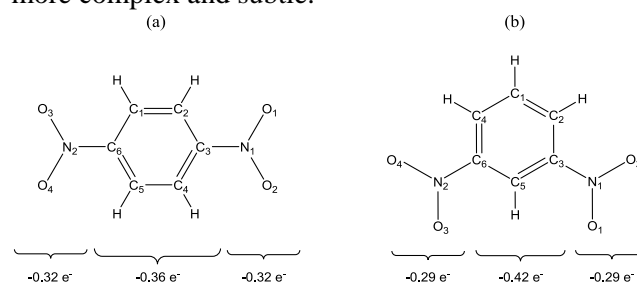
Scheme 1. Atomic numbering and spin density for: (a) **1b** and (b) **2b.**

Structural Analysis

The nitro groups in the free molecules of p- and m-dinitrobenzene are expected to be coplanar with the phenyl ring. Taking this into account, we maintained the symmetry of **1a**, as well as of the corresponding RA **1b**, during geometry optimization as D$_{2h}$, while this of the m-derivatives **2a** and **2b** was fixed as C$_{2v}$.

The calculated bond lengths included in Table 1 are denoted according to the atomic numbering presented in Scheme 1. For simplicity, in Table 1 the bond length duplicates resulting from the molecular symmetry are omitted. According to the DFT calculations, m- and p-dinitrobenzene in neutral form have comparable N-O and C-N bond lengths, very close to the values reported for nitrobenzene [27]. The data are also in excellent agreement with the bond lengths found by crystallographic studies on **1a** and **2a** [28,29].

Table 1. Bond lengths R (in Å) in **1a**, **2a** and their RAs **1b** and **2b.**

Species	Neutral molecules	RAs	ΔR^a
p-Dinitrobenzene	**1a**	**1b**	
R(C^1-C^2)	1.390	1.377	-0.013
R(C^2-C^3)	1.391	1.414	0.023
R(C^1-C^6)	1.391	1.414	0.023
R(C^3-N^1)	1.486	1.413	-0.073
R(N^1-O^1)	1.222	1.258	0.033
R(N^1-O^2)	1.222	1.258	0.033
m-Dinitrobenzene	**2a**	**2b**	
R(C^1-C^2)	1.392	1.392	0.00
R(C^2-C^3)	1.393	1.420	0.027
R(C^3-C^5)	1.392	1.392	0.00
R(C^3-N^1)	1.485	1.431	-0.054
R(N^1-O^1)	1.222	1.253	0.031
R(N^1-O^2)	1.223	1.254	0.031

^{a} $\Delta R = R_{RA} - R_{molecule}$ (Å)

The conversion into RAs leads to simultaneous shortening of the C-N bond and lengthening of the N-O bonds (Table 1). The differentiation is greater concerning the C-N bond length – in the p-substituted compound **1b** the C-N bond is much shorter than in **2b**. Compared to nitrobenzene, the C-N bond lengths decrease in the following order: **2b** (1.431 Å) > **1b** (1.413 Å) > $NO_2C_6H_5^-$ (1.395 Å).

As it can be seen from Table 1, the N-O bonds in both RAs are in the range 1.254–1.258 Å – by approximately 0.03 Å shorter than the N-O bonds in the RA of nitrobenzene. The geometry of the phenyl ring is also affected as a result of the conversion into RAs. In **1b** and **2b** the phenylene bond lengths are no longer identical, but altered in such a manner that their values are much closer to the C-N bond lengths and they form a quinoid-like structure influenced by the position of the NO_2 substituents. Hence, the structural changes reveal that the mesomeric interaction between the NO_2 groups and the phenyl ring is strongly enhanced in comparison to the neutral form and the electronic conjugation is extended over the whole RA species.

Important information for the distribution of the odd electron upon negative radical formation could be derived from atomic spin population analysis of **1b** and **2b**. Based on experimental and computational FTIR studies, it was found that the lowering of the stretching vibrations of the main functional groups of aromatic compounds accompanying their conversion into RAs is mainly related to the localization of spin density within the corresponding functional groups [30]. The spin population over the functional groups correlates to the experimentally observed lowering of the stretching vibrations and thus provides a reliable approach to predict and explain the spectral changes caused by the radicalization. The distribution of the odd electron over the fragments in **1b** and **2b** is illustrated in Scheme 1.

In both RAs, the two NO_2 groups bear equal parts of the odd electron: 0.36 e⁻ in the case of **1b** and 0.29 e⁻ in the case of **2b**. In comparison to the RA of nitrobenzene, where the corresponding value is 0.64 e⁻ [27], the spin density over the NO_2 groups of **1b** and **2b** is about twice lower. As a consequence, the changes in the bond lengths characterizing the conversion of **1a** and **2a** into RAs are smaller than in the case of nitrobenzene. Furthermore, this should also result in smaller frequency shifting of the N-O stretching vibrations upon radicalization. However, concerning the differences between the two species studied here, we could conclude that the electronic conjugation

between the nitro groups of the p-isomer is more effective, as evidenced by the greater spin density over them and the shorter C-N distances in **1b**.

Force Field Analysis

The distribution of the odd electron in RAs may be further characterized by investigating the force field in these systems. For this purpose we computed the diagonal and coupling force constants with respect to the natural internal coordinates and used them to assist the analysis of the electronic and spectral changes resulting from the conversion. The shift of the frequencies of the characteristic groups is of particular interest since the participation of a small number of bonds in the vibration allows comparison of the frequencies with certain parameters describing the electronic structure of the RAs. Selected diagonal and coupling constants for the species studied are listed in Table 2.

In accordance with the structural changes upon radicalization, the corresponding diagonal force constants are larger for the C-N bonds and smaller for the N-O bonds for both RAs. The ΔK values of transitions **1a** → **1b** and **2a** → **2b** are smaller in comparison to nitrobenzene and its RA ($\Delta K_{C-N} = 2.03$ and $\Delta K_{C-N} = -3.18$), but they show the same tendency as found by the atomic spin density. A considerable frequency shifting of the N-O and C-N stretching vibrations should be expected for **1b** and **2b**.

It is known that the coupling constants of distant functional groups in p- and m-disubstituted aromatic nitriles increase substantially when the corresponding RAs are formed, thus indicating an enhanced electron coupling between the vibrating groups [27]. As it could be seen from the values of the coupling constants presented in Table 2, this relation also holds in case of the dinitrobenzene RAs investigated by us. The coupling constants of the N-O bonds increase up to two orders of magnitude with the negative radical formation. The force constants describing the interaction of the C-N bonds also indicate enhanced coupling in the RAs.

IR Spectral analysis

The described electronic and structural changes accompanying the formation of the RAs of p- and m-dinitrobenzene are related to the essential changes occurring in the IR spectral behavior of the studied species. The altered bond lengths and the enhanced electronic coupling between the nitro

Table 2. Selected diagonal and coupling force constants K (in mdyn.Å^{-1}) for **1a**, **2a** and their RAs **1b** and **2b.**

Species	Neutral molecules	RAs	ΔK^a
p-Dinitrobenzene	**1a**	**1b**	
Diagonal Force Constants			
K(C^3-N^1)	4.02	5.51	1.49
K(N^1-O^1)	10.31	7.97	-2.33
K(N^1-O^2)	10.31	7.97	-2.33
Interaction Force Constants			
K(C^3-N^1)/(C^6-N^2)	0.02	0.05	0.03
K(N^1-O^1)/(N^2-O^3)	0.01	0.33	0.32
K(N^1-O^1)/(N^2-O^4)	0.00	0.30	0.30
m-Dinitrobenzene	**2a**	**2b**	
Diagonal Force Constants			
K(C^3-N^1)	4.04	4.93	0.88
K(N^1-O^1)	10.34	7.88	-2.46
K(N^1-O^2)	10.26	7.90	-2.36
Interaction Force Constants			
K(C^3-N^1)/(C^6-N^2)	0.00	0.20	0.20
K(N^1-O^1)/(N^2-O^3)	0.03	0.64	0.61
K(N^1-O^2)/(N^2-O^4)	0.02	0.55	0.53
K(N^1-O^1)/(N^2-O^4)	0.00	0.56	0.56

^{a} $\Delta K = K_{RA} - K_{molecule}$ (mdyn Å^{-1})

groups in the RAs would lead to considerable shifting of the IR band positions and the character of the vibrational modes. Having in mind the above described differences between **1b** and **2b**, the spectral changes should be expected to be larger in the case of **1b**. In order to check this assumption, we studied the IR spectra of the neutral compounds and the corresponding anion species and compared them to experimental data in solid state and DMSO-d$_6$ solution obtained earlier by Juchnovski and Andreev [22,32,33].

The IR spectra (1600-800 cm^{-1}) of **1a** and **1b** and those of **2a** and **2b** are shown in Fig. 1. The most important vibrations of the nitro groups in the neutral dinitrobenzenes and their RAs arise from the stretching of the N-O bonds and the C-N bonds. Table 3 summarizes those vibrations and the proposed assignments based on the contribution of a given mode to the corresponding normal vibration according to the PED matrix.

Assignments of the nitro vibrations in 1b

Similarly to the neutral p-dinitrobenzene, RA **1b** belongs to the point group D$_{2h}$. As a result of the electronic coupling, the two nitro groups vibrate coherently which leads to the formation of four N-O stretching modes - two antisymmetric: in-phase v^{as}_{NO2} *(ip)* and out-of-phase v^{as}_{NO2} *(op)*, and two symmetric: in-phase v^{s}_{NO2} *(ip)* and out-of-phase v^{s}_{NO2} *(op)* vibrations. According to the analysis of

the theoretical IR frequencies of **1b**, only two of them, v^{as}_{NO2} *(ip)* and v^{s}_{NO2} *(op)*, are IR active – Fig. 1a.

The band of v^{as}_{NO2} *(ip)* is predicted to appear at 1397 cm^{-1}, which agrees well with the experimentally found value – 1417 cm^{-1} and the assignment suggested earlier by Juchnovski and Andreev [22]. On the other hand, according to the calculations, v^{s}_{NO2} *(op)* is expected at a much lower frequency – 1096 cm^{-1}, than suggested in Ref. [22]. However, this theoretical value could not be compared to an experimental one since no IR data below 1100 cm^{-1} were reported in [22] due to the limitations of the spectral technique used. The band assigned as v^{s}_{NO2} in [22] is registered at 1212 cm^{-1}. It is the most intensive band in the IR spectrum of **1b** and based on the theoretical calculations should be attributed to a mixed $v_{C-N}+\delta_{NO2}$ *(op)* vibration.

Assignments of the nitro vibrations in 2b

In the m-dinitrobenzene **2a** and its AR **2b**, point group C$_{2v}$, all four N-O stretching modes should be IR active. Nevertheless, in the case of the neutral m-dinitrobenzene **2a** only two bands could be identified in the theoretical IR spectrum – Fig. 1b. This is a result of the small splitting between the in-phase and out-of-phase components of v^{as}_{NO2} and v^{s}_{NO2} and the higher intensity of the out-of-phase components.
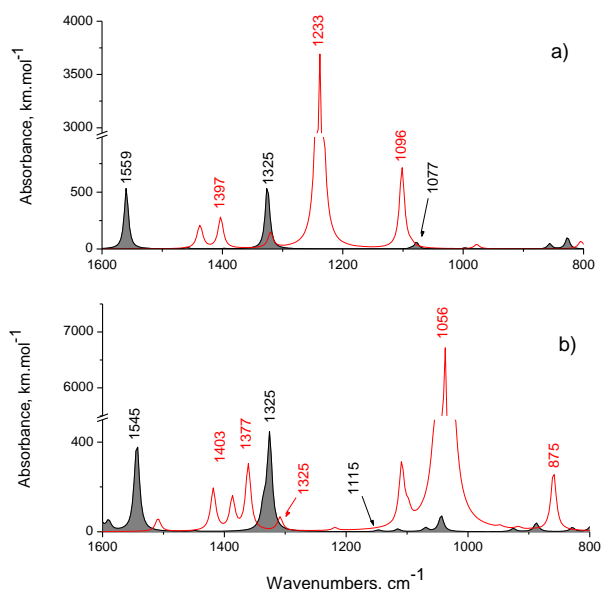
Fig. 1. Theoretical (B3LYP/6-311++G**) IR spectra of: a) **1a** (shaded) and **1b**; b) **2a** (shaded) and **2b**.

Our calculations show that among the N-O stretching vibrations of **2b**, v^{as}_{NO2} (op) absorbs at the highest frequency: 1403 cm^{-1}. v^{as}_{NO2} (ip) participates in a mixed $v_{CC} + v^{as}_{NO2}$ (ip) mode and gives rise to a band at 1377 cm^{-1}. The in-phase symmetric N-O stretching vibration v^{s}_{NO2} (ip) has similar character and position to this of **1b**: mixed mode $v_{CN} + v^{s}_{NO2}$ (ip) at 1325 cm^{-1}. On the other hand, in the case of **2b** the out-of-phase component v^{s}_{NO2} (op) is mixed with δ_{NO2} and the corresponding band is the strongest band in the whole spectrum. In the RA of m-dinitrobenzene the coordinate v_{CN} also participates in a lower-frequency mixed vibration: $v^{as} + \delta_{CCC} + v_{C-N}$ (op) appearing at 878 cm^{-1}. These findings support in general the assignments made in [22], but the experimental values measured for some of these vibrations are much higher: 1516 cm^{-1} for v^{as}_{NO2} (op) and 1274 cm^{-1} for v^{s}_{NO2} (op). The discrepancy must be due to the great complexity of the nitro vibrational modes revealed by the theoretical data reported here. As a result of the strong conjugation of the nitro groups and the benzene ring, all characteristic nitro vibrations in the RA **1b** and **2b** show mixed character. On the other hand, the benzene ring vibrations are also affected and appear at new positions and with enhanced intensity – Fig. 1. Further IR studies of the p- and m-dinitrobenzene anions isolated in solid argon might be decisive for the accurate vibrational assignment.

IR spectral changes upon conversion into RAs

The spectral changes concerning the most important nitro vibrations could be best described if the average v^{as}_{NO2} and v^{s}_{NO2} are calculated [$v^{as}_{NO2} = (v^{as}_{NO2}(ip) + v^{as}_{NO2}(op))/2$ and $v^{s}_{NO2} = (v^{s}_{NO2}(ip) + v^{s}_{NO2}(op))/2$]. The changes are summarized below:

1) Decrease of v^{as}_{NO2} by 162 cm^{-1} for **1b** and 154 cm^{-1} for **2b**, respectively.

2) Decrease of v^{s}_{NO2} by 170 cm^{-1} for **1b** and 140 cm^{-1} for **2b**, respectively.

3) Increase of v_{CN} by 156 cm^{-1} for **1b** and 220 cm^{-1} for **2b**, respectively. In the case of **1b** the coordinate v_{CN} is delocalized over two vibrations: $v_{CN} + v^{s}_{NO2}(ip)$ and $v_{CN} + \delta_{NO2}(op)$ (see Table 3).

4) Strong enhancement of the *intensity of one main band* upon radicalization:

The IR spectra of the RAs studied are dominated by one extremely intensive band. In the spectrum of **1b**, this band originates from $v_{CN} + \delta_{NO2}$ vibration and absorbs about 60 times stronger than in the neutral compounds. In the IR spectrum of **2b** the intensity of the band is even higher, but corresponds to a mixed vibration $v^{s}_{NO2}(op) + \delta_{NO2}$, without contribution of v_{CN}. Taking into account the assignments in both cases, one could conclude that a great migration of π-electron density in the conjugated system is connected to the δ_{NO2} motion and it is contributing at the largest extent to the very high intensities of these bands.

5) The uniform distribution of the odd electron upon both nitro groups accounts for the smaller reduction in frequency in the studied RAs as compared with those of nitrobenzene RA. In the case of nitrobenzene, v^{as}_{NO2} and v^{s}_{NO2} are shifted downwards with 278-275 cm^{-1} (B3LYP/6-311++G**) [27]. The reported experimental values in DMSO-d$_6$ solution are 285-289 cm^{-1} [34].

Table 3. Experimental and theoretical (B3LYP/6-311++G**) vibrational frequencies (ν in cm^{-1}) and IR intensities (A in km.mol^{-1}, in parentheses), and approximate assignments of the bands for the neutral p-dinitrobenzenes **1a** and **2a**, and the corresponding radical anions **1b** and **2b**

Species	Neutral molecules					RAs				
p-Dinitrobenzene			**1a**					**1b**		
Assignment	$\nu^{as}_{NO2}(ip)$	$\nu^{as}_{NO2}(op)$	$\nu^{s}_{NO2}(ip)$	$\nu^{s}_{NO2}(op)$	$\nu_{CN}+\delta_{CCC}$	$\nu_{CC}+\nu^{as}_{NO2}(ip)$	$\nu^{as}_{NO2}(op)$	$\nu_{CN}+\nu^{s}_{NO2}(ip)$	$\nu_{CN}+\delta_{NO2}(op)$	$\delta_{CCC}+\nu^{s}_{NO2}(op)$
IR [a]	1556	-	-	1339	1106	-	-	-	-	-
Raman [a]	-	1535	1358	-	-	-	-	-	-	-
DMSO-d$_6$ [b]	1552	-	-	1343	-	1417	-	-	1212	-
Calc. [c]	1559 (535.7)	1535 (0)	1336 (0)	1325 (540.2)	1077 (60.7)	1397 (274.4)	1373 (0)	1334 (0)	1233 (3710.9)	1096 (710.6)
m-Dinitrobenzene			**2a**					**2b**		
Assignment	$\nu^{as}_{NO2}(ip)$	$\nu^{as}_{NO2}(op)$	$\nu^{s}_{NO2}(ip)$	$\nu^{s}_{NO2}(op)$	$\nu_{NC}+\delta_{CCC}$	$\nu^{as}_{NO2}(op)$	$\nu_{CC}+\nu^{as}_{NO2}(ip)$	$\nu_{CN}+\nu^{s}_{NO2}(ip)$	$\nu^{s}_{NO2}+\delta_{NO2}(op)$	$\nu_{CN}+\delta_{CCC}+\nu^{as}_{NO2}(op)$
IR [d]	1540	1529	1352	1348	1147	-	-	-	-	-
Raman [d]	1538	1528	1353	1348	1147	-	-	-	-	-
DMSO-d$_6$ [b]	1540	-	-	1349	-	-	1360	1336	1274	-
Calc. [c]	1543 (95.2)	1545 (320.3)	1335 (96.4)	1325 (427.8)	1115 (11.87)	1403 (145.5)	1377 (296.0)	1325 (58.1)	1056 (6862.4)	878 (263.1)

[a] Experimental IR and Raman spectra in solid state [32] [b] Experimental IR spectra in DMSO-d$_6$ solution [22] [c] Calculated frequencies - B3LYP/6-311++G**, scaling factor – 0.9688; [d] Experimental IR and Raman spectra in solid state [33]

CONCLUSIONS

We show in this work that the conversion of p- and m-dinitrobenzene into RAs causes very essential structural, electronic and spectral changes. The two RAs studied exhibit uniform distribution of the odd electron over the two nitro groups, and quinoid-like structure with shorter C-N bonds and longer N-O bonds. The RA species are characterized by a larger and stronger conjugated system than the neutral form. The analysis of the N-O and C-N vibrations allows concluding that the formation of the RAs leads to a considerable increase of the electronic and vibrational interaction between the distant nitro groups. This conclusion is confirmed by the quantum chemical evaluation of the coupling force constants of the two nitro groups in the investigated neutral molecules and corresponding RAs.

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ОХАРАКТЕРИЗИРАНЕ НА СТРУКТУРАТА, ЕЛЕКТРОННОТО СПРЕЖЕНИЕ И ВИБРАЦИОННИТЕ СПЕКТРИ НА РАДИКАЛ-АНИОНИТЕ НА p- И m-ДИНИТРОБЕНЗЕН: ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ

Д. Я. Янчева

Лаборатория „Структурен органичен анализ“, Институт по органична химия с център по фитохимия, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 9, 1113 София

(Резюме)

Структурата, разпределението на заряда и електронното спрежение между функционалните групи, съпътстващи превръщането на два основни нитробензена (p- и m-динитробензен) в съответните радикал-аниони, бяха изследвани чрез B3LYP/6-311++G** пресмятания. Вибрационните спектри на неутралните съединения и радикал-анионите, които са тясно свързани с промените в пространствената и електронната структура, също бяха изследвани и дискутирани. Засиленото вибрационно взаимодействие между нитро групите в радикал-анионните производни беше описано въз основа на анализ на силовото поле и понижение на ИЧ честотите при превръщането в радикали. Анализът на електронната плътност показа, че и в двата случая нитро групите носят равни части от допълнителния електрон: 0.36 е⁻ при p-динитробензена и 0.29 е⁻ при m-изомера. Радикал-анионите се характеризират с хиноидна структура, както и с по-силно електронното спрежение от неутралните съединения, което обхваща по-голяма част от молекулата.