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Electronic structure of 1,3-dinitrobenzene radical anion: a multiconfigurational quantum chemical study

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The structure of 1,3-dinitrobenzene radical anion in the doublet ground and lowest excited states was studied by *ab initio* multiconfiguration CASSCF methods. The results of calculations suggest the existence of one symmetrical and two asymmetrical structures of the radical anion. The energies of these structures were estimated.

Key words: radical anion, 1,3-dinitrobenzene, intramolecular electron transfer, *ab initio* quantum chemical calculations, CASSCF method.

The results of experimental and theoretical studies show that transfer of an electron to a neutral molecule resulting in a radical anion is accompanied by changes in geometric parameters.[1] A particular case is the electron transfer to a symmetrical molecule followed by formation of several isomeric asymmetrical radical anions that are in fast dynamic equilibrium. This phenomenon, which manifests itself in the broadening of spectral lines, was observed[2] in ESR studies of radical anions of aromatic dinitro derivatives.

The available theoretical interpretations of this phenomenon are ambiguous. One of them treats the asymmetrical geometry of radical anions formed from symmetrical neutral molecules as a result of either asymmetrical specific solvation of such molecules[3] or higher stabilization (compared to symmetrical structures) of the asymmetrical structure due to non-specific solvation.[4] An alternative concept[2] assumes an asymmetrical structure of isolated radical anion. To confirm this assumption, *ab initio* UHF и MP2 calcuations of 1,3-dinitrobenzene (DNB) radical anion were carried out,[2] but the calculated spin densities and S^2 values were found to be incorrect and the authors had to use the AM1 semiempirical method. However, they failed to obtain unambiguous results[2] because the energy difference between the symmetrical and asymmetrical forms of the DNB radical anion was too small to state with certainty that isolated DNB radical anion has an asymmetrical structure.

The electronic structure of radical anions of aromatic nitro derivatives is of interest for both basic and applied chemical research.[4] Therefore, we carried out an *ab initio* multideterminant quantum chemical study of the electronic structure of DNB radical anion. The electronic structure of radical anions of aromatic compounds has an antibonding molecular orbital (MO) occupied by an electron; therefore, one should expect that in this case the energy differences between the highest occupied and lowest unoccupied MOs will be much smaller than in the starting neutral molecule and, hence, the effects of configuration interaction witl be much more pronounced.

The aim of this work was to study the electronic structure of the radical anion formed from symmetrical neutral DNB molecule by modern multideterminant methods.

Calculation Procedure

Calculations were carried out using the multiconfiguration complete active space self-consistent field (CASSCF) method[5] with the 6-31G basis set augmented with polarization functions on all atoms and diffuse functions on all heavy atoms (6-31+G** basis set). Full geometry optimization was performed.

The active space used in the calculations of DNB radical anion included twelve valence p-orbitals (six C2p-orbitals, four O2p-orbitals, and two N2p orbitals) and fifteen electrons (CASSCF(15,12)). The system´s wave function included a total of 392040 configurations (doublet state). Calculations of neutral DNB molecule were carried out by the CASSCF(14,12) method with inclusion of 627264 configurations. The dynamic electron correlation was included at the second-order level of multiconfiguration perturbation theory,[6] namely, MRMP2 for the structures with C_{2v} symmetry (electronic states A_2 and B_2) and MCQDPT2 for the structures with C_s symmetry (electronic state A″), using the CASSCF(11,10) wave function.

The calculations were carried out at the Computer Assistance to Chemical Research Center (Russian Academy of Sciences)[7] using the GAMESS US progam package.[8]

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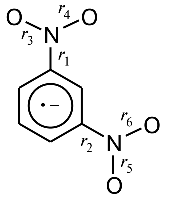


Fig. 1. 1,3-Dinitrobenzene radical anion.

Table 1. Bond lengths (r/Å) in 1,3-dinitrobenzene (DNB) molecule and radical anion (RA) optimized by the CASSCF(15,12)/6-31+G** method

Species	r_1	r_2	r_3	r_4	r_5	r_6
DNB★ molecule	1.460	1.460	1.206	1.205	1.206	1.205
RA-A_2	1.411	1.411	1.222	1.222	1.222	1.222
RA-B_2	1.419	1.419	1.227	1.218	1.227	1.218
RA-A″	1.366	1.463	1.263	1.263	1.210	1.206

★ Calculated by the CASSCF(14,12)/6-31+G** method.

Results and Discussion

Our study of the potential energy surfaces (PESs) of neutral DNB molecule and DNB radical anion revealed minima corresponding to the ground states of these molecular systems. The minimum on the PES of DNB molecule corresponds to the structure with C_{2v} symmetry (DNB-A_2). Three minima were located on the PES of DNB radical anion, two corresponding to asymmetrical structures (RA-A″) and one corresponding to the structure with C_{2v} symmetry (RA-A_2). The geometric parameters of these structures (Fig. 1) are listed in Table 1.

The nitro groups in the neutral molecule and in the RA-A_2 structure are equivalent (see Table 1). However, the energy of the symmetrical RA-A_2 structure is 7 kcal mol^{-1} higher* than those of the RA-A″ structures with significantly different geometric parameters of nitro groups (in particular, the C—N bond lengths differ by 0.09 Å while the N—O bond lengths differ by 0.05 Å).

The results obtained suggest that asymmetry of DNB radical anion is not due to solvation effects, as was assumed earlier,[3,4] being a consequence of higher thermodynamic stability of the asymmetrical RA-A″ structures compared to the symmetrical RA-A_2 structure.

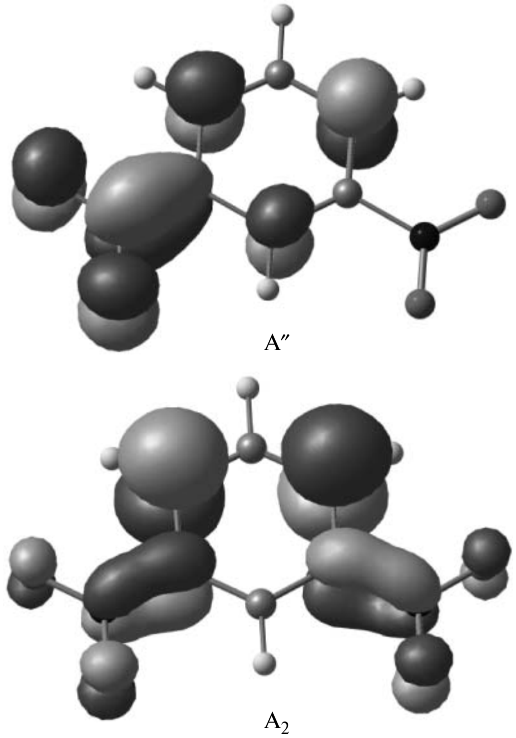
The natural orbital populations calculated for the DNB molecule and RA are listed in Table 2. The wave functions of both neutral molecule and radical anion have essentially multiconfiguration characters with 75% contributions of the main determinant (configuration). In addition, the populations of the first two orbitals exceed a value of 1.98, which allowed us to reduce the size of the active space to ten orbitals. The natural orbitals, on which the unpaired electron density is localized, calculated for the RA-A″ and RA-A_2 structures are shown in Fig. 2.

Table 2. Natural orbital populations calculated for 1,3-dinitrobenzene (DNB) molecule and radical anion (RA)

Orbital	DNB★	RA-A_2★★	RA-B_2★★	RA-A″★★
1	1.986	1.986	1.987	1.993
2	1.986	1.986	1.987	1.991
3	1.960	1.966	1.972	1.986
4	1.902	1.957	1.948	1.962
5	1.900	1.938	1.935	1.916
6	1.896	1.938	1.931	1.911
7	1.895	1.924	1.922	1.908
8	0.134	1.014	1.013	1.008
9	0.128	0.104	0.119	0.122
10	0.093	0.079	0.084	0.089
11	0.083	0.069	0.064	0.079
12	0.036	0.040	0.040	0.037

★ Obtained from CASSCF(14,12)/6-31+G** calculations.
★★ Obtained from CASSCF(15,12)/6-31+G** calculations.

In contrast to the RA-A_2 structures the electronic structure of RA-A″ is characterized by almost zero unpaired electron density on one nitro group (see Fig. 2). As a result, the C—N distance in this group increases to 1.46 Å while the N—O bonds are reduced to 1.21 Å (see Table 1). Therefore, a conversion between the RA-A″ structures can be interpreted as intramolecular electron



A″

A_2

Fig. 2. Natural orbitals with 1.0 populations calculated for the RA-A″ and RA-A_2 structures of 1,3-dinitrobenzene radical anion.

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* Calculated without inclusion of dynamic electron correlation.

transfer, as was actually detected by spectral methods.[2] In the case of DNB radical anion this process can not be described by a concentional model,[9] which approximates the reaction profile by two electron terms. This is associated with the possibility for a maximum (analog of B$_2$ point in Fig. 3) to appear in the transition state on crossing of the terms corresponding to the RA-A″ structures (see Fig. 3). However, the results of our calculations show that the RA-A$_2$ structure corresponds to a minimum on the PES. Therefore, it seems appropriate to use the three-level model,[10,11] thich treats the minimum corresponding to the RA-A$_2$ structure as a result of symmetry-allowed mixing with excited state.

In order to interpret the nature of stationary points on the PES, we calculated the PES sections along the coordinate of intramolecular electron transfer for DNB radical anion in the ground and excited doublet electronic states by the multiconfiguration perturbation theory methods. The structures with A″ symmetry (see Table 1) were calculated using the state-averaged CASSCF (SA-CASSCF) method with equal weights of the ground and excited states followed by the use of quasi-degenerate perturbation theory, MCQDPT2. The structures with the A$_2$ and B$_2$ symmetries were calculated using the MRMP2 theory for pure states.

The sections of the PESs for the doublet ground and excited states are shown in Fig. 3.* Here, a salient feature is that the curves avoided crossing in certain regions. As a result, the curve for the ground state has three minima. Two somewhat deeper minima correspond to the RA-A″ structure while the minimum lying 4 kcal mol^{-1} higher in energy corresponds to the RA-A$_2$ structure. Probably, intramolecular electron transfer involves the structure with A$_2$ symmetry (local minimum) and is characterized by an effective activation energy of ~6 kcal mol^{-1}.

Thus, our CASSCF quantum chemical calculations showed that DNB radical anion in the ground state exists as two structures with C_s and C_{2v} symmetries (electronic states A″ and A$_2$, respectively) and energies differnig by 4 kcal mol^{-1}. The more stable structure has asymmetrical geometry and the unpaired electron localized on one NO$_2$ group.

Detailed elucidation of the dymanic behavior of DNB radical anion requires the inclusion of vibronic interaction and the use of quantum dynamics methods and may be a subject of further studies.

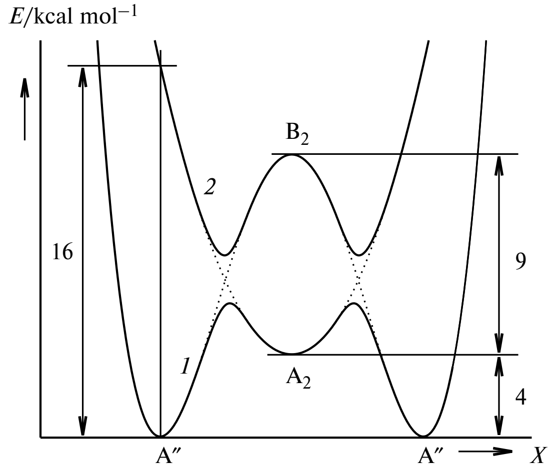

Fig. 3. Sections of the potential energy surface along the intramolecular electron transfer coordinate (X) in 1,3-dinitrobenzene radical anion in the ground (*1*) and lowest excited (*2*) electronic states, obtained from CASSCF(11,10)/6-31+G**//MRMP2/6-31+G** and SA-CASSCF(11,10)/6-31+G**//MCQDPT2/6-31+G** calculations.

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* Here, the reaction coordinate characterizes the degree of deviation of the system´s geometry from symmetrical C_{2v}-conformations.