Brief Communications

Structure of the 1,3-dinitrobenzene dianion studied by multiconfigurational methods

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The structure of the 1,3-dinitrobenzene dianion in the ground and lowest excited electron states was studied by quantum chemical methods. The dianion, unlike the radical anion, is characterized by the symmetrical structure in both the ground triplet ($^3B_1$) and lowest excited singlet ($^1A_1$) states. The wave function of the singlet state has the biradical character to a great extent. The singlet-triplet splitting calculated by the CASSCF and MRMP2 methods is 6 and 2 kcal mol^{-1}, respectively.

Key words: dianion, 1,3-dinitrobenzene, quantum chemical calculations.

Dianions (DAs) formed as a result of the transfer of two electrons to a neutral molecule, as well as radical anions (RAs), play an important role in many reactions involving organic compounds.[1] However, the electronic structure of DAs has been studied so poorly compared to the electronic structure of RAs.

An important feature of the RA and DA is the presence of electrons on the antibonding MO, due to which differences in energies of the highest occupied and lowest unoccupied MOs are much lower than those in the initial neutral molecule and in contrast to the effects of configuration interaction that are stronger. We have earlier[2] studied the structure of the 1,3-dinitrobenzene (DNB) RA in the ground and lowest excited doublet states by the CASSCF method. The calculations showed the presence of two asymmetrical and one symmetrical structures of the RA, and the latter has a greater (compared to the asymmetrical structures) energy. Since the major facors determining the direction and rate of reactions of RA and DA is the electron density distribution on the frontier MOs, it was of interest to elucidate whether the asymmetry is retained on going from RA to DA.

Calculation Methods

Calculations were performed by the multiconfigurational self-consistent field method in the variant of complete active space (CASSCF).[3] The 6-31G basis set augmented by the polar-

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ization functions on all atoms and diffuse functions on all heavy atoms (6-31+G**) was used. In the calculation of the 1,3-DNB DA, the active space consisted of 12 valent p-orbitals (six C-2p-orbitals, four O-2p-orbitals, and two N-2p-orbitals) and 16 electrons, *i.e.*, the CASSCF(16,12) was applied. The wave function included 245 025 and 174 240 configurations for the singlet ($^1A_1$) and triplet ($^3B_1$) states, respectively. The dynamic electron correlation was taken into account in the MRMP2 second-order multireference perturbation theory[4] based on the CASSCF(16,12) wave function. The calculations were performed at the Computer Center for Chemical Investigation Support[5] of the Russian Academy of Sciences using the PC GAMESS quantum chemical program package.[6,7]

Results and Discussion

Unlike the earlier[2] studied RA, the study of the potential energy surfaces of the DNB dianion showed only the minima corresponding to the symmetrical (C_{2v}) structures in both the triplet ($^3B_1$) and singlet ($^1A_1$) states. The geometric parameters of these structures (Fig. 1) are presented in Table 1. As can be seen from the data in Table 1, the DNB DA in the $^3B_1$ and $^1A_1$ states is characterized by almost the same geometric parameters. The most significant distinction is the elongation of the C—N bonds by 0.02 Å on going from the triplet to singlet state. Another peculiarity is a very low value of the singlet-triplet splitting. The $^3B_1$ triplet state is more stable than the $^1A_1$ singlet state by only 6 kcal mol^{-1} (CASSCF). The perturbation theory (MRMP2) gives still lower value: 2 kcal mol^{-1}. These two specific features indicate the possible existence of the point of intersection of terms in the vicinity of the minima and, as a consequence, the singlet-triplet transition upon vibrational motion of the nuclei proceed more readily.

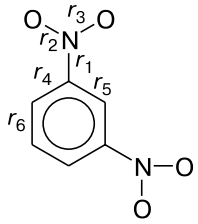

Fig. 1. Molecule of the 1,3-dinitrobenzene dianion and introduced designations.

Table 1. Optimized (CASSCF(16,12)/6-31+G**) bond lengths (Å) for the DNB molecule and its DA

Bond	DNB*	DA-$^1A_1$	DA-$^3B_1$
r_1	1.460	1.404	1.381
r_2	1.206	1.282	1.285
r_3	1.205	1.274	1.273
r_4	1.392	1.408	1.418
r_5	1.389	1.406	1.414
r_6	1.394	1.396	1.395

* See Ref. 2.

Table 2. Occupancies of the natural orbitals (CASSCF(16,12)/6-31+G**) for the DNB molecule and its DA

Orbital	DNB*	DA-$^1A_1$	DA-$^3B_1$
1	1.986	1.998	1.998
2	1.986	1.998	1.998
3	1.960	1.995	1.994
4	1.902	1.993	1.994
5	1.900	1.964	1.961
6	1.896	1.918	1.911
7	1.895	1.911	1.903
8	0.134	1.150	1.006
9	0.128	0.864	1.004
10	0.093	0.094	0.102
11	0.083	0.081	0.091
12	0.036	0.035	0.039

* See Ref. 2.

The site occupancies of the natural orbitals for the DNB molecule and its DA are given in Table 2. The data in Table 2 show that the wave functions of both the neutral molecule and RA are multiconfigurational. In addition, an analysis of the occupancies of the frontier orbitals for the $^1A_1$ state (Fig. 2) suggests that the DNB DA in the

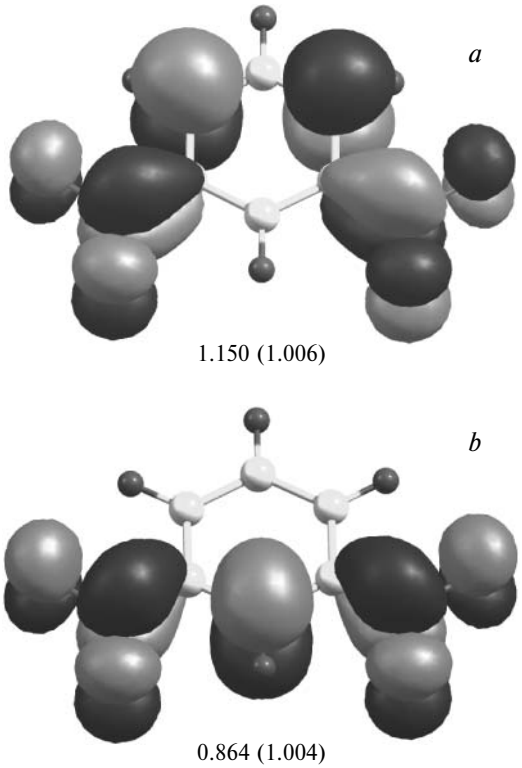

Fig. 2. Frontier natural orbitals and their occupancies for the DA-$^1A_1$ (*a*) and DA-$^3B_1$ (*b*) structures; occupancies for DA-$^3B_1$ are given in parentheses.

singlet state represents a biradical particle. The considerable destabilization of the singlet state and the decrease in the singlet-triplet splitting are related to the biradical nature.

The question about multiplicity of organic dianions, including electrochemically generated ones, remains yet unanswered.[8] The formation of triplet DAs was experimentally detected only for the two-electron cathodic reduction of 2,2´,4,4´-tetranitrobiphenyl[8] and the interaction of two 1,3,5-trinitrobenzene radical anions accompanied by π-complex formation.[9] In the both cases,[8,9] an electron pair was distributed between two unconjugated benzene rings. The results obtained show that the triplet state can also be characteristic of DAs of mononuclear aromatic derivatives.

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