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X-ray Diffraction and Ab Initio Quantum-Chemical Study of the Charge Density in the Crystals of Meisenheimer Complexes−Derivatives of 2,4,6-Trinitrobenzene and 5,7-Dinitroquinoline

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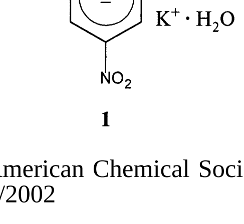
The experimental charge density in the crystals of two Meisenheimer complexes (MC), hydrate of potassium 2′,4′,6′-trinitro-3′,5′-dihydrospiro(1,3-dioxolane-2,8′-cyclohexadienide) **1** and potassium 5′,7′-dinitro-5′,8′-dihydrospiro(1,3-dioxolane-2,8′-quinolinide) **2** has been studied using low-temperature, high-resolution X-ray diffraction data. A theoretical study of this charge density obtained from HF/6-311++G** and B3LYP/6-311++G** calculations has been carried out as well for comparison. It was shown that potassium cations coordinated with σ-complex in these crystals considerably affect the charge density distribution. Each anionic σ-complex in both structures is surrounded by five cations, and the specific influence of the cation in each position on the charge density characteristics has been revealed.

Introduction

The formation of the Meisenheimer complexes, or anionic σ-complexes, is a key step for the two major mechanisms of reactions of the nucleophilic aromatic substitution: $S_{N}Ar$, and the vicarious nucleophilic substitution (VNS).[1,2] These intermediate σ-complexes are further converted into various products depending on structure and stability of organic anions.[3−5] Therefore, there has been a great interest in the molecular and electronic structure of the MC during past decade.[1−7] However, explicit determination of the geometry of MC is a difficult task because these compounds usually form poor single crystals.[1−4] Moreover, the accuracy of most of the published X-ray diffraction data[8−16] for MC is not enough to analyze their geometries in detail. Probably, structural investigations of spirocyclic anionic σ-complexes are more promising in this respect because these MCs were found to form relatively good and stable single crystals. Our recent studies of MCs were devoted to the conformational analysis of similar spirocyclic compounds,[17,18] or the study of zwitterionic Meisenheimer complexes.[19−22] Moreover, we have investigated, for the first time, the charge density distribution in the crystal of the Meisenheimer complex of the potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-oxazolidine-2,8′-quinolinide).[23] This preliminary study has demonstrated that the electronic structure of the anionic σ-complex is drastically influenced by the manner of potassium cation coordination to the organic anion. On the other hand, we met with some difficulties in reproducing of some topological characteristics of the charge density distribution of this σ-complex studied by Hartree−Fock calculations.[23]

Previous theoretical studies of the MC demonstrated some contradictions between results of calculations using different semiempirical[17,24,25] and ab initio[17,26,27] methods as well. For example,[26] the study of the nucleophilic aromatic substitution reaction between 4-Cl−Ph-CO−SMe and CH_3COO^- by the PM3 and DFT methods indicated a formation of the stable MC during reaction. However, the same calculation using the HF/6-31G** method resulted in the opposite conclusion. The most probable reason for such a contradiction is an accurate description of the charge density distribution in anionic σ-complexes using different quantum-chemical methods.

In the present paper, we report results of the experimental determination of the charge density distribution in the crystals of two Meisenheimer complexes, hydrate of potassium 2′,4′,6′-trinitro-3′,5′-dihydrospiro(1,3-dioxolane-2,8′-cyclohexadienide)-**1** and potassium 5′,7′-dinitro-5′,8′-dihydrospiro(1,3-dioxolane-2,8′-quinolinide) **2**. Ab initio calculations of the charge density for **1** and **2** have been carried out as well for comparison.



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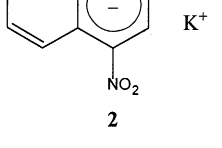

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TABLE 1: Crystal Data and Results of the Multipole Refinement for Compounds 1 and 2

	1	2
formula	$C_8H_8N_3O_9K\ H_2O$	$C_{11}H_8N_3O_6K$
M_r	329.27	317.3
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a(Å)	8.523(1)	7.759(2)
b(Å)	11.456(2)	8.677(2)
c(Å)	11.989(2)	9.347(3)
α(°)	90	88.45(2)
β (°)	91.351(4)	77.77(2)
γ(°)	90	75.46(2)
V (Å^3)	1170.2(3)	595.1(3)
Z	4	2
D_c (g/cm^3)	1.869	1.771
μ (mm^{-1})	0.512	0.482
F(000)	672	324
T (K)	110(2)	153(2)
crystal size (mm)	0.5 × 0.4 × 0.3	0.5 × 0.4 × 0.2
scans	φ and ω	$\theta/2\theta$
diffractometer	Bruker SMART CCD	Siemens P3/PC
radiation	Mo K_α	Mo K_α
$2\theta_{max}$ (°)	115	82
total reflections	55315	10232
unique reflections	15884	7886
R_{int}	0.038	0.029
used reflections with $F > 3\sigma(F)$	10349	4391
no. of parameters	406	411
wR2	0.099	0.101
R1 [$F > 4\sigma(F)$]	0.029	0.0297
S	0.98	0.92

Experimental Section

Preliminary X-ray structural data for compounds **1** and **2** were reported in the recent past.[28,18] Single crystals of **1** and **2** were obtained by a slow evaporation of the water and acetonitrile solutions, respectively. Crystallographic data and results of the multipole refinements are summarized in Table 1.

Data reduction was carried out with the SAINT,[29] SADABS[30] programs for **1**, and the XDISK[31] for **2**. The structures were solved by direct method using the SHELXTL-97 and SHELXTL PLUS program packages.[32,33] Positions of hydrogen atoms were located from the Fourier difference maps. Full-matrix least-squares refinement against F^2 in anisotropic approximation for non-hydrogen atoms and in isotropic one for H atoms was used.

The multipole refinement of both structures in the framework of the Hansen−Coppens multipole formalism[34] was carried out using the XD software package.[35] The multipole description of all C, N, and O atoms in **1**, **2** was extended to the octupolar level. To reduce the number of multipole parameters, all carbon and oxygen atoms in both structures were restricted by the local symmetry *m*, with the exception of the C(sp^3) spiro-atoms. No symmetry restrictions were applied to these C(sp^3) atoms. The nitrogen atoms of the nitro groups were assigned the *mm2* symmetry. At last, the N(1) atom in **2** was assumed to has the local symmetry *m*. Definitions of the local coordinate systems for the structures **1**, **2** are given in the Supporting Information.

Before start the multipole refinement, the H atom positions were adjusted “ideal” C−H (1.085 Å) and O−H (0.96 Å) distances taken from the neutron diffraction data and were held constant. All H-atoms were treated at the dipole level. In both cases, the potassium cation was kept spherical and no charge transfer between the cation and organic anion was allowed. Bond lengths for the compounds **1**, **2** are listed in Tables 2 and 3. Atomic coordinates, selected bond and torsion angles, as well as data of the rigid body analysis are given the in Supporting Information.

Experimental charge density distributions in **1** and **2** were analyzed in the framework of Bader’s theory of “Atoms in Molecules” (AIM).[36] It is important for further considerations that the magnitude of $\rho(\boldsymbol{r})$ at the bond critical point (3, −1), which is usually denoted as $\rho_b(\boldsymbol{r})$, reflects and is proportional to a bond strength and its order. Moreover, the ellipticity ϵ of a bond is also directly related to the values of its π component.[36]

Results of topological analyses of the charge density distribution for compounds **1**, **2** were derived using XDPROP module of the XD package, and are presented in Tables 2,3. Experimental atomic charges in **1** and **2** were estimated as difference between the number of electrons in the valence shell of the given atom and its monopole populations. They are given in the Supporting Information. The static deformation density (DD) was obtained as the difference between the total charge density and the superposition of the atomic spherical densities. The DD maps were plotted using the XDGRAPH routine.

Rigid body analysis based on results of the multipole refinement of **1** states that all bonds are satisfying the Hirshfeld criteria,[37] and the maximum value of the MSDA ($8 \cdot 10^{-4}$ Å) is observed for the O(7)−C(7) bond. For structure **2**, the maximum value of MSDA ($15 \cdot 10^{-4}$ Å) was found for the O(5)−C(8) bond.

Quantum-chemical calculations were performed for different systems anion−cation K^+ realized in the crystal structures. Each organic anion in the crystals of **1** or **2** is surrounded by five potassium cations (Figures 1, 4). Therefore, the systems calculated consisted of the corresponding anions (**1** or **2**) and one of the surrounding cation. All five positions of the K^+ cations were taken into account. The single anions **1** and **2** were calculated as well. The geometry of all of the systems and the single MC was taken from the X-ray data without optimization. Computations were performed at the HF/6-311++G** level of theory using the GAMESS program,[38] and at the B3LYP/6-311++G** level with the GAUSSIAN package.[39] Topological analysis of theoretical charge density distribution was carried out with the program EXTREME, incorporated into the program package AIMPAC.[40] These results are presented in Tables S1 and S2 of the Supporting Information. Geometry optimization of the MC **1** at the HF/6-31+G* and B3LYP/6-31+G* levels has been done as well using GAMESS and GAUSSIAN programs.

Results and Discussion

Molecular and Crystal Structure of 1. Low-temperature X-ray diffraction study of **1** (Figure 1, Table 2) has demonstrated that the six-membered ring C(1)...C(6) adopts a flattened sofa conformation and the deviation of the C(1) atom from the plane of the other atoms (r.m.s. deviation 0.015 Å) of this ring is equal to −0.0746(5) Å. The dioxolane ring has a flattened twist conformation. The C(8) and O(8) atoms are deviated from the plane of three remaining atoms of the ring by −0.048(1) and 0.064(1) Å, respectively. The interplanar angle between least-squares planes of the five and six-membered rings is equal to 88.56(2)°.

The C(2)−C(3) and C(5)−C(6) bond lengths in **1** are almost equal, and their values, (1.3653(5) and 1.3679(5) Å), are considerably shorter than those for the C(3)−C(4) and C(4)−C(5) bonds (1.4034(5) and 1.3985(6) Å, respectively).

The nitro groups in **1** are rotated with respect to the conjugated part of the six-membered ring C(2)...C(6); the corresponding torsion angles O(2)−N(1)−C(2)−C(3), O(3)−N(2)−C(4)−C(3) and O(6)−N(3)−C(6)−C(1) are equal to −8.36(6), −11.26(6), and 16.96(5)°, respectively.

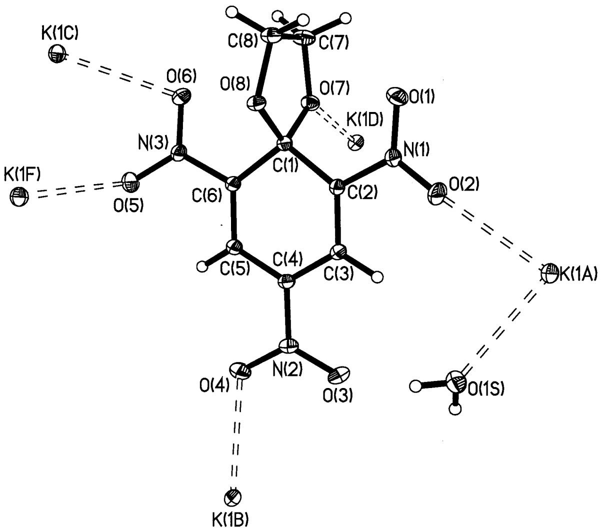


Figure 1. Molecular structure and arrangement of the anion **1** by potassium cations in the crystal. The K(1B), K(1C), K(1D), and K(1F) atoms are obtained by the $x - 0.5, -y + 0.5, z + 0.5$; $x, y + 1, z$; $-x + 0.5, y + 0.5, -z + 1.5$ and $-x + 1, -y + 1, -z + 2$ symmetry operations, respectively.

TABLE 2: Bond Lengths (l, Å) and Topological Characteristics ($\rho_b(\boldsymbol{r})$, e/Å^3, $\nabla^2\rho(\boldsymbol{r})$, e/Å^5, ϵ) of the Bond Critical Points for the Structure 1 from the Multipole Refinement

bond	l	$\rho_b(\boldsymbol{r})$	$\nabla^2\rho(\boldsymbol{r})$	ϵ
C(2)−N(1)	1.4362(7)	1.88(2)	−13.19(9)	0.18
C(4)−N(2)	1.4183(6)	1.99(2)	−15.27(9)	0.21
C(6)−N(3)	1.4288(6)	1.97(2)	−15.69(9)	0.20
C(1)−C(2)	1.5140(6)	1.77(2)	−11.87(6)	0.09
C(2)−C(3)	1.3654(7)	2.22(2)	−21.39(8)	0.23
C(3)−C(4)	1.4027(7)	2.08(2)	−18.38(8)	0.16
C(4)−C(5)	1.3992(6)	2.15(2)	−17.60(8)	0.27
C(5)−C(6)	1.3692(7)	2.22(2)	−20.99(8)	0.32
C(1)−C(6)	1.5115(6)	1.75(2)	−12.19(6)	0.06
O(1)−N(1)	1.2356(8)	3.27(3)	−7.0(1)	0.10
O(2)−N(1)	1.2382(7)	3.11(3)	−2.2(1)	0.11
O(3)−N(2)	1.2363(7)	3.30(3)	−7.3(1)	0.03
O(4)−N(2)	1.2484(8)	3.26(3)	−6.5(1)	0.10
O(5)−N(3)	1.2471(8)	3.15(3)	−3.1(1)	0.09
O(6)−N(3)	1.2394(7)	3.24(3)	−6.1(1)	0.07
O(7)−C(1)	1.4275(7)	1.89(2)	−11.23(9)	0.08
O(8)−C(1)	1.4298(6)	1.83(2)	−8.73(9)	0.14
O(7)−C(7)	1.4332(7)	1.78(2)	−10.06(9)	0.09
O(8)−C(8)	1.4344(7)	1.85(2)	−8.40(9)	0.01
C(7)−C(8)	1.5283(7)	1.58(2)	−9.68(5)	0.07
K(1A)-O(2)	2.6888(6)	0.103(5)	2.02(3)	0.04
K(1B)-O(4)	2.7608(6)	0.090(6)	1.80(3)	0.00
K(1C)-O(6)	2.7959(6)	0.084(6)	1.68(3)	0.05
K(1D)-O(7)	2.7326(6)	0.098(6)	1.96(3)	0.04
K(1F)-O(5)	3.1927(6)	0.028(5)	0.56(3)	0.01

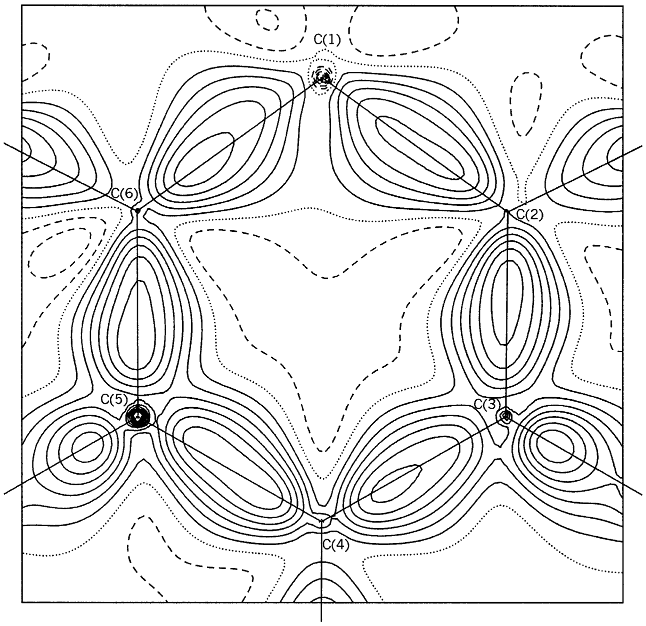
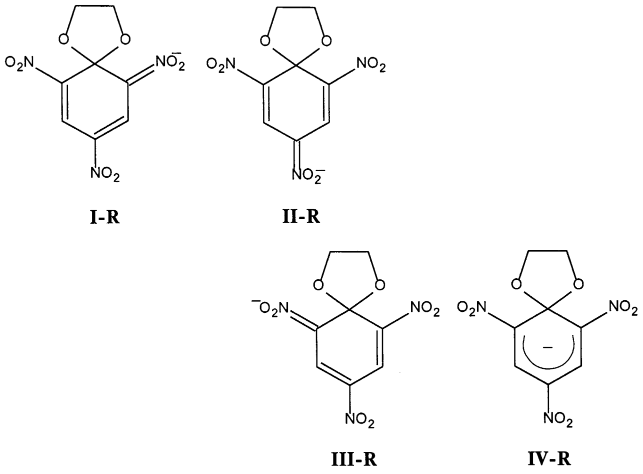


Figure 2. Static deformation density map in the section passing through the atoms C(1), C(3), and C(5) of MC **1**. The map is contoured at intervals of 0.1 e/A^3.

SCHEME 1



The bonds lengths C(2)−N(1) and C(6)−N(3) of the nitro groups in the *ortho*-positions are similar and equal to 1.4369(5) and 1.4299(5) Å. On the contrary, the "*para*" C(4)−N(2) bond length 1.4178(5) Å is considerably shorter.

It is reasonable to assume that four resonance forms **I−R−IV−R** contribute to the molecular and electronic structure of **1** (Scheme 1).[41] Our analysis based on the bond length distribution in **1** (see Table 2) has driven us to a conclusion that contribution of the resonance form **II−R** is predominant.

In the crystal of **1**, each anion is surrounded by five potassium cations (Figure 1). Thus, five oxygen atoms of different anions coordinate each cation. Moreover, two neighboring K$^+$ cations separated by 3.8254(5) Å, are bounded by two bridged solvate water molecules (K(1A)−O(1S) 2.8247(5) Å, K(1A)−O(1S)^i (1-x, $-y$, 2-z) 2.9337(5) Å). Thus, the coordination number of K$^+$ cation in the structure of **1** is equal to 7. Hydrogen atoms of the water molecule form three H-bonds with participation of the oxygen atoms of the nitro groups in *ortho*-positions and the O(6) atom of the dioxolane ring. Geometry of H-bonds is given in the Supporting Information.

Charge Density Distribution in the Crystal of 1. All peaks of the positive DD on the C−C bonds of the conjugated part of the C(1)...C(6) ring have approximately the same magnitude about 0.6 e/Å^3 (Figure 2). This is in some contradiction with above-mentioned alternation of the bond lengths in the ring. Topological analysis of the charge density was found to be more fruitful in consideration of peculiarities of the bonding in the structure of **1** (Table 2).

The values of the $\rho_b(\boldsymbol{r})$ and ellipticities ϵ of the ring bonds are considerably different. First of all, the $\rho_b(\boldsymbol{r})$ values for the C(2)−C(3) and C(5)−C(6) bonds are larger than those for the C(3)−C(4) and C(4)−C(5) bonds. This supports conclusion about predominant contribution of the resonance form **II−R** to the electronic structure of the anion **1**. The most interesting is the fact that both the $\rho_b(\boldsymbol{r})$ value (2.15(2) e/Å^3) and ellipticity

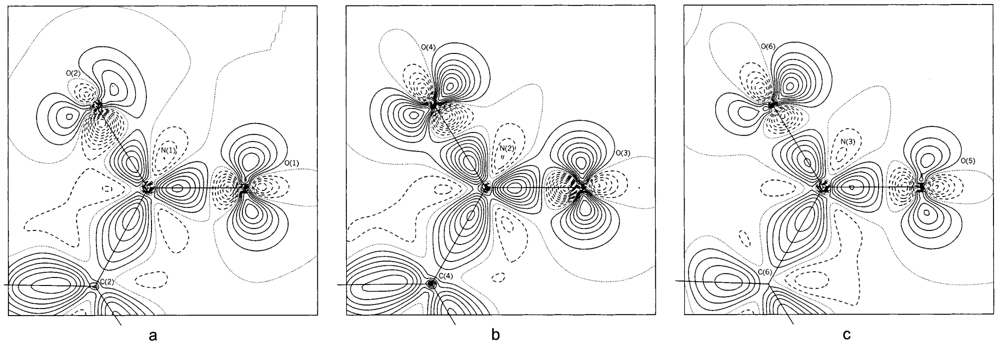


Figure 3. Static deformation density map in the section passing through the atoms O(1), N(1), and O(2) (*a*), O(3), N(2), and O(4) (*b*) and O(5), N(3), and O(6) (*c*) of MC **1**. The map is contoured at intervals of 0.1 e/A^3.

(0.27) of the C(4)−C(5) bond are essentially larger than corresponding values (2.08(2) e/Å^3 and 0.16) for the C(3)−C(4) bond. This may indicate that contribution of the canonic forms **I−R** and **III−R** are not equal, and the contribution of the **III−R** form is larger. Thus, the electronic structure of MC **1** in the crystal is different from that of the isolated anion **1** optimized by using various quantum-chemical approaches. For instance, our optimization of the isolated anion **1** at the B3LYP/6-31+G* and HF/6-31+G* levels resulted to the structure **1** having symmetry C_{2v} for which contributions of the **I−R** and **III−R** forms have to be equal. Further analysis of the experimental charge density gives other evidences supporting inequality of contribution of the **I−R** and **III−R** forms. Despite the equality the peak heights of DD for the C−N bonds of the nitro groups in *ortho*-positions (Figure 3), magnitudes of the $\rho_b(\boldsymbol{r})$ (1.88(2) e/Å^3) and ϵ (0.18) for the N(1)−C(2) bond are lower than those for the N(3)−C(6) bond (1.97(2) e/Å^3 and 0.20, respectively). Moreover, topological values for the N(3)−C(6) bond are very close to those for the C−N bond of the *para*-nitro group (Table 2).

On the contrary, according to topological analysis of the charge density based on the B3LYP/6-311++G** calculations[42] of the single anionic σ-complex **1**, the values of the $\rho_b(\boldsymbol{r})$ and ϵ for the C−N bonds of the nitro groups in *ortho*-positions are essentially the same and lower than those for the C(4)−N(2) bond. In addition, the $\rho_b(\boldsymbol{r})$ values for the C(3)−C(4) and C(4)−C(5) bonds are much closer to each other than corresponding experimental data. Thus, theoretically obtained charge density of the single MC **1** does not reveal significant difference in contribution of the resonance forms **I−R** and **III−R**. However, the contribution of the resonance form **II−R** remains predominant in this case.

Experimental charge density of the anion **1** is influenced by the crystal packing field. This might be a reason of a discrepancy between features of the experimental and theoretical charge density for the single anionic σ-complex **1**. Each MC **1** in the crystal is coordinated by the five potassium cations, and an important suggestion can be made that influence of the crystal field on the charge density distribution is primary due to an influence of the potassium cations directly surrounding MC in the crystal.[23]

It should be mentioned that for all coordination bonds K−O in the crystal of **1** the critical points (3, −1) have been found. The values of the $\rho_b(\boldsymbol{r})$ for all K−O bonds except the K(1F)−O(5) are in the range 0.08−0.1 e/Å^3. The lower value of the $\rho_b(\boldsymbol{r})$ 0.03 e/Å^3 for the K(1F)−O(5) contact results from the fact that this coordination bond is longer. The values of the Laplacian $\nabla^2\rho(\boldsymbol{r})$ for the K−O contacts are in the range 0.6−2.0 e/Å^5. Thus, coordination bonds K−O are typical examples of the closed-shell interactions in the framework of the AIM theory.[36]

Influence of Potassium Cations on the Charge Density in MC 1. A manner in which each cation affects charge density of the anionic σ-complex in the crystal may be established by calculation of the theoretical charge density of a corresponding system anion **1**− cation. Five systems **1** −K$^+$ referred as (A)−(F) with different positions of cations K(1A)−K(1F) have been calculated.

In the system (A), cation K(1A) coordinates the oxygen atom O(2) of the nitro group in the *ortho* position to the spiro-carbon atom C(1). In this system, according to B3LYP/6-311++G** calculation, the ellipticity of the C(2)−N(1) is enlarged, whereas it is decreased for the other C−N bonds in comparison with corresponding values for the single MC **1**. All changes of ϵ have magnitudes about $\Delta\epsilon = 0.04$. As a result, the ellipticity of the C(2)−N(1) bond in (A) becomes larger than that for the other C−N bonds. The values of $\rho_b(\boldsymbol{r})$ for C−N bonds are changed in the similar way. The order n of the C(2)−N(1) bond is increased as well, whereas similar values for C(4)−N(2) and C(6)−N(3) bonds become lower according to Hartree−Fock calculations. Moreover, considerable changes are observed for bond orders of the C−C bonds for the conjugated part of the six-membered ring of (A). The values n(C(2)−C(3)) and n(C(4)−C(5)) are decreased ($\Delta n = -0.15$ and -0.05, respectively), whereas values n(C(3)−C(4)) and n(C(5)−C(6)) are enlarged ($\Delta n = 0.11$ and 0.04, respectively) as compared with corresponding bond orders of the single MC **1**.

According to both DFT and Hartree−Fock calculations, the values of $\rho_b(\boldsymbol{r})$ and ϵ of these C−C bonds in (A) are changed in the same way as their bond orders but absolute magnitudes of these changes are less significant. Redistribution of the charge density in (A) as compared to the single MC **1** due to the influence of the K(1A) cation may be described by increasing the contribution of the **I−R** resonance form to the electronic structure of the anion.

In the system (B) the charge density is redistributed by another way. Values of the $\rho_b(\boldsymbol{r})$ and ϵ of the *para* N(2)−C(4) bond as well as its bond order are increased, but these characteristics for the two other C−N bonds in the *ortho*-positions are decreased in comparison with the single MC **1**. In addition, an increase of the C(2)−C(3) and C(5)−C(6) bond orders and decreasing the C(3)−C(4) and C(4)−C(5) ones are seen in the system (B). The similar trend is also observed for ellipticities of these C−C bonds. Thus, we may conclude that there is an increase of the **II−R** resonance form contribution in the system (B).

Effects of cations in the systems (C) and (F) are similar and opposite to that in the system (A). The values of the $\rho_b(\boldsymbol{r})$ and ϵ for the C(6)−N(3) bond are increased, bond orders n(C(2)−C(3)) and n(C(4)−C(5)) are also increased, but n(C(3)−C(4)) and n(C(5)−C(6)) are decreased as compared to those values for the single MC **1**. In general, the influence of both K(1C) and K(1F) cations gives rise to increasing the contribution of the form **III−R**. Nevertheless, effect of the K(1C) is stronger than that of K(1F). For instance, the value of the $\rho_b(\boldsymbol{r})$ for the C(6)−N(3) bond is equal to 1.885 e/Å^3 and 1.869 e/Å^3 with the bond ellipticity 0.32, 0.28 in the (C) and (F) systems, respectively.

Charge density redistribution is relatively small for the system (D) where anion is coordinated by K$^+$ cation via the O(7) atom of the dioxolane ring. However, the values of $\rho_b(\boldsymbol{r})$ of all C−N bonds become lower. Very likely, this may indicate increasing the **IV−R** canonic form contribution.

Thus, results of theoretical topological analysis of the charge density for systems (A)—(F) demonstrate that effects of cations in each position give rise to noticeably changes of the bond orders, ellipticities, and values of the $\rho_b(\boldsymbol{r})$ for the C−N bonds of the nitro groups, and the C−C bonds of the conjugated part of the six-membered ring. Characteristics of these bonds determine contribution of the various canonic forms to the structure of anionic σ-complex **1**. The changes of the ϵ and $\rho_b(\boldsymbol{r})$ values caused by cations are considerable for the C−N bonds, whereas their orders are slightly changed. For the C−C bonds, the opposite situation is observed.

It is clear that the total influence of the potassium cations located at different positions with respect to the organic anion in the crystal **1** should be a some superposition of individual cation impacts. In particular, contribution of the forms **I−R** and **II−R** to the electronic structure of **1** are enlarged by effects of the K(1A) and K(1B) cations, respectively. Both the K(1C) and K(1F) cations favor to increase contribution of the **III−R** form. Finally, coordination of cation with the oxygen atom of the dioxolane ring gives rise to increase contribution of the **IV−R** form. Thus, two positions of the cation favor contribution of the **III−R** form, whereas contribution of the each other form is favored just by one cation. This may explain the inequality in contributions of the **I−R** and **III−R** forms to the electronic structure of the anion observed in the experimental charge density. On the other hand, the form **III−R** does not dominate because for the single MC **1** contribution of the **II−R** form is considerable.

Further details of influence of the cations on the charge density distribution in MC were obtained during investigation of the compound **2**.

Molecular and Crystal Structure of the Compound 2. The X-ray structural study of the crystal **2** (Figure 4) has shown that six-membered ring C(4)...C(9) adopts a sofa conformation. The deviation of the C(8) atom from the plane of the other atoms of the ring is equal to 0.248(1) Å. The dioxolane ring adopts twist conformation and deviations of the O(6) and C(11) atoms from plane of the three rest atoms of the ring are equal to −0.218(2) and 0.313(2) Å, respectively.

The C(6)−C(7) 1.374(1) Å and C(4)−C(9) 1.420(1) Å bond lengths (Table 3) are elongated in comparison to similar bonds in MC **1** and other anionic σ-complexes of 2,4,6-trinitrobenzene.[9,43] It is important, that the C(5)−C(6) bond length (1.396(1) Å) is almost the same as the corresponding bond in the structure **1** and hence, the difference between the C(5)−C(6) and C(6)−C(7) bonds is less pronounced in **2**. It should be noted the C(8)−C(9) bond length (1.540(1) Å) in **2** is significantly longer than the average value[44] 1.503 Å for the C(sp^3)−C(Ar) bond. This may be attributed to the presence of intramolecular shortened contacts between the nitrogen atom of quinoline fragment and the carbon atom of dioxolane ring: N(1)...C(11) 3.054(1) Å (the sum of the van der Waals radii[45] is 3.21 Å). In the anionic σ-complexes of the trinitrobenzene where similar shortened contacts are absent, the C(sp^3)−C(Ar) bond lengths have normal values.[9,43]

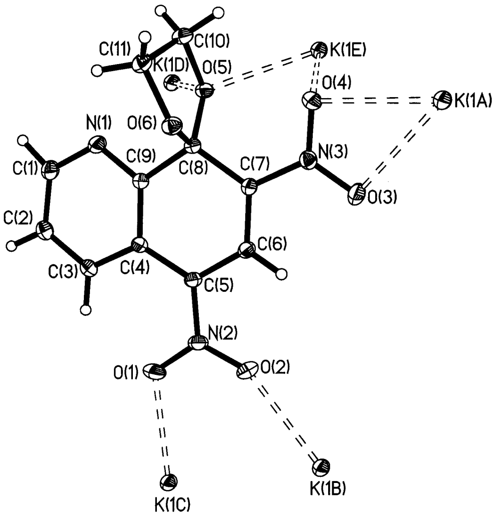


Figure 4. Molecular structure and arrangement of the anion **2** by potassium cations in the crystal. The K(1B), K(1C), K(1D), and K(1E) atoms are obtained by the $-x, -y + 2, -z - 1$; $x + 1, y, z - 1$; $x + 1, y, z$ and $-x, -y + 2, -z$ symmetry operations, respectively.

TABLE 3: Bond Lengths (l, Å) and Topological Characteristics ($\rho_b(\boldsymbol{r})$, e/Å^3, $\nabla^2\rho(\boldsymbol{r})$, e/Å^5, ϵ) of the Bond Critical Points for the Structure 2 from the Multipole Refinement

	l	$\rho_b(\boldsymbol{r})$	$\nabla^2\rho(\boldsymbol{r})$	ϵ
C(5)−N(2)	1.399(1)	2.10(4)	−18.4(1)	0.22
C(7)−N(3)	1.414(1)	1.93(4)	−15.1(1)	0.21
C(1)−N(1)	1.338(1)	2.30(5)	−23.1(1)	0.02
C(9)−N(1)	1.347(1)	2.39(5)	−22.9(1)	0.13
C(1)−C(2)	1.393(1)	2.11(5)	−16.6(1)	0.35
C(2)−C(3)	1.388(1)	2.11(5)	−18.0(1)	0.20
C(3)−C(4)	1.410(1)	2.12(4)	−17.4(1)	0.17
C(4)−C(5)	1.462(1)	1.91(4)	−13.57(9)	0.22
C(4)−C(9)	1.420(1)	1.98(4)	−14.55(9)	0.24
C(5)−C(6)	1.396(1)	2.12(4)	−17.99(9)	0.27
C(6)−C(7)	1.374(1)	2.20(4)	−20.0(1)	0.30
C(7)−C(8)	1.500(1)	1.78(4)	−12.04(9)	0.19
C(8)−C(9)	1.540(1)	1.59(4)	−9.46(9)	0.18
N(2)−O(1)	1.257(1)	2.97(6)	1.3(2)	0.05
N(2)−O(2)	1.252(1)	3.06(6)	−3.8(2)	0.08
N(3)−O(3)	1.246(1)	3.04(6)	−0.3(2)	0.18
N(3)−O(4)	1.259(1)	3.13(6)	−6.4(2)	0.09
O(5)−C(8)	1.432(1)	1.75(5)	−10.5(1)	0.05
O(5)−C(10)	1.444(1)	1.79(5)	−9.4(1)	0.05
O(6)−C(8)	1.430(1)	1.74(5)	−8.9(1)	0.12
O(6)−C(11)	1.436(1)	1.83(5)	−11.3(1)	0.05
C(10)−C(11)	1.517(1)	1.67(4)	−12.47(8)	0.01
K(1A)-O(3)	2.818(1)	0.081(8)	1.60(5)	0.23
K(1A)-O(4)	2.810(1)	0.080(8)	1.58(5)	0.21
K(1B)-O(2)	2.658(1)	0.112(8)	2.17(5)	0.01
K(1C)-O(1)	2.753(1)	0.088(7)	1.74(5)	0.02
K(1D)-O(5)	2.793(1)	0.086(8)	1.68(5)	0.01
K(1E)-O(4)	2.889(1)	0.065(7)	1.27(5)	0.02
K(1E)-O(5)	2.957(1)	0.057(8)	1.12(4)	0.03

The geometry of the nitro groups in **2** is not similar. The C(5)−N(2) bond 1.399(1) Å is shorter than the C(7)−N(3) bond 1.414(1) Å. It should be noted as well that both C−NO$_2$ bonds are significantly shorter in the anion **2** as compared to the anionic

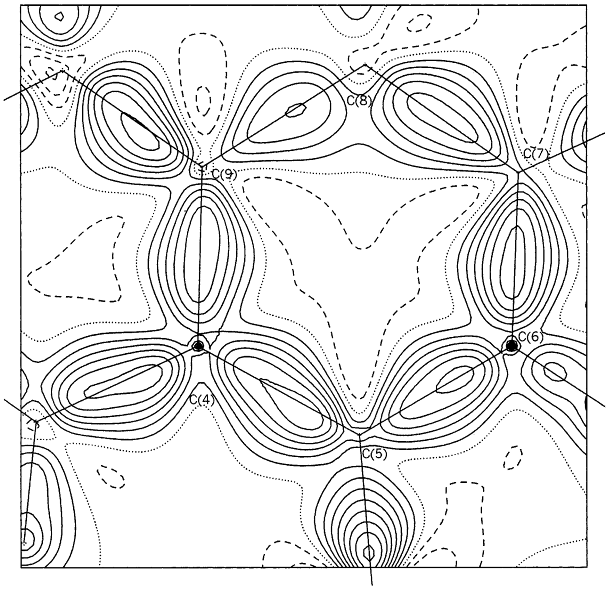


Figure 5. Static deformation density map in the section passing through the C(4), C(6) and C(8) atoms of MC **2**. The map is contoured at intervals of 0.1 e/A^3.

σ-complex **1** (see also[9,43]), but are much longer than the C−N bond (1.36(2) Å) in the Meisenheimer complex of 9-nitroanthracene.[17] This indicates an essential increase of the partially double character of the C−NO$_2$ bonds with expansion of the aromatic π-system. Nitro groups in the anion **2** are nearly coplanar to the ring plane C(4)...C(9) (the O(3)−N(3)−C(7)−C(6) and O(2)−N(2)−C(5)−C(6) torsion angles are equal to 6.0(1) and 1.9(1)°, respectively).

In the crystal phase, each anion **2** is linked to five cations K(1A)−K(1E). Namely, three potassium atoms (K1(A), K(1D), and K(1E)) are coordinated with the oxygen atoms of the nitro group at the *ortho* position and the O(5) atom of the dioxolane ring, whereas the oxygen atoms of the nitro group at the *para* position are coordinated to the potassium atoms K(1B) and K(1C) (Figure 4). The corresponding K−O distances are listed in Table 3.

Charge Density Distribution in the Crystal 2. A static DD map in the plane of the C(4), C(6), and C(9) atoms of **2** shows that heights of the DD peaks on the C-C bonds in the conjugated part of the six-membered ring are nearly equal and hence bond length alternation within this fragment is not reflected by this map (Figure 5). However, topological analysis of the experimental charge density has revealed that both the ϵ and $\rho_b(\boldsymbol{r})$ values of the C(4)-C(5) and C(4)-C(9) bonds are significantly lower that those of the C(5)-C(6) and C(6)-C(7) bonds (Table 3). The similar trend is observed for the charge density obtained by ab initio calculations.

According to the DD maps in the planes of the nitro groups DD peaks at the C−N bonds are close. (Figure 6). In the crystal **2**, ellipticities of the C−N bonds are the same, but the value of the $\rho_b(\boldsymbol{r})$ for the C(5)-N(2) bond (2.10(4) e/Å^3) is somewhat larger than that for the C(5)-N(2) bond (1.93(4) e/Å^3) (Table 3).

By analogy with the MC **1** we can assume that three canonic forms **I−Q−III−Q** (Scheme 2) contribute to the electronic structure of MC **2**. Because both the C(5)−N(2) and C(7)−N(3) bonds have significant double character, contribution of the **III−Q** form seems to be negligible. Probably, the electronic structure of **2** is determined by a balance of the **I−Q** and **II−Q** forms. This is reflected in characteristics of the C(5)−N(2), C(7)−N(3) and C(5)−C(6), C(6)−C(7) bonds. For instance, $\rho_b(\boldsymbol{r})$ values of the C(5)−C(6) and C(6)−C(7) bonds in the crystal of **2** are nearly equal but the ellipticity of the later bond is slightly larger. It was mentioned above that the $\rho_b(\boldsymbol{r})$ value of the C(5)−N(2) bond is larger than that of the C(7)−N(3) bond, but their ellipticities are equal. Nevertheless, the form **I−Q** seems to be predominant in the crystal **2**. It is interesting to note that the same is true for the single MC **2** according to

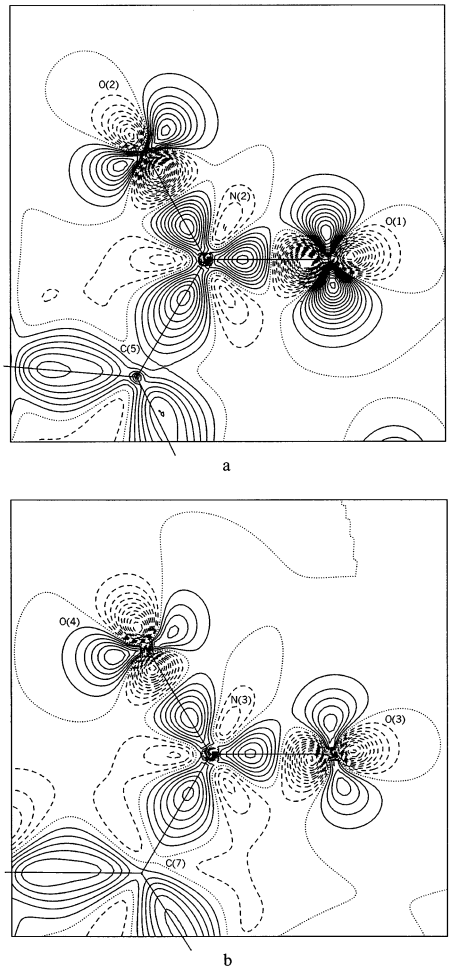
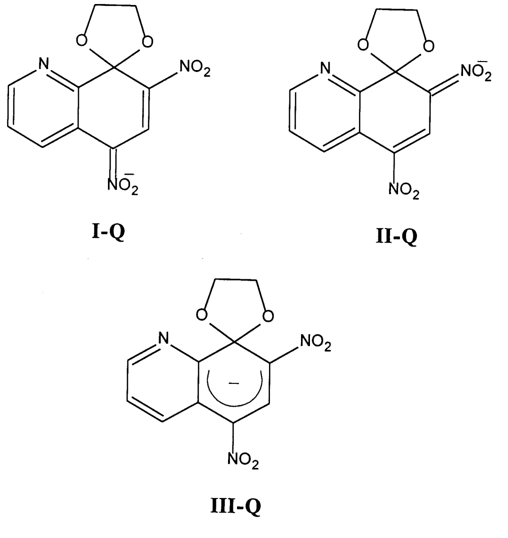


Figure 6. Static deformation density map in the section passing through the O(1), N(2) and O(2) (*a*) and O(3), N(3), and O(4) (*b*) atoms of MC **2**. The map is contoured at intervals of 0.1 e/A^3.

SCHEME 2



ab initio calculations, but in this case contribution of the **I−Q** form is larger. For instance, according to the B3LYP/6-311++G** calculations both the ellipticity and $\rho_b(\boldsymbol{r})$ values for the C(5)−N(2) bond are noticeably larger than those for the C(7)−N(3) bond.

Potassium cations coordinating the anion in the crystal of **2** definitely affect the charge density distribution. Therefore, five systems **2** − K$^+$ (A)−(E) were calculated taking into account each position of the cations around the organic anion to evaluate an influence of the cation on the charge density. These systems are similar to those in the case of **1**.

It should be mentioned in general that no changes of characteristics of the bonds within the quinoline fragment except the C(5)−C(6) and C(6)−C(7) bonds were seen under variation of the cation coordination. The $\rho_b(\boldsymbol{r})$ values of the N−O bonds and their orders become somewhat lower in the anion−cation systems only if corresponding oxygen atoms are directly involved in coordination. For example, for the $\rho_b(\boldsymbol{r})$ values this decreasing does not exceed 0.02 e/Å^3. No other N−O bonds are subject of changing in the particular system. The characteristics of the C(5)−C(6) and C(6)−C(7) bonds, and C−N bonds of the both nitro groups are the most sensitive to influence of the cations. Orders of the C−C bonds vary in the wider range than their topological values, and opposite observation can be made for the C−N bonds. The similar situation was found for the **1**−K$^+$ systems.

The influence of the potassium cations on the electronic structure of the MC **2** in the systems (À) and (Å) is very similar. According to the topological analysis of the charge density based on the B3LYP calculations, values of the $\rho_b(\boldsymbol{r})$ and ϵ for the C(7)−N(3) bond are increased, whereas they are decreased for the C(5)−N(2) bond. It is interesting that ellipticity of the C(7)−N(3) bond (0.34 and 0.33) becomes larger than that of the C(5)−N(2) bond (0.28 and 0.30) in both (A) and (E) systems.

According to the Hartree−Fock calculations, the order of the C(5)−C(6) bond is increased, whereas the order of the C(6)−C(7) bond is decreased in these systems. As a result, relation between bond orders in (A) and (E) is opposite to that observed for the single MC **2**.

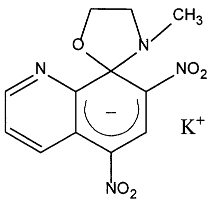
Thus, the magnitudes of the $\rho_b(\boldsymbol{r})$, ϵ and n for the mentioned C−N and C−C bonds in (A) and (E) lead to a conclusion that the form **II−Q** is predominant contrary to the situation found for the single anion **2**.

Coordination of the cation with oxygen atoms of the nitro group in the *para*-position (the systems (B) and (C)) gives rise to opposite results. The $\rho_b(\boldsymbol{r})$, ϵ and n values of the C(5)−N(2) and C(6)−C(7) bonds are increased while corresponding values of the C(7)−N(3) and C(5)−C(6) bonds are decreased. We can conclude therefore that contribution of the **I−Q** form in the systems (B) and (C) is noticeably larger than that for the single MC **2**.

The system (D) with the cation arranged over the fused rings is close to that for the MC **1**−K(1D) system. Thus, a structure bearing the negative charge within the fused rings could be additionally stabilized due to such position of the cation. As a result, the contribution of the **III−Q** form is somewhat enlarged in (D) that is confirmed by decreasing the $\rho_b(\boldsymbol{r})$ and n values of the C−N bonds of the both nitro groups.

Two cations K(1A) and K(1E) favor to contribute the **II−Q** form, whereas the influence of both the K(1B) and K(1C) cations leads to stabilization of the **I−Q** form. The overall effect of these cations depends on the strengths of their effects. Probably, in the crystal of **2** the influence of these two pair of cations largely mutually cancels because the **I−Q** form is predominant for both experimental electronic structure of the anion and for the single MC **2**.

A more interesting situation has been found earlier[23] during the study of the charge density distribution in the crystal of the related anionic σ-complex, namely potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-oxazolidine-2,8′-quinolinide) **3**.



3

According to experimental data,[23] both the $\rho_b(\boldsymbol{r})$ (1.92 e/Å^3) and ϵ (0.29) values for the C(5)−N(2) bond are lower than those (2.04 e/Å^3 and 0.38) for the C(7)−N(3) bond in **3**. This fact may indicate that contribution of the **II−Q** form to electronic structure of **3** in the crystal is predominant, contrary to the compound **2**. It was shown,[46] however, that charge densities within the 5,7-dinitroquinolinide fragment are very close for the single MC **2** and MC **3**. Anions in the crystal phase[23] of **3** are surrounded by cations in the same manner as in the crystal of **2**. It is important to note that lengths of the coordination bonds between cations and the oxygen atoms of the nitro group in the *para*-position in the crystal of **3** are close to those in **2**. However, lengths of other coordination K−O bonds are different in these two structures. In particular, the distances K(1A)−O(4) (2.731(2) Å) and K(1E)−O(4) (2.750(2) Å) in the crystal of **3** are considerably shorter than corresponding distances in the crystal **2**. On the other hand, the distance K(1A)−O(3) (2.863(1) Å) in **3** is somewhat elongated with comparison to that in **2**. The mentioned shortening of the two K−O distances in **3** probably gives rise to strengthening of the corresponding potassium effects in this structure. Really, comparison results of theoretical topological analysis for the systems[23,46] MC **3** − K$^+$ with those for the systems MC **2**−K$^+$ leads to the conclusion that in the (A) and (E) systems contribution of the **II−Q** resonance form is greater in the case of MC 3. On the other hand, topological characteristics of bonds in the systems (B) and (C) are essentially the same for **2** and **3**. Therefore, more stronger effect of the pair cations K(1A)−O(4) and K(1E) in the crystal **3** than in **2** causes predomination of the **II−Q** form in the electronic structure of **3**.

Summary and Conclusions

Experimental study of the charge density in the crystal of the anionic σ-complex **1** has revealed that contribution of the resonance forms **I−R** and **III−R** to the electronic structure of the anion is different. However, theoretical investigation of the single MC **1** shows nearly equal contribution of the mentioned canonic forms. Influence of the cations surrounding the anion in the crystal phase was analyzed to explain that contradiction. According to ab initio calculations, effect of cations gives rise to change of characteristics of the C−N bonds and C−C bonds of the conjugated part of the six-membered ring which determine contributions of canonic forms to the structure of the anion. It was stated that influence of potassium cations situated in the different positions is not consistent, and total effect of all cations is a some superposition of individual cation impacts. In particular, two cations K(1C) and K(1F) favor to increase contribution of the **III−R** form, whereas **I−R** is favored by just one cation K(1A). This explains larger contribution of the **III−R** form as compared to the **I−R** one observed experimentally.

The electronic structure of the anionic σ-complex **2** is determined by a balance of the **I−Q** and **II−Q** canonic forms. The **I−Q** form is predominant for both the anion in the crystal and the single MC **2**. According to ab initio calculations, effect of two cations K(1A) and K(1E) increases of the contribution of the **II−Q** form whereas the pair K(1B) and K(1C) favors to contribution of the **I−Q** form. In the crystal of **2** effects of these cations largely cancel each other. In the case of the related MC **3** studied previously, the influence of pair cations K(1A) and K(1E) is considerably stronger than that in the crystal of **2**. As a result, the **I−Q** resonance form becomes predominant for MC **3**.

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Supporting Information Available: Definitions of the local coordinate systems for the structures **1**, **2**; atomic coordinates, selected bond and torsion angles, as well as data of the rigid body analysis; experimental atomic charges in **1** and **2**; topological analysis of theoretical charge density distribution (Tables S1 and TS2); and geometry of the H-bonds are provided as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) The structure **IV−R** is the generalized formula for three canonic forms with single C−N bonds. In these three resonance forms negative charge is localized at the C(2), C(4) and C(6) atoms, respectively. Similarly, the structure **III−Q** at Scheme 2 is the generalized formula for two canonic forms with single C−N bonds of the nitro groups.

(42) Hartree−Fock calculations lead to unreasonable values of $-\nabla^2\rho(\mathbf{r})$ and ϵ for C−N bonds, which respectively are considerably lower and greater than corresponding experimental values. In fact, curvatures λ_2 and λ_3 are estimated incorrectly in the case of C−N bonds. The λ_2 magnitude seems to be underestimated, whereas λ_3 is overestimated.

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