Electron density distribution in the crystal of the Meisenheimer complex of potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-oxazolidine-2,8′-quinolinide) based on X-ray diffraction data at 153 K

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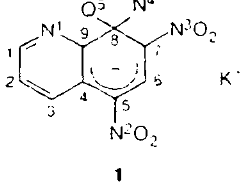
The electron density distribution in the crystal of the Meisenheimer complex of potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-oxazolidine-2,8′-quinolinide) (**1**) was studied based on the data of precision X-ray diffraction study. The experimental data were compared with the results of quantum-mechanical calculations. The electron density distributions in the regions of the nitro groups are substantially different in spite of the similarity in the geometric parameters of these groups. In addition, there is a discrepancy between the experimental and theoretical data on this distribution. The effect of the cation on the electronic structure of the anion in the crystalline phase is the most probable cause of the differences observed. To reveal this effect, *ab initio* calculations of different anion **1**—K^+ systems were performed and a topological analysis of the electron density distributions was carried out. Depending on the mode of coordination of the cation to the anion, the former determines the contribution of alternative resonance forms to the structure of the anion.

Key words: potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-oxazolidine-2,8′-quinolinide), Meisenheimer complexes, molecular structure, *ab initio* calculation, electron density distribution, X-ray diffraction study, Bader's theory, resonance forms.

Nucleophilic substitution reactions, which play a great role in the chemistry of electron-deficient aromatic compounds, proceed according to two major mechanisms,[1,2] *viz.*, S_NAr and vicarious nucleophilic substitution (VNS). These reactions afford various products depending on the structure and the electron density distribution in the key intermediate, which is a negatively charged σ-complex or a Meisenheimer complex (MC).[3-9] Owing to this fact, molecular and electronic structures of MC attracted increased interest over the last decades.[4-13] X-ray diffraction studies of a number of MC[14-26] made it possible to reveal some characteristic features of the spatial structure of the organic anion. In particular, it was demonstrated that the nitro groups in Meisenheimer complexes of 2,4,6-trinitrobenzene are substantially different. One of them (at the *para* position with respect to the saturated carbon atom) has a shorter C—N bond and longer N—O bonds compared to other nitro groups. This fact reflects a large contribution of the *aci*-resonance form to the structure of the nitro group at the *para* position. This conclusion agrees well with the noticeable alternation of the endocyclic C—C bonds in the six-membered ring[23,26] as well as with the spectral data.[27]

Investigation of the electronic structure and the electron density distribution in MC is a more challenging task. Presently, the results of experimental studies of these characteristics are limited primarily to spectral data due to the low stability of MC. Many of these compounds cannot be isolated from reaction mixtures.[1] Calculations by semiempirical and *ab initio*[13,24,28] quantum-chemical methods often gave contradictory results.[13] Besides, in this case the effect of the cation on the molecular and electronic structure of the Meisenheimer complex is ignored.

In the present work, experimental data on the electron density distribution in the crystal of potassium 3-methyl-5′,7′-dinitro-5′,8′-dihydrospiro(1,3-



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oxazolidine-2,8′-quinolinide) (**1**) were obtained for the first time by X-ray diffraction analysis and the results were compared with the data of *ab initio* quantum-chemical calculations. These data were interpreted with the use of the results of topological analysis of the electron density function, which allowed us to state the principal characteristic features of chemical bonding in MC **1** in terms of the experimentally observed characteristics of the electron density.

Experimental

Compound **1** was synthesized according to a procedure reported previously.[29] Single crystals were prepared by slow cooling of a solution of **1** in MeCN.

X-ray diffraction study of compound 1. Crystals of $C_{12}H_{11}N_4O_5K$ are monoclinic at 153(2) K, a = 25.118(5) Å, b = 7.686(2) Å, c = 18.178(4) Å, β = 132.71(3)°, V = 2579(3) Å^3, crystal dimensions 0.5×0.3×0.2 mm, space group $C2/c$, Z = 8, d_{calc} = 1.702 g cm^{-3}, $F(000)$ = 1360, μ = 0.445 mm^{-1}.

Intensities of 8154 reflections (8028 independent reflections, R_{int} = 0.068) were measured at 153(2) K on an automated four-circle Siemens P3/PC diffractometer equipped with a low-temperature LT-2 unit (graphite monochromator, Mo Kα radiation, θ/2θ scanning technique, $2\theta_{max}$ = 80°). The results of preliminary X-ray structural analysis of compound **1**, which has been carried out with the use of the SHELXTL PLUS program package,[30] have been reported previously.[25]

Analysis of the electron density function in compound **1** was carried out within the framework of Hansen—Coppens's multipole model,[31] which allows one to analytically represent this function as an expansion in terms of spherical harmonics, as well as with the use of the topological approach proposed by Bader.[32,33] The multipole refinement based on F^2 was performed with the use of the XD program package[34] using 4198 reflections (458 parameters) to R = 0.032, GOF$_w$ = 0.98. For the carbon, nitrogen, and oxygen atoms, the multipole expansion was broken off at the octupole level (l_{max} = 3). For the hydrogen and potassium atoms, the expansion was broken off at the dipole level (l_{max} = 1). It was assumed that the local symmetry m is true for all oxygen and carbon atoms, except for the C(8) and C(12) atoms, for which the symmetries 1 and $3m$, respectively, were assumed. The local symmetry $mm2$ was used for the nitrogen atoms of the nitro groups and the symmetry m was used for the N(1) and N(4) atoms. According to the accepted local symmetries, restrictions reported previously[35] were imposed on the indices of spherical harmonics for the above-mentioned atoms. The coordinates of the nonhydrogen atoms in the structure of **1** obtained by the multipole refinement and the complete tables of the bond lengths and bond angles were deposited with the Cambridge Structural Database. The principal bond lengths and their electronic and topological characteristics, in particular, the total electron density ρ(r), its Laplacian $\nabla^2\rho(r)$, and the ellipticity ε at the critical points of the bonds (3, −1), are given in Table 1.

Table 1. Bond lengths and their topological characteristics at the critical points (3, −1) in the crystal of compound **1** according to X-ray structural data (a multipole model)

Bond	d/Å	ρ(r) /e · Å^{-3}	$\nabla^2\rho(r)$ /e · Å^{-5}	ε
N(2)—O(1)	1.2496(14)	3.315	−7.98	0.19
N(2)—O(2)	1.2494(14)	3.515	−14.25	0.12
N(3)—O(3)	1.2452(14)	3.301	−14.70	0.17
N(3)—O(4)	1.2510(13)	2.884	−2.14	0.11
O(5)—C(8)	1.433(2)	1.496	−5.77	0.16
O(5)—C(10)	1.449(2)	1.414	−6.14	0.22
N(1)—C(1)	1.335(2)	2.307	−25.81	0.17
N(1)—C(9)	1.3415(14)	2.332	−28.14	0.15
N(2)—C(5)	1.3995(14)	1.915	−14.76	0.29
N(3)—C(7)	1.408(2)	2.044	−17.92	0.38
N(4)—C(8)	1.476(2)	1.663	−6.27	0.19
N(4)—C(11)	1.460(2)	1.689	−9.50	0.17
N(4)—C(12)	1.454(2)	2.012	−13.98	0.05
C(1)—C(2)	1.385(2)	1.972	−14.45	0.15
C(2)—C(3)	1.380(2)	2.152	−19.09	0.16
C(3)—C(4)	1.402(2)	2.079	−17.33	0.19
C(4)—C(5)	1.458(2)	1.881	−14.25	0.23
C(4)—C(9)	1.418(2)	1.919	−13.49	0.24
C(5)—C(6)	1.392(2)	2.021	−18.50	0.31
C(6)—C(7)	1.371(2)	2.018	−16.18	0.39
C(7)—C(8)	1.502(2)	1.757	−11.95	0.13
C(8)—C(9)	1.540(2)	1.655	−10.08	0.15
C(10)—C(11)	1.515(2)	1.636	−8.98	0.16
O(3)—K(1A)	2.8633(14)	0.071	1.375	0.56
O(4)—K(1A)	2.731(2)	0.099	1.985	0.12
O(2)—K(1B)	2.655(2)	0.113	2.180	0.03
O(1)—K(1C)	2.7480(14)	0.088	1.703	0.02
O(5)—K(1D)	2.772(2)	0.092	1.799	0.05
O(4)—K(1E)	2.750(2)	0.091	1.778	0.02
O(5)—K(1E)	3.160(2)	0.036	0.681	0.15

Ab initio quantum-chemical calculations of the wave functions for anion **1** and the anion **1**—K$^+$ system (for five possible positions of the cation, *viz*., K(1A)—K(1E)) were carried out with the use of the GAMESS program[36] in the HF/6-311++G** approximation with fixed geometric parameters taken from the X-ray structural data. The topological analysis of the theoretically calculated electron density distribution was performed within the framework of Bader's theory[32,33] using the EXTREME program included in the AIMPAC program package.[37]

When interpreting the results, we used the following concepts of Bader's theory[32,33]: the structure of the many-electron system with a given nuclear configuration {R} is completely determined by a set and types of critical points of the electron density ρ(r,R) in which the gradient of the electron density vanishes ($\nabla\rho(r) = 0$). The second derivatives ρ(r) calculated at these points comprise a real symmetrical Hessian matrix. Each critical point is characterized by the rank p and the signature q, which are determined by the eigenvalues of the Hessian λ_i at this point. The rank is the number of nonzero eigenvalues, and the signature is the algebraic sum of their signs. Four types of nondegenerate critical points, *i.e.*, points with p = 3, are possible, *viz*., (3, −3), (3, −1), (3, +1), and (3, +3). Critical points of the (3, −1) type or saddle points of the electron density, which determine bonding interactions between two atoms of the molecular system, are of prime importance from the chemical standpoint. Their presence is a necessary condition for chemical bonding. It is believed that a bonding interaction occurs between two atoms if there is a line (bonding path) linking their nuclei, along which the electron density is maximum with respect to any one side shift and which has a minimum at the critical saddle point (3, −1). One of the important topological characteristics of the chemical bond is its ellipticity ε, determined by the ratio between two negative eigenvalues λ_1 and λ_2 normal to the direction of the bond ($\varepsilon = \lambda_1/\lambda_2 - 1$). The ellipticity of the bond is directly (and quantitatively) related to the value of its π component[38] and, therefore, this parameter is very useful in the analysis of the nature of electron conjugation. Yet another important characteristic of the electron density $\rho(r)$ is its Laplacian $\nabla^2\rho(r)$, *viz.*, the sum of three eigenvalues of the Hessian λ_i (the second partial derivatives of the electron density). Thus negative values of the Laplacian determine regions of the molecular space, where the local concentration of the electron charge occurs and bonding covalent interactions between atoms prevail. The positive Laplacian determines regions of the so-called interactions of closed shells, which are realized, in particular, in ionic and hydrogen bonds as well as in van der Waals molecules.

Results and Discussion

As is evident from the X-ray structural data (Fig. 1), the C(6)—C(7) and C(4)—C(9) bonds (1.371(2) and 1.418(2) Å, respectively) in the six-membered C(4)...C(9) ring are elongated compared to the corresponding bonds in the Meisenheimer complexes of 2,4,6-trinitrobenzene derivatives (1.348(2) and 1.357(2) Å)[23] and are similar to bonds of the C(Ar)—C(Ar) type. The length of the formally single C(8)—C(9) bond (1.540(2) Å) is substantially larger than the average value (1.503 Å)[39] for bonds of the C(Ar)—C(sp^3) type, due, apparently, to the shortened intramolecular N(1)...C(11) contact (3.09 Å; the sum of the van der Waals radii[40] is 3.21 Å). In anionic σ-complexes of trinitrobenzene in which such shortened contacts are absent, the C(Ar)—C(sp^3) bond length has a standard value.[17,19,23]

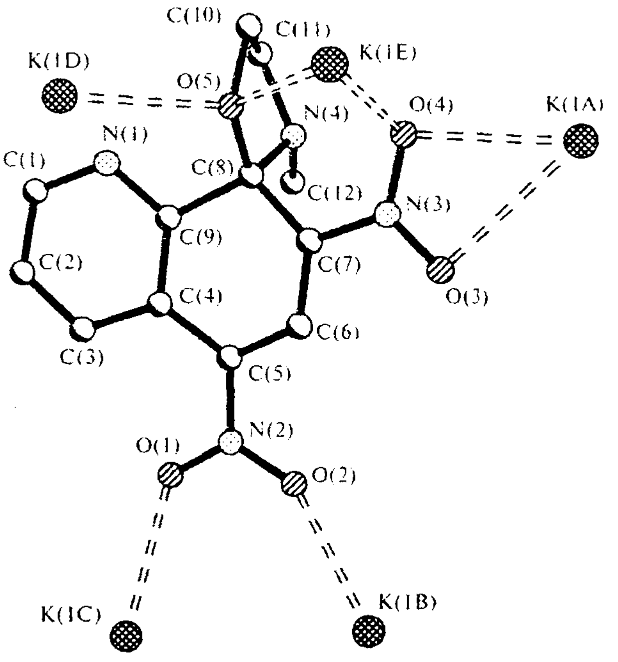
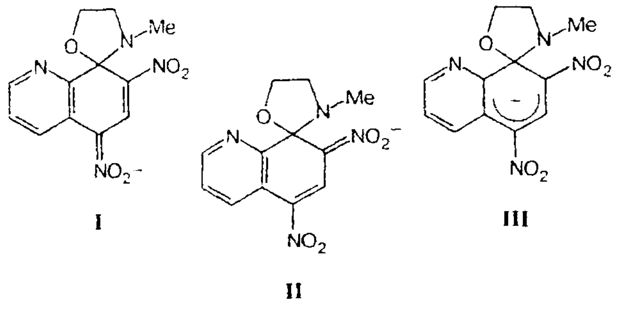


Fig. 1. Overall view of anion **1** and the atomic numbering scheme. Coordination of the potassium atoms by the oxygen atoms of anion **1** in the crystal is indicated by dashed lines.

The C(5)—N(2) and C(7)—N(3) bonds in anion **1** (1.400(1) and 1.408(2) Å, respectively; see Fig. 1) are substantially shorter than those in the anionic σ-complexes of 2,4,6-trinitrobenzene derivatives[17,19,23] but are essentially longer than the C—N bond (1.36(2) Å) in the Meisenheimer complex of the 9-nitroanthracene derivative.[24] This may be indicative of a substantial enhancement of the partially double character of the C—NO_2 bond upon extension of the π-system of the anion. However, the nitro groups in anion **1**, unlike those in the MC of trinitrobenzene, are virtually identical in geometry (see Table 1). It is also difficult to draw a conclusion about the character of localization (delocalization) of the C—C bonds in the central six-membered ring. Consequently, in the case of **1**, the preference of the contribution of any one of structures **I**—**III** (Scheme 1) to the electronic structure of the anion cannot be stated based only on the geometric data. In this case, the use of the topological analysis of the electron density distribution in compound **1** for studying the electronic structure of the anion (the contributions of forms **I**—**III**) seems to be particularly fruitful. In particular, the ellipticity of the bond is considerably superior to the molecular geometry in sensitivity with respect to the conjugation effects.

Scheme 1



The nitro groups in compound **1** are coplanar with the plane of the conjugated system of the C(4)...C(9) ring (the O(3)—N(3)—C(7)—C(6) and O(2)—N(2)—C(5)—C(6) torsion angles are −7.3(1)° and −6.1(1)°, respectively) in spite of the shortened intramolecular contacts O(1)...C(3) (2.77 Å; the sum of the van der Waals radii[40] is 3.00 Å), O(1)...H(3) (2.18 Å; the sum of the van der Waals radii is 2.45 Å), O(2)...H(6) (2.33 Å), and O(3)...H(6) (2.29 Å). (The conformations of the rings in molecule **1** and the factors determining these conformations have been considered in detail previously.[25])

In the crystal of compound **1**, the potassium cations form infinite zigzag chains along the (0 1 0) direction. In these chains, the distances between the metal atoms are equal (4.172(2) Å). The chains are linked to each other through coordination of the metal ions by the oxygen atoms of the anions to form a stack structure along the (0 1 0) direction. As a result, the oxygen atoms of the

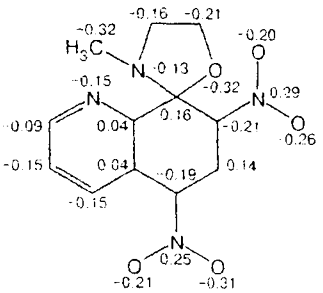


Fig. 2. Experimental charge distribution in anion **1** determined on the basis of coefficients of monopole populations.

five-membered ring and the nitro groups at the *ortho* positions are coordinated to three successively linked potassium atoms of one chain (the distances are as follows: O(3)—K(1A), 2.863(1) Å; O(4)—K(1A), 2.731(2) Å; O(5)—K(1D), 2.772(2) Å; O(4)—K(1E), 2.750(2) Å; and O(5)—K(1E), 3.160(2) Å), whereas the oxygen atoms of the nitro group at the *para* position of this anion are coordinated to two successively located potassium atoms of the adjacent chain (O(2)—K(1B), 2.655(2) Å; and O(1)—K(1C), 2.748(1) Å). Therefore, each anion is coordinated to five cations K(1A)—K(1E) (see Fig. 1). Each potassium ion, in turn, is coordinated by five oxygen atoms of five anions to form seven coordination bonds. Apparently, the coordination number of the potassium atom can be taken equal to 6 and the coordination polyhedron can be considered as an octahedron since the O(5)—K(1E) distance is substantially longer than the remaining K—O distances.

Precision X-ray diffraction study made it possible to perform the analysis of the distribution of the electron density function in the crystal of complex **1**. The experimental charge distribution in anion **1** calculated on the basis of coefficients of monopole populations (Fig. 2) demonstrated that the negative charge is localized primarily on the oxygen atoms of the nitro groups and the oxazolidine ring. On the whole, the results of quantum-chemical calculations of the charge distribution in isolated anion **1** (Fig. 3) agree well with the experimental data. However, these calculations gave higher negative charges on the oxygen atoms of the nitro groups and a lower charge on the O(5) atom in the five-membered ring. Therefore, the absence of the concentration of a negative charge on the carbon atoms of the six-membered ring indicates that the contribution of structure **III** to the structure of the anion is insignificant.

Analysis of the static deformation electron density maps in the section passing through the C(4), C(6), and C(9) atoms (Fig. 4) demonstrated that the peak heights of the deformation electron density in these bonds are

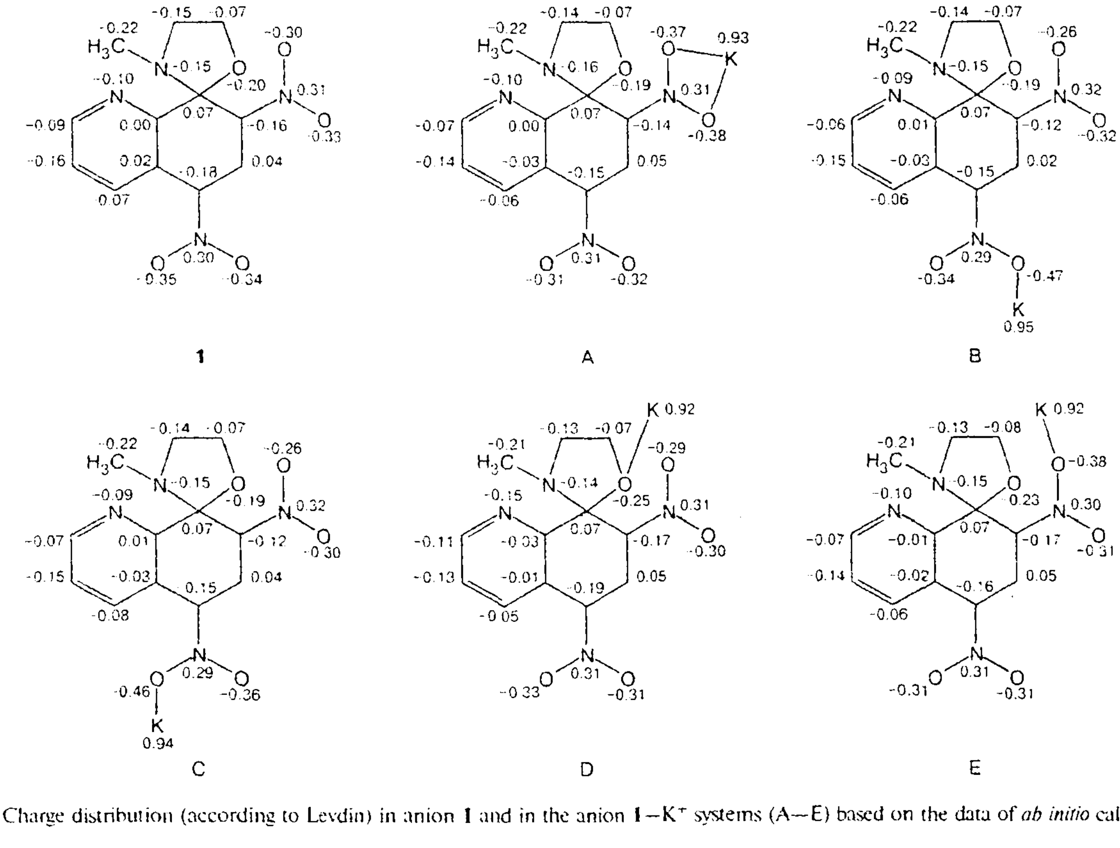


Fig. 3. Charge distribution (according to Levdin) in anion **1** and in the anion **1**—K$^+$ systems (A—E) based on the data of *ab initio* calculations.

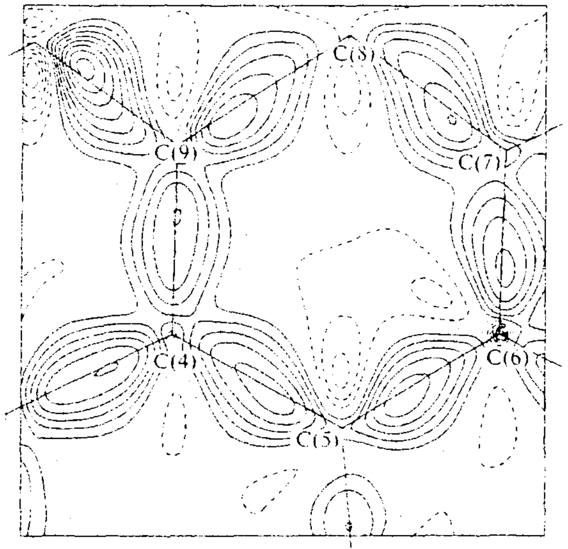


Fig. 4. Static deformation electron density map in the section passing through the C(4), C(6), and C(9) atoms. The map is contoured at intervals of 0.1 e · Å^{-3}.

approximately equal in spite of a noticeable difference in the bond lengths in the conjugated portion of the six-membered ring. However, the topological analysis of the electron density function revealed that the electron density at the critical points (3, −1) in the C(4)—C(5) and C(4)—C(9) bonds is somewhat lower than that in the C(5)—C(6) and C(6)—C(7) bonds and the ellipticities of the latter bonds are substantially larger, which is also consistent with their smaller lengths (Table 2). The data of theoretical topological-analysis calculations for the dihydrocycle in anion **1** agree not only qualitatively but also virtually quantitatively with the experimental data (see Table 2).

According to the deformation electron density maps (Figs. 5 and 6), two nitro groups are noticeably different in spite of the similarity in their geometric characteristics. The peak height of the deformation electron density in the C(7)—N(3) bond is actually twice as large as that in the C(5)—N(2) bond. The topological analysis confirmed this nonequivalence. The C(7)—N(3) bond is characterized by somewhat larger values of the electron density and its Laplacian at the critical point (3, −1) in the C—N bond and the ellipticity of this bond is substantially larger than that of the C(5)—N(2) bond (see Table 1). However, the topological analysis of the theoretically calculated electron density distribution in isolated anion **1** gave opposite results (see Table 2). The ellipticity of the C(5)—N(2) bond (0.67) is larger than that of the C(7)—N(3) bond (0.45). The same is true for the values of the electron density at the critical points (3, −1) in the above-mentioned bonds (see Table 2). This contradiction seems to be of fundamental importance because the ellipticity of the bond gives an estimate of its π character[38] and allows one to judge the contribution of resonance forms **I** and **II** to the structure of anion **1**.

It can be suggested that the observed contradiction between the theoretical and experimental data stems from the polarizing effect of the potassium cations that coordinate the oxygen atoms of the anion. To verify this suggestion, we carried out the topological analysis of the theoretically calculated electron density distribution in

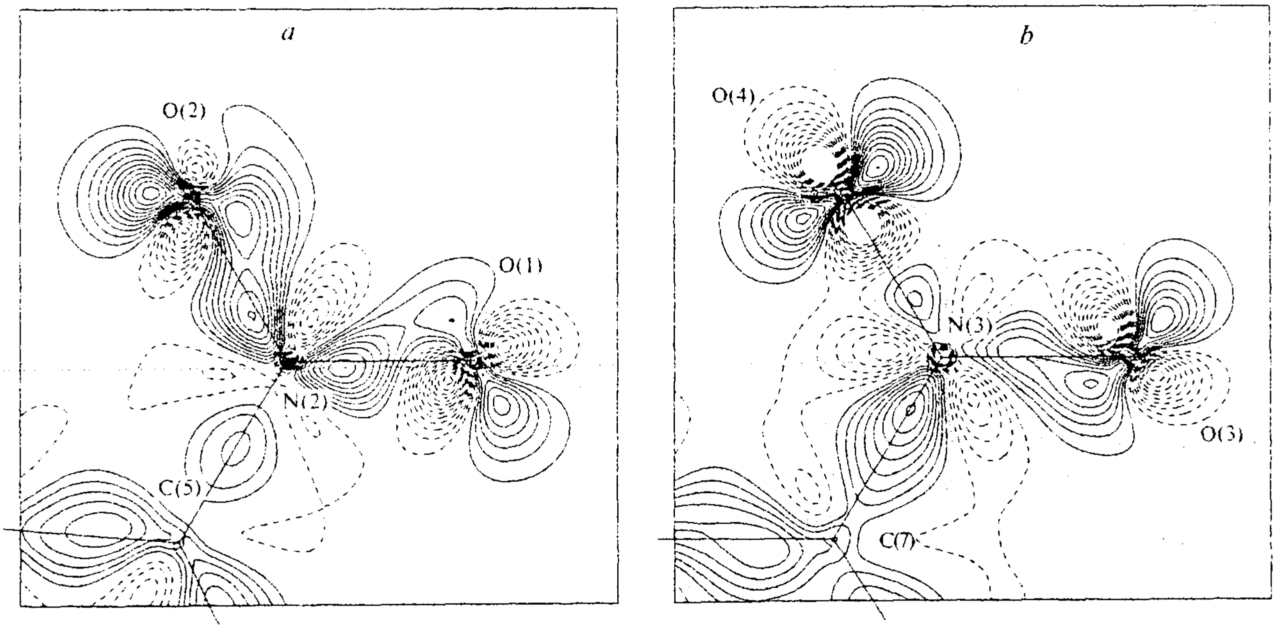


Fig. 5. Static deformation electron density maps in the sections passing through the O(1), N(2), and O(2) atoms (*a*) and through the O(3), N(3), and O(4) atoms (*b*). The maps are contoured at intervals of 0.1 e · Å^{-3}.

Table 2. Topological characteristics of the bonds at the critical points (3, −1) and the orders of these bonds (n) in anion **1** and in the anion **1**—K$^+$ system according to the data of *ab initio* calculations taking into account possible positions of the cation, *viz.*, K(1A)—K(1E))

Bond	Anion, system	$\rho(r)$ /e · Å^{-3}	$\nabla2\rho(r)$ /e · Å^{-5}	ε	n
N(2)—C(5)	**1**	1.899	−0.991	0.67	1.14
	1—K(1A)	1.914	−2.393	0.50	1.08
	1—K(1B)	1.879	0.195	0.73	1.19
	1—K(1C)	1.877	0.272	0.75	1.20
	1—K(1D)	1.912	−1.983	0.65	1.12
	1—K(1E)	1.915	−2.357	0.53	1.09
N(3)—C(7)	**1**	1.866	−1.234	0.45	1.12
	1—K(1A)	1.823	2.207	0.61	1.20
	1—K(1B)	1.881	−2.640	0.32	1.08
	1—K(1C)	1.889	−3.293	0.30	1.07
	1—K(1D)	1.876	−2.040	0.48	1.09
	1—K(1E)	1.840	0.946	0.60	1.16
C(4)—C(5)	**1**	1.912	−19.668	0.19	1.10
	1—K(1A)	1.915	−19.904	0.17	1.08
	1—K(1B)	1.914	−19.899	0.17	1.14
	1—K(1C)	1.915	−19.856	0.17	1.09
	1—K(1D)	1.911	−19.521	0.21	1.14
	1—K(1E)	1.915	−19.821	0.18	1.07
C(5)—C(6)	**1**	2.158	−24.072	0.27	1.31
	1—K(1A)	2.152	−23.469	0.32	1.51
	1—K(1B)	2.167	−24.676	0.23	1.23
	1—K(1C)	2.169	−24.837	0.21	1.25
	1—K(1D)	2.156	−23.953	0.28	1.32
	1—K(1E)	2.153	−23.540	0.32	1.45
C(6)—C(7)	**1**	2.229	−24.804	0.35	1.56
	1—K(1A)	2.242	−25.767	0.27	1.40
	1—K(1B)	2.227	−24.481	0.38	1.69
	1—K(1C)	2.226	−24.413	0.38	1.71
	1—K(1D)	2.228	−24.813	0.34	1.55
	1—K(1E)	2.237	−25.503	0.29	1.46
C(7)—C(8)	**1**	1.857	−19.218	0.09	0.87
	1—K(1A)	1.854	−19.305	0.08	0.84
	1—K(1B)	1.857	−19.425	0.08	0.88
	1—K(1C)	1.859	−19.431	0.08	0.89
	1—K(1D)	1.857	−19.083	0.11	0.84
	1—K(1E)	1.855	−19.133	0.10	0.86
C(8)—C(9)	**1**	1.770	−17.664	0.06	0.40
	1—K(1A)	1.771	−17.651	0.06	0.39
	1—K(1B)	1.770	−17.673	0.05	0.42
	1—K(1C)	1.770	−17.679	0.05	0.41
	1—K(1D)	1.768	−17.577	0.06	0.51
	1—K(1E)	1.772	−17.639	0.06	0.39
C(4)—C(9)	**1**	2.079	−22.267	0.24	1.39
	1—K(1A)	2.076	−22.100	0.25	1.39
	1—K(1B)	2.077	−22.139	0.25	1.41
	1—K(1C)	2.078	−22.211	0.25	1.39
	1—K(1D)	2.079	−22.320	0.24	1.44
	1—K(1E)	2.075	−22.100	0.25	1.41
N(2)—O(1)	**1**	3.291	−28.077	0.11	2.02
	1—K(1A)	3.292	−27.647	0.12	2.06
	1—K(1B)	3.288	−27.783	0.11	2.01
	1—K(1C)	3.280	−30.013	0.10	1.85
	1—K(1D)	3.292	−27.812	0.11	2.02
	1—K(1E)	3.292	−27.676	0.12	2.05
N(2)—O(2)	**1**	3.293	−27.522	0.11	2.09
	1—K(1A)	3.294	−27.292	0.11	2.10
	1—K(1B)	3.280	−29.894	0.09	1.69
	1—K(1C)	3.291	−27.678	0.11	2.00
	1—K(1D)	3.293	−27.087	0.12	2.12
	1—K(1E)	3.294	−27.187	0.12	2.11
N(3)—O(3)	**1**	3.326	−28.402	0.11	2.12
	1—K(1A)	3.326	−29.505	0.11	2.01
	1—K(1B)	3.325	−28.436	0.11	2.09
	1—K(1C)	3.326	−28.147	0.12	2.13
	1—K(1D)	3.326	−27.978	0.12	2.14
	1—K(1E)	3.327	−28.206	0.11	2.14
N(3)—O(4)	**1**	3.282	−27.299	0.12	2.18
	1—K(1A)	3.280	−28.383	0.11	2.08
	1—K(1B)	3.282	−26.955	0.13	2.22
	1—K(1C)	3.282	−26.986	0.13	2.21
	1—K(1D)	3.282	−27.271	0.12	2.15
	1—K(1E)	3.279	−28.455	0.10	1.93

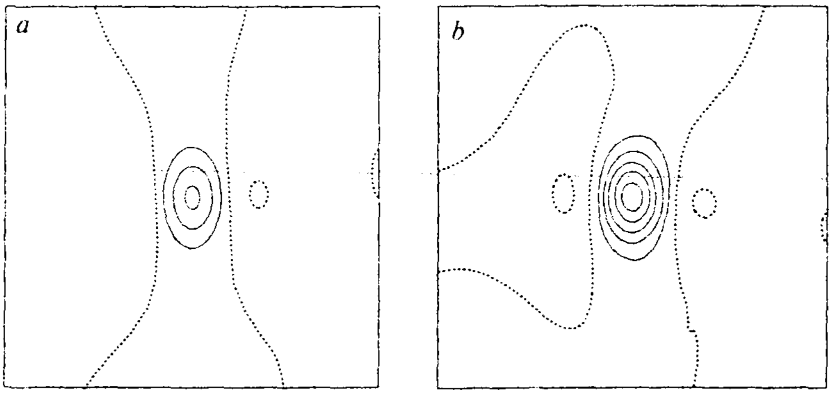


Fig. 6. Static deformation electron density maps in the sections perpendicular to the C(5)—N(2) (*a*) and C(7)—N(3) (*b*) bonds and passing through their midpoints. The maps are contoured at intervals of 0.1 e · Å^{-3}.

the anion **I**—K^+ systems for five possible positions of the cation, *viz.*, K(1A)–K(1E) (see Table 2 and Fig. 3).

The effect of the cation in the systems A and E on the electronic structure of anion **I** is very similar. In particular, a slight increase in the negative charges on the O(3) and O(4) atoms compared to those in the isolated anion is observed. However, the charge distribution as a whole remains fundamentally the same (see Fig. 3). Note also a substantial decrease in the N—O bond orders and an increase in the C—N bond order in the nitro group at the *ortho* position as well as a decrease in the C—N bond order in the nitro group at the *para* position. As a result, for example, the C(7)—N(3) bond order (1.20) in the system A is substantially larger than the C(5)—N(2) bond order (1.08) although the inverse ratio is observed in isolated anion **I**. In addition, the C(5)—C(6) and C(6)—C(7) bond orders in the central ring change substantially and the equalization of these bond orders in the system E occurs (see Table 2). The orders of the remaining bonds in the systems under consideration remain virtually unchanged.

The topological analysis of the electron density distribution demonstrated that the ellipticity of the C(7)—N(3) bond in the systems A and E (0.61 and 0.60, respectively) is larger than that of the C(5)—N(2) bond (0.50 and 0.53, respectively) although, as mentioned above, the opposite situation is observed in isolated anion **I** (see Table 2). Interestingly, the topological characteristics of the N—O bonds in this case remain virtually unchanged, while the ellipticity of the C(5)—C(6) bond increases and the ellipticity of the C(6)—C(7) bond decreases compared to the values observed in anion **I** (see Table 2). Therefore, the character of the changes in the order and ellipticity of the bonds indicates that the cation in the systems A and E causes an increase in the contribution of resonance form **II** (see Scheme 1) to the structure of anion **I**.

In the systems B and C, the negative charge on the oxygen atom of the nitro group bound to the potassium atom increases substantially and the order of the corresponding N—O bond decreases compared to the values observed in isolated anion **I** (see Figs. 3 and 4). In addition, the ratio between the C(5)—N(2) and C(7)—N(3) bond orders as well as the ratio between the C(5)—C(6) and C(6)—C(7) bond orders are identical to those observed in anion **I** (and opposite to those observed in the system A), but the difference in these values is more pronounced. However, the topological analysis of the electron density distribution demonstrated that, as in the cases of the systems A and E, noticeable changes are observed only for the C—N bonds of the nitro groups as well as for the C(5)—C(6) and C(6)—C(7) bonds. Note that the ellipticities of the C(5)—N(2) and C(6)—C(7) bonds increase and the ellipticities of the C(7)—N(3) and C(5)—C(6) bonds decrease compared to those observed in anion **I**. In these systems, the contribution of resonance form **I** to the structure of anion **I**, apparently, increases.

In the system D, the C(8)—O(5) bond order decreases substantially, the C(sp^3)—C bond orders are somewhat increased, and the C—N bond orders in both nitro groups are slightly decreased. Apparently, the last-mentioned fact is indicative of a slight increase in the contribution of form **III**. At the same time, the topological characteristics of the electron density function for the dinitroquinoline fragment of the molecule are virtually identical to those for the isolated anion.

Therefore, it can be concluded that the effect of the field generated by the potassium cations leads primarily to noticeable changes in the order and ellipticity of the C—N bonds of the nitro groups and of the C(5)—C(6) and C(6)—C(7) bonds in anion **I**, which are responsible for the contributions of resonance forms **I** and **II** to its structure. In this case, the ellipticities of the C—N bonds vary in wider ranges than those observed for the bond orders. For the C—C bonds, the opposite situation is observed. Changes in the bond orders and their ellipticities in the systems A and E result in an increase in the contribution of resonance form **II** to the structure of anion **I**, whereas these changes in the systems B and C lead to an increase in the contribution of resonance form **I**. Evidently, the experimental data on the electronic structure of compound **I** are characterized by a superposition of the field effects generated by each potassium atom bound to the anion. It was demonstrated that these effects are not consistent but favor the contribution of alternative resonance forms to the structure of the anion.

References

1. G. A. Artamkina, M. P. Egorov, and I. P. Beletskaya, *Chem. Rev.*, 1982, **82**, 427.
2. E. Buncel, J. M. Dust, and F. Terrier, *Chem. Rev.*, 1995, **95**, 2261.
3. F. Terrier, *Chem. Rev.*, 1982, **82**, 77.
4. G. A. Artamkina, S. V. Kovalenko, I. P. Beletskaya, and O. A. Reutov, *Usp. Khim.*, 1990, **59**, 1288 [*Russ. Chem. Rev.*, 1990, **59** (Engl. Transl.)].
5. V. N. Knyazev and V. N. Drozd, *Zh. Org. Khim.*, 1995, **31**, 3 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
6. V. N. Knyazev, O. Ya. Borbulevich, and O. V. Shishkin, *Zh. Org. Khim.*, 2000, No. 4 [*Russ. J. Org. Chem.*, 2000, No. 4 (Engl. Transl.)].
7. Yu. M. Atroshchenko, N. I. Blokhina, I. V. Shakhkel'dyan, Yu. D. Grudtsyn, S. S. Gitis, O. Ya. Borbulevich, I. V. Blokhin, A. Ya. Kaminskii, O. V. Shishkin, and V. F. Andrianov, *Zh. Org. Khim.*, 2000, No. 4 [*Russ. J. Org. Chem.*, 2000, No. 4 (Engl. Transl.)].
8. V. N. Knyazev, O. Ya. Borbulevich, and O. V. Shishkin, *Zh. Org. Khim.*, 2000 [*Russ. J. Org. Chem.*, 2000 (Engl. Transl.)].
9. Yu. M. Atroshchenko, S. S. Golotvin, I. V. Shakhkel'dyan, O. V. Shishkin, Zh. O. Lavrik, O. Ya. Borbulevich, M. Yu. Antipin, E. N Alifanova, S. S. Gitis, I. V. Ivanov, and A. Ya. Kaminskii, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1713 [*Russ. Chem. Bull.*, 1999, **48** (Engl. Transl.)].
10. B. Y. Simkin, E. B. Gluz, M. N. Glukhovtsev, and V. I. Minkin, *J. Mol. Struct. (THEOCHEM)*, 1993, **103**, 123.

11. E. Buncel, R. M. Tarkka, and J. M. Dust, *Can. J. Chem.*, 1994, **72**, 1709.
12. V. N. Solkan and S. A. Shevelev, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 624 [*Russ. Chem. Bull.*, 1995, **44**, 603 (Engl. Transl.)].
13. Y. J. Zheng and T. C. Bruice, *J. Am. Chem. Soc.*, 1997, **119**, 3868.
14. S. S. Gitis, E. G. Kaminskaya, A. I. Ivanova, N. V. Grigor'eva, N. V. Margolis, and A. Ya. Kaminskii, *Zh. Strukt. Khim.*, 1976, **17**, 671 [*J. Struct. Chem. USSR*, 1976, **17** (Engl. Transl.)].
15. H. Ueda, N. Sakabe, J. Tanaka, and A. Furusaki, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2866.
16. E. G. Kaminskaya, S. S. Gitis, A. I. Ivanova, N. V. Margolis, A. Ya. Kaminskii, and N. V. Grigor'eva, *Zh. Strukt. Khim.*, 1977, **18**, 386 [*J. Struct. Chem. USSR*, 1977, **18**, (Engl. Transl.)].
17. R. Destro, T. Pilati, and M. Simonetta, *Acta Cryst.*, 1979, **B35**, 733.
18. G. G. Messmer and G. J. Palenik, *Acta Cryst.*, 1971, **B27**, 314.
19. R. Destro, C. M. Gramaccioli, and M. Simonetta, *Acta Cryst.*, 1968, **B24**, 1369.
20. F. Terrier, J. Lelievre, A. P. Chatrousse, T. Boubaker, B. Bachet, and A. Cousson, *J. Chem. Soc. Perkin Trans. 2*, 1992, 361.
21. C. K. Lowe-Ma, *Acta Cryst.*, 1986, **C27**, 38.
22. V. N. Drozd, V. N. Knyazev, N. L. Khilkova, D. S. Yufit, Yu. T. Struchkov, I. V. Stankevich, and A. L. Khistyakov, *Zh. Org. Khim.*, 1993, **29**, 770 [*Russ. J. Org. Chem.*, 1993, **29** (Engl. Transl.)].
23. O. Ya. Borbulevych, O. V. Shishkin, A. Yu. Kovalevsky, Yu. M. Atroschenko, E. N. Alifanova, S. S. Gitis, A. Ya. Kaminsky, and E. Yu. Tarasova, *Monatsh. Chem.*, 1998, **129**, 467.
24. O. V. Shishkin, O. Ya. Borbulevich, I. V. Blokhin, Yu. M. Atroshchenko, and S. S. Gitis, *Izv. Akad. Nauk. Ser. Khim.*, 1998, 438 [*Russ. Chem. Bull.*, 1998, **47**, 423 (Engl. Transl.)].
25. O. Ya. Borbulevych, M. Yu. Antipin, O. V. Shishkin, and V. N. Knyazev, *J. Mol. Struct.*, 2000, in press.
26. O. Ya. Borbulevych, O. V. Shishkin, and V. N. Knyazev, *Acta Cryst.*, 1999, **C55**, 1704.
27. E. G. Kaminskaya, S. S. Gitis, and A. Ya. Kaminskii, *Zh. Prikl. Spektrosk.*, 1975, **23**, 243 [*J. Appl. Spectr.*, 1975, **23** (Engl. Tranl.)].
28. O. V. Shishkin, O. Ya. Borbulevich, I. V. Blokhin, Yu. M. Atroshchenko, and S. S. Gitis, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2142 [*Russ. Chem. Bull.*, 1998, **47**, 2074 (Engl. Transl.)].
29. N. L. Khilkova, V. N. Knyazev, N. S. Knyazev, N. S. Patalakha, and V. N. Drozd, *Zh. Org. Khim.*, 1992, **28**, 1048 [*Russ. J. Org. Chem.*, 1992, **28** (Engl. Transl.)].
30. G. M. Sheldrick, SHELXTL PLUS, PC Version, *A system of computer programs for the determination of crystal structure from X-ray diffraction data*, Rev. 5. 02, Siemens Analytical X-ray Instruments Inc., Germany, 1994.
31. N. K. Hansen and P. Coppens, *Acta Cryst.*, 1978, **A34**, 909.
32. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1990.
33. R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893.
34. T. Koritsanszky, S. T. Howard, P. R. Mallinson, Z. Su, T. Richter, and N. K. Hansen, *XD-Computer program package for multipole refinement and analysis of electron densities from diffraction data*, Version 1995.
35. K. Kurki-Suonio, *Isr. J. Chem.*, 1977, **16**, 115.
36. M. W. Schmidt, K. K. Baldridge, J. A. Bootz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Masunega, K. A. Nguyen, S. Su, T. L. Windees, M. Dupois, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
37. F. W. Biegler-König, R. F. W. Bader, and T. H. Tang, *J. Comput. Chem.*, 1982, **3**, 317.
38. V. G. Tsirel'son, *Itogi nauki i tekhniki. Kristallokhimiya*, [*Results of Science and Engineering. Crystal Chemistry*], VINITI, Moscow, 1993, **27**, 3 (in Russian).
39. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. J. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1.
40. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1989, **58**, 713 [*Russ. Chem. Rev.*, 1989, **58** (Engl. Transl.)].

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