Molecular and electronic structures and conformational analysis of derivatives of 9-nitroanthracene, anionic σ-complexes

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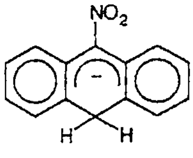
Potassium 10-methoxy-9-nitroanthracenide was studied by X-ray diffraction analysis. The central ring of the anthracene fragment adopts an asymmetrically flattened boat conformation. The bond lengths in the C(Ar)—C(NO_2)—C(Ar) fragment are indicative of the presence of conjugation between the π-systems of the benzene rings and the nitro group owing to a substantial contribution of the *aci* form to the structure of the nitro group. Quantum-chemical calculations of anionic σ-complexes of 9-nitroanthracene derivatives were performed. In all cases, the central ring adopts two conformations with the pseudoaxial and pseudoequatorial orientations of the substituents at the saturated C(10) atom, respectively. The relative stability of the conformers and the factors determining the stability were considered. The minima on the potential energy surface have a flattened shape in spite of relatively high barriers to the conformational transition (2—4 kcal mol^{-1}). The deviation of the C(Ar)—C(Ar)—C(sp^3)—C(Ar) torsion angle from the equilibrium value by ±20° causes an increase in the energy of the anion by less than 1 kcal mol^{-1}. The effect of the substituents on the charge distribution was considered.

Key words: 9-nitroanthracene, anionic σ-complexes, molecular structure, conformational analysis, X-ray diffraction analysis, semiempirical quantum-chemical AM1 method.

Anionic σ-complexes of aromatic polynitro compounds are intermediates in reactions of nucleophilic substitution.[1] Studies of the spatial structures of these compounds can provide important data on the reactivity and fine details of the reaction mechanisms. Unfortunately, because of the instability of σ-complexes, it is generally not only difficult to study them by X-ray diffraction analysis but even impossible to isolate these compounds from solutions. Because of this, experimental data[2—8] on the structures of these compounds are scarce.

The aim of this work is to theoretically and experimentally study the molecular and electronic structures of anionic σ-complexes of 9-nitroanthracene **1—3**.



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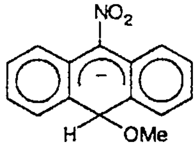

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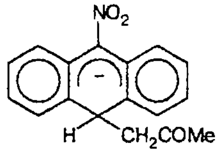

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Experimental

Potassium salt of anion **2** was prepared according to a procedure reported previously.[9] Crystals were grown by slow cooling of a solution of the salt in methanol.

X-ray diffraction analysis. Crystals of the salt $2 \cdot K^+ \cdot 5MeOH \cdot 3H_2O$ are monoclinic. At −80 °C, a = 21.398(8) Å, b = 7.564(3) Å, c = 13.295(5) Å, β = 107.21(3)°, V = 2056(3) $Å^3$, space group $C2$, Z = 4, d_{calc} = 1.342 g cm^{-3}, μ = 0.295 mm^{-1}. Intensities of 1900 independent reflections (R_{int} = 0.08) were measured on a four-circle automated Syntex $P2_1$/PC diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique, $2\theta_{max}$ = 50°). We carried out the profile analysis of the X-ray diffraction data according to a known procedure,[10] which made it possible to improve substantially the quality of the data set.

The structure was solved by the direct method with the use of the SHELXTL PLUS 4.2 program package.[11] The positions of the hydrogen atoms of the anthracene fragment were calculated geometrically and refined using the riding model with fixed values of U_{iso} = 0.08 $Å^2$. We failed to reveal the positions of the remaining H atoms. The refinement based on F was carried out by the full-matrix least-squares method with

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Table 1. Coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$/Å) of nonhydrogen atoms in the structure of the potassium salt of anion **2**

Atom	*x*	*y*	*z*	U_{eq}
K(1)	5000	19507(21)	0	161(2)
K(2)	5000	24206(14)	0	96(2)
O(1)	5555(5)	17107(22)	1401(7)	71(2)
O(2)	5066(4)	16782(19)	2616(6)	35(2)
O(3)	6559(5)	11849(16)	3203(8)	45(2)
N(1)	5604(4)	16806(19)	2334(6)	17(2)
C(1)	5853(6)	16800(25)	4747(8)	30(2)
C(2)	5959(7)	16015(25)	5762(13)	61(2)
C(3)	6348(6)	14613(23)	6183(9)	34(2)
C(4)	6714(7)	13954(19)	5610(10)	32(2)
C(4A)	6640(7)	14438(22)	4527(10)	41(2)
C(10)	6979(8)	13373(21)	3922(11)	42(2)
C(5A)	7149(7)	14666(21)	3235(10)	39(2)
C(5)	7778(5)	14506(23)	2932(8)	39(2)
C(6)	7955(9)	15681(23)	2184(13)	49(2)
C(7)	7534(5)	16910(21)	1787(9)	20(2)
C(8)	6912(7)	16730(26)	1966(10)	55(2)
C(8A)	6772(7)	16055(19)	2693(11)	25(2)
C(9)	6190(8)	16391(27)	3036(12)	73(2)
C(1A)	6173(7)	15840(19)	4122(12)	34(2)
C(11)	6415(9)	10740(21)	3595(17)	74(2)
O(1M)	4092(7)	18918(27)	1306(15)	155(3)
C(1M)	3573(10)	17666(26)	987(13)	87(3)
O(2M)	3979(10)	21358(33)	267(12)	196(3)
C(2M)	3394(12)	21283(35)	−603(16)	240(3)
O(3M)	4643(8)	22182(30)	−1574(10)	164(3)
O(1S)	4618(11)	10035(37)	3046(22)	303(3)
C(1S)	4721(14)	11031(25)	3891(15)	99(3)
O(1W)	4626(8)	13422(30)	2741(16)	185(3)

Table 2. Selected bond lengths (*d*) in the structure of the potassium salt of anion **2**

Bond	*d*/Å	Bond	*d*/Å
K(1)—O(1)	2.62(2)	K(1)—O(1M)	3.00(2)
K(1)—O(2M)	2.71(2)	K(1)—O(3M)	2.85(2)
K(2)—O(2M)	3.16(2)	K(2)—O(3M)	2.52(2)
O(1)—N(1)	1.24(1)	O(2)—N(1)	1.31(1)
N(1)—C(9)	1.36(2)	C(4A)—C(10)	1.47(2)
C(4A)—C(1A)	1.45(2)	C(10)—C(5A)	1.46(2)
C(5A)—C(8A)	1.39(2)	C(8A)—C(9)	1.47(2)
C(9)—C(1A)	1.51(2)		

anisotropic thermal parameters using 836 reflections with $F > 6\sigma(F)$ and converged to $R = 0.096$, $R_w = 0.096$, $S = 2.55$. The final coordinates of the nonhydrogen atoms are given in Table 1. The selected bond lengths and bond angles are listed in Tables 2 and 3, respectively.

The spatial structures of anions **1**—**3** were calculated by the semiempirical quantum-chemical AM1 method[12] with full geometry optimization. The conformational flexibility of the dihydrocycle was studied by scanning the C(Ar)—C(Ar)—C(sp^3)—C(Ar) torsion angle in the range of ±50° with a step of 5° and with optimization of the remaining geometric parameters at each point.

The *ab initio* quantum-chemical calculations were carried out using the GAMESS program[13] with the 3-21G basis set.

Results and Discussion

X-ray diffraction analysis of the potassium salt of anion **2** demonstrated that in the crystal, this compound exists as a complex of composition 2 **2**$\cdot$2K$^+\cdot$4MeOH$\cdot$4H$_2$O (Fig. 1). In addition, the asymmetric unit contains H$_2$O and MeOH molecules of solvation.

The N(1)—C(9) bond is substantially shorter (1.36(2) Å) than those in the nitro derivatives of anthracene[14,15] (1.47 Å) and 9,10-dihydroanthracene[16,17] (1.54 Å), which indicates that this bond is partially multiple. This fact as well as the planar configuration of the C(9) atom (the sum of the bond angles is 358(2)°) suggest a substantial contribution of the *aci* form to the structure of the nitro group.

The central ring of the dihydroanthracene fragment adopts an asymmetrical boat conformation (the C(8a)—C(5a)—C(10)—C(4a) and C(4a)—C(1a)—C(9)—C(8a) torsion angles are 41(2)° and 24(2)°, respectively). The methoxy and nitro groups are in the pseudoaxial and pseudoequatorial positions, respectively (the C(1a)—C(4a)—C(10)—O(3) and C(4a)—C(1a)—C(9)—N(1) torsion angles are 83(2)° and −140(2)°, respectively). A substantial flattening of the portion of the ring that contains the nitro group as well as the equatorial orientation of the nitro group are also indicative of the presence of conjugation between the π-systems of the substituent and the benzene rings.

In the crystal, the potassium atoms occupy special positions, namely, the twofold axes (Fig. 2), and form infinite chains along the OY axis. In the chains, metal

Table 3. Selected bond angles (ω) in the structure of the potassium salt of anion **2**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—K(1)—O(1M)	73.8(4)	N(1)—C(9)—C(8A)	121(1)	O(2)—N(1)—C(9)	121(1)
O(1M)—K(1)—O(2M)	46.7(6)	C(8A)—C(9)—C(1A)	121(1)	C(4A)—C(10)—C(5A)	103(1)
O(1M)—K(1)—O(3M)	116.9(6)	K(1)—O(2M)—K(2)	74.1(6)	C(5A)—C(8A)—C(9)	113(1)
K(1)—O(1)—N(1)	137(1)	O(1)—K(1)—O(2M)	118.7(5)	N(1)—C(9)—C(1A)	116(2)
O(1)—N(1)—C(9)	121(1)	O(1)—K(1)—O(3M)	168.8(4)	C(4A)—C(1A)—C(9)	110(1)
C(10)—C(4A)—C(1A)	127(1)	O(2M)—K(1)—O(3M)	71.1(6)	K(1)—O(3M)—K(2)	82.7(5)
C(10)—C(5A)—C(8A)	128(2)	O(1)—N(1)—O(2)	117.9(8)		

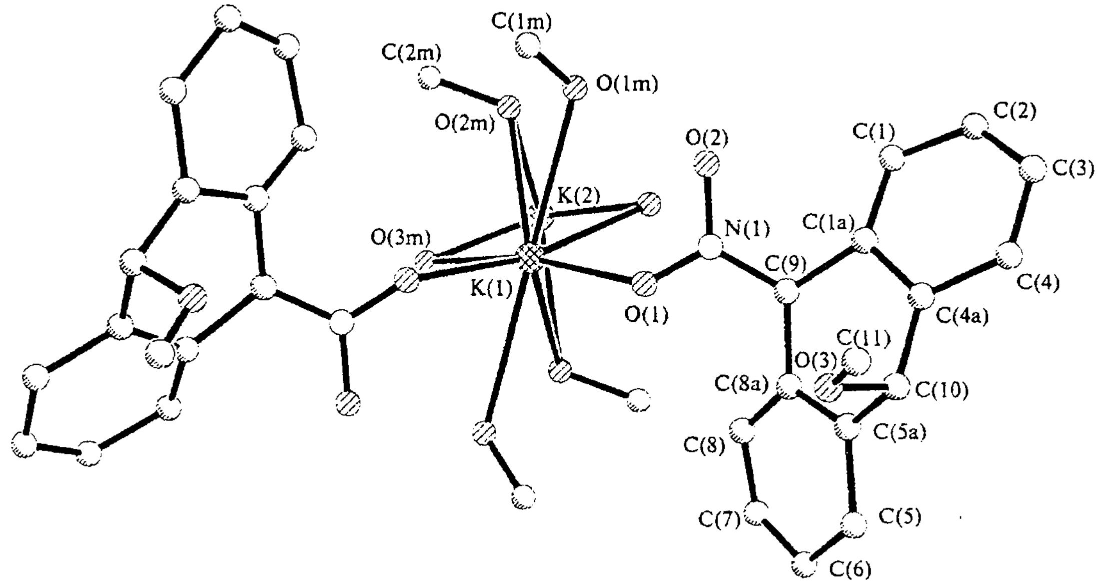

Fig. 1. Structure of the potassium salt of anion 2 (hydrogen atoms are omitted).

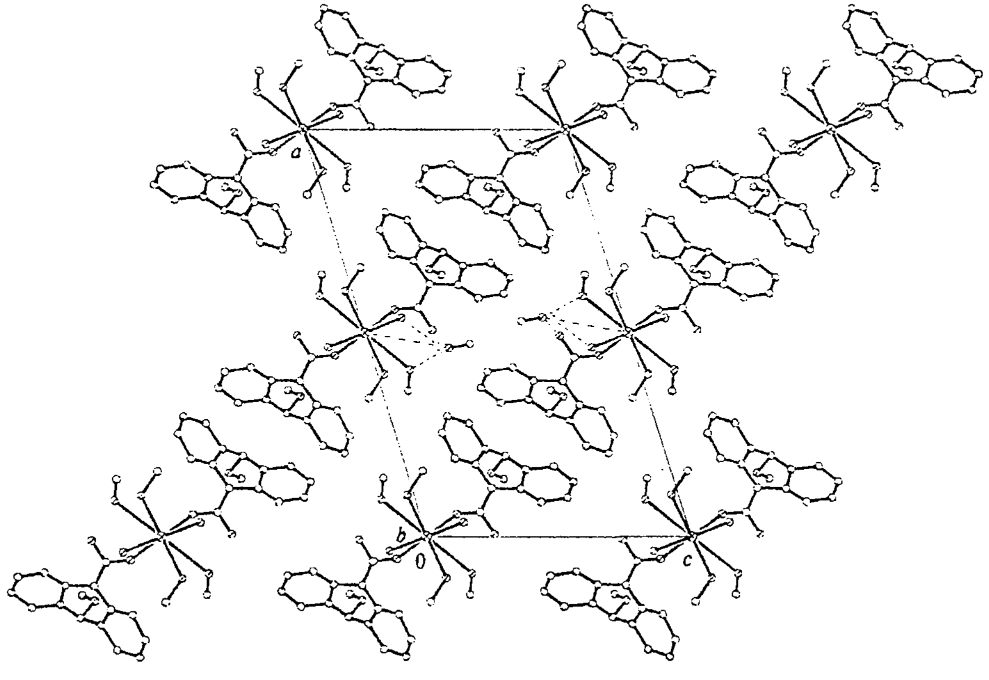

Fig. 2. Crystal structure of the potassium salt of anion 2. Projection onto the XOZ plane.

atoms with coordination numbers 6 and 8 alternate. Each potassium ion is bonded to the adjacent ions through two bridging H_2O molecules and two bridging MeOH molecules along one direction and through two bridging oxygen atoms of the nitro group along the other direction. In addition, one potassium atom (K(1), Fig. 1) is additionally coordinated to two MeOH molecules. Based on the arrangement of the MeOH and H_2O molecules of solvation, it can be suggested that these molecules can be linked to the O(2) atom of the nitro group, the coordinated nonbridging MeOH molecule, and the bridging H_2O molecule through hydrogen bonds (O(2)...O(1S), 1.76 Å; O(1M)...O(1S), 2.41 Å; O(2)...O(1W), 2.73 Å; O(3M)...O(1W), 2.68 Å; and O(1S)...O(1W), 2.60 Å). Unfortunately, the poor quality of the crystals did not allow us to reveal the positions of the hydrogen atoms of the H_2O and MeOH molecules and also results in poor accuracy of the determined geometric parameters. Therefore, it is impossible to discuss the experimental geometry of the molecule in detail.

The poor accuracy of the experimental geometric parameters of anion **2** induced us to carry out *ab initio* quantum-chemical calculations of anions **1—3** with the 3-21G basis set. However, the use of this basis set resulted in a substantial overestimation of the contribution of the *aci* form to the structure of the nitro group. The C(9)—N bond length is close to the average value for the double C=N bond (1.273 Å),[18] and the N—O bond lengths are close to the those of the single bonds, which is inconsistent with the experimental data for anionic σ-complexes of aromatic nitro compounds.[2—8] In spite of this, the calculated conformation of the dihydroanthracene fragment agrees well with the results of X-ray diffraction analysis.

Therefore, *ab initio* calculations with the 3-21G basis set cannot be used in the analysis of the geometry of anionic σ-complexes. Apparently, it is necessary to use substantially larger basis sets for obtaining reliable data with the use of *ab initio* quantum-chemical methods.

In a number of works (see, for example, Refs. 19 and 20), the semiempirical quantum-chemical AM1 method was used in theoretical studies of this class of compounds. This method gave results which agree closely with the experimental data on both the geometric and thermodynamic characteristics. Therefore, we used the results of calculations by the AM1 method in the analysis of the electronic structures and conformational dynamics of anions **1—3**.

Based on the results of calculations by the AM1 method (Table 4), the dihydrocycle in unsubstituted anion **1** adopts an asymmetrically flattened boat conformation. The deviation of the C(9) atom from the plane through the central atoms of the ring (0.28 Å) is substantially smaller than that of the C(10) atom (0.37 Å). The C(9)—N bond length (1.420 Å) agrees well with the experimental data on other σ-complexes.[2—7] The coordination environment about the C(9) atom is planar (the sum of the bond angles is 360°). The C(9)—C(1a) and C(9)—C(8a) bond lengths (1.446 Å) are substantially smaller than the average value of the C(Ar)—C(sp^3) bonds (1.501 Å).[18] On the whole, these results confirm the presence of conjugation between the nitro group and the aromatic rings.

Table 4. Selected geometric parameters of anions **1—3** calculated by the AM1 method

Parameter	Anion				
	1	**2**		**3**	
		axial	equat.	axial	equat.
Bond			*d*/Å		
C(9)—N	1.420	1.424	1.423	1.422	1.419
N—O(1)	1.222	1.221	1.221	1.221	1.221
N—O(2)	1.222	1.220	1.221	1.221	1.221
C(1a)—C(9)	1.446	1.445	1.444	1.444	1.446
C(4a)—C(10)	1.487	1.497	1.498	1.496	1.498
C(10)—R	—	1.444	1.437	1.535	1.519
Bond angle			ω/deg		
C(1a)—C(9)—C(8a)	117.5	117.7	117.9	117.3	116.4
C(4a)—C(10)—C(5a)	112.4	112.0	112.9	111.3	109.3
Torsion angle			φ/deg		
C(4a)—C(1a)—C(9)—N	155.3	155.8	155.1	155.6	154.0
C(1a)—C(4a)—C(10)—R	—	−97.0	153.7	−92.4	174.5
C(4a)—C(1a)—C(9)—C(8a)	−25.0	−23.5	−23.8	−25.3	−29.5
C(1a)—C(4a)—C(10)—C(5a)	31.4	26.9	25.7	30.9	45.8
Puckering parameters:					
S	0.49	0.44	0.43	0.49	0.67
θ	81.4	83.8	86.3	82.1	74.48
Ψ	0.1	0.9	0.4	0.2	0.26

In unsubstituted anion **1**, the dihydrocycle exists as two mirror-symmetrical conformers, which are separated by the inversion barrier of the ring of 2.07 kcal mol^{-1} (Fig. 4). The introduction of the methoxy group at the C(10) atom leads to a slight decrease in the degree of puckering of the dihydrocycle, which is, apparently, due to repulsion between the oxygen atom of this substituent and the nitro group. Apparently, this accounts also for a decrease in the inversion barriers of the dihydrocycle to 1.40 kcal mol^{-1} and destabilization of the pseudoaxial conformer compared to the pseudoequatorial one (ΔE_{a-e} = −0.2 kcal mol^{-1}), which is, on the whole, untypical of derivatives of 9,10-dihydroanthracene.[21] In this case, when the methoxy group is in the pseudoaxial orientation, the repulsion between the substituents is stronger than the repulsion between the substituent at the C(10) atom and the adjacent hydrogen atoms in the *peri* positions of the benzene rings.

Sharp strengthening of the last-mentioned interactions in acetonyl derivative **3** leads to substantial destabilization of the pseudoequatorial conformer (ΔE_{a-e} = 1.62 kcal mol^{-1}) and to an increase in its degree of puckering (Table 4). Steric repulsions account also for a sharp increase in the inversion barrier of the dihydrocycle (3.33 kcal mol^{-1}) compared to unsubstituted anion **1**.

Because the nitro group exists partially in the tautomeric *aci* form, the structures of anions **1—3** are close to those of the 9-imino-substituted derivatives of 9,10-dihydroanthracene.[22,23] Previously, it has been demonstrated[21,24] that these compounds can exhibit high conformational flexibility. This property is determined by two groups of factors that affect the equilibrium conformation of the ring. The first group involves conjugation, which favors flattening of the molecule. The second group of factors involves the bending strain occurring owing to the deformation of the endocyclic bond angle at the saturated carbon atom; this strain is maximum in the case of a planar conformation. There are also additional factors that affect the conformation of the dihydrocycle in anions **1—3**. Nonbonded interactions between the substituents at the C(9) and C(10) atoms and the hydrogen atoms in the *peri* positions of the

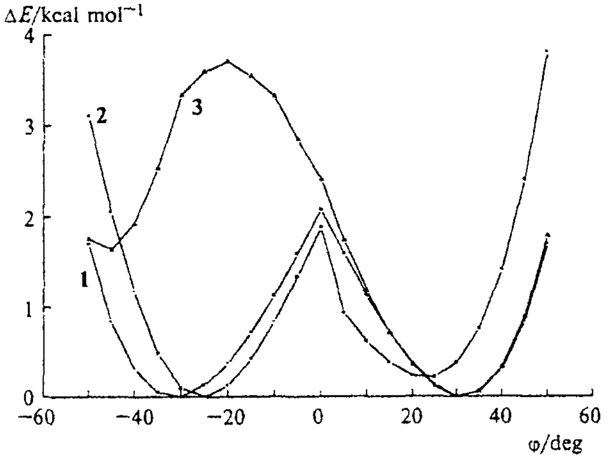

Fig. 3. Dependence of the energy on the C(Ar)—C(Ar)—C(sp^3)—C(Ar) torsion angle in anions **1**—**3** according to the results of AM1 calculations.

aromatic rings have a dual character. In the case of the nitro group, O...H interactions are favorable and should result in a planar conformation of the dihydrocycle. However, in this case, substantially shortened intramolecular O...C(Ar) contacts appear, which results in destabilization of the planar geometry of the molecule. Interactions with the participation of the substituents at the C(10) atom have also a dual character. In the case of unsubstituted anion **1**, the nonbonded interactions between the hydrogen atoms of the methylene group and the benzene rings favor the planar conformation of the dihydrocycle owing to the symmetry of these interactions relative to the mean plane of the anthracene fragment. However, the replacement of one H atom at the C(10) atom by the radical leads to distortion of the symmetry of the nonbonded interactions and, as a result, to destabilization of the planar geometry of the ring.

In all the anions, the minima on the potential energy surface have a rather flattened shape in spite of rather high values of the inversion barriers of the ring. The deviation of the C(Ar)—C(sp^3)—C(Ar)—C(Ar) torsion angle from the equilibrium value by ±20° leads to an increase in the energy by less than 1 kcal mol^{-1} (Fig. 3). In the case of methoxy derivative **2**, the above-considered unfavorable interactions with the participation of the ether group are observed for both orientations of the substituent and lead to a slight increase in the conformational flexibility of the dihydrocycle. In the case of the axial conformer, an increase in the volume of the substituent in anion **3** affects only slightly the degree of flattening of the minimum. However, in the case of the equatorial orientation, the dihydrocycle is substantially more rigid, which is, apparently, associated with the peculiarities of the nonbonded interactions between the planar acetonyl group and the hydrogen atoms in the *peri* positions of the benzene rings. Apparently, this fact is also responsible for the nonplanar structure of the intermediate state of the inversion of the ring in anion **3**.

To summarize, the dihydrocycle in anions **1**—**3** exhibits rather high conformational flexibility owing to the

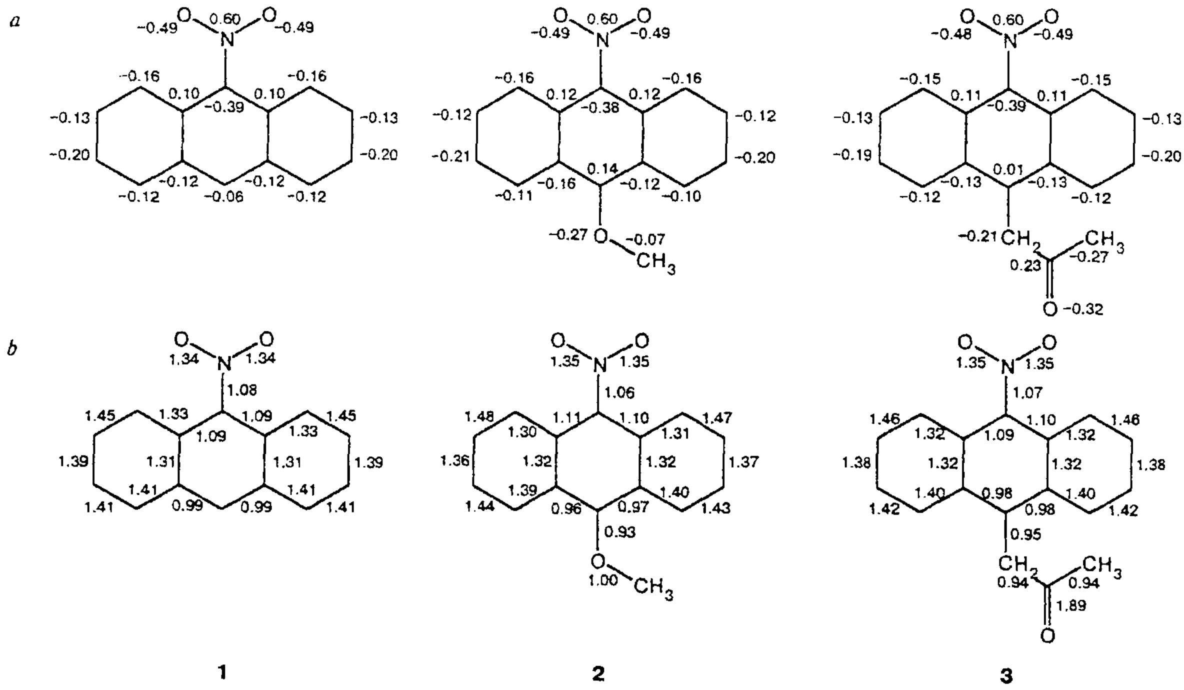

Fig. 4. Charge distribution (*a*) and bond orders (*b*) in anions **1**—**3**.

flattened shape of the minima on the potential energy surface. On the whole, the data obtained demonstrate that anionic σ-complexes based on 9-nitroanthracene follow the general regularities of the conformational analysis, which have been found for ylidene derivatives of 9,10-dihydroanthracene.[21]

Analysis of the charge distribution and bond orders in anions **1**—**3** (Fig. 4) demonstrated that in **1**, the negative charge is located mainly on the oxygen atoms of the nitro group, the carbon atoms of the benzene ring, and the C(10) atom. The introduction of substituents at position 10 of the anthracene fragment leads to a change in the sign of the charge on the C(10) atom and affects only slightly the charges on the remaining atoms of the molecule. The most pronounced effect is observed in the case of methoxy derivative **2**. It should be also noted that the C—N bond has opposite polarization compared to imines,[25] and the C(9) atom carries a high negative charge.

The values of the orders of the bonds with the participation of the C(9) atom are substantially larger than unity, which is indicative of the presence of a conjugation interaction in this fragment and confirms a substantial contribution of the *aci* form of the nitro group to the structure of the anion. The introduction of substituents does not lead to a noticeable change in these values in compounds **2** and **3**.

Therefore, according to the results of quantum-chemical AM1 calculations, the anionic σ-complexes under consideration (the derivatives of 9-nitroanthracene) exhibit high conformational flexibility.

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