Physical Chemistry

Molecular and electronic structures of anionic σ-complexes of 9-nitroanthracene and its derivatives studied by *ab initio* HF/6-31G** calculations

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The molecular structures of anionic σ-complexes of 9-nitroanthracene and its 10-methoxy and 10-acetonyl derivatives were calculated by the *ab initio* quantum-chemical HF/6-31G** method. The central ring of the anthracene fragment adopts a boat conformation. The values of the bond lengths and bond orders in the compounds under study indicate that the contribution of the *aci*-resonance form to the structure of the nitro group is substantially larger than that estimated for 2,4,6-trinitrobenzene derivatives. The substituents have no substantial effect on the geometry of the anion. The negative charge is localized mainly on the oxygen atoms of the nitro group and of the substituents.

Key words: 9-nitroanthracene, anionic σ-complexes, molecular structure, charge distribution, *ab initio* calculations.

Reactions of nucleophilic substitution play an important role in the chemistry of electron-deficient aromatic compounds. These reactions proceed according to two principal mechanisms,[1,2] namely, as S_NAr and vicarious nucleophilic substitution (VNS). Negatively charged σ-complexes, or Meisenheimer complexes, are key intermediates in these reactions.

Previously,[3] we have studied the structures of the anionic σ-complexes of 9-nitroanthracene derivatives by X-ray diffraction analysis. However, the poor quality of the crystals did not allow us to determine the geometric parameters of the anions with sufficient accuracy. Therefore, the data of X-ray diffraction analysis were supplemented by the results of calculations by the semiempirical quantum-chemical AM1 method.[1] An attempt to use more reliable *ab initio* (HF/3-21G) methods failed.[3] The calculated values of the bond lengths in the nitro group were inconsistent with the available experimental data. Apparently, it is necessary to use larger basis sets for obtaining reliable data.

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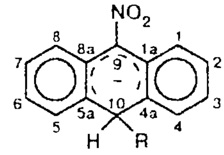
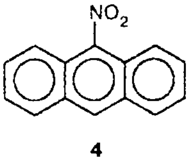
In this work, we report the results of calculations of the molecular and electronic structures of anionic σ-complexes **1**—**3** by the HF/6-31G** method. Previously, it has been demonstrated[4] that these complexes are intermediates in the synthesis of derivatives of anthracene and 9,10-dihydroanthracene.



1: R = H
2: R = OMe
3: R = $CH_2\underset{\underset{O}{\|}}{C}CH_3$



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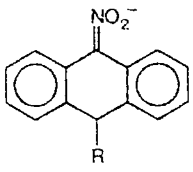
Calculation procedure

The molecular structures of compounds **1**—**4** were calculated by the HF/6-31G** method with full geometry optimization. In the case of molecule **4**, its point symmetry group (C_2) was taken into account. All calculations were carried out using the GAMESS program.[5] The results of calculations are given in Tables 1—3. The conformations of the central anthracene fragments were described by Zefirov—Palyulin's puckering parameters,[6] namely, by the degree of puckering S and the polar angles θ and ψ (θ = 90° and ψ = 0° for the ideal boat conformation and θ = 45° and ψ = 0° for the sofa conformation).

Results and Discussion

The structures of anions **1**—**3** can be represented as a combination of two resonance forms:



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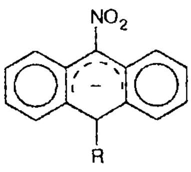


II

The experimental[7—14] and theoretical[15—18] studies of various anionic σ-complexes demonstrated that the contributions of both forms are significant.

The results of our calculations agree with the published data. In particular, the C(9)—N bond in anions **1**—**3** is substantially shorter than that in 9-nitroanthracene (**4**) (Table 1), which is indicative of a substantial contribution of resonance form **I**. It should be noted that this bond is noticeably shorter than the corresponding bonds in the anionic trinitrobenzene σ-complexes (1.41 Å).[11] The atoms of the C(9),C(1a),C(8a),N fragment are in a single plane (to within 0.005 Å). The bond lengths and bond angles at the C(9) atom are indicative of its sp^2-hybridization.

Table 1. Bond lengths in compounds **1**—**4** according to the data of *ab initio* HF/6-31G** calculations

Bond	d/Å			
	1	**2**	**3**	**4**
C(1a)—C(4a)	1.404	1.404	1.404	1.425
C(4a)—C(10)	1.508	1.503	1.513	1.387
C(10)—C(5a)	1.508	1.508	1.514	1.387
C(5a)—C(8a)	1.404	1.406	1.404	1.425
C(8a)—C(9)	1.475	1.467	1.474	1.393
C(1a)—C(9)	1.475	1.470	1.474	1.393
C(9)—N	1.347	1.353	1.348	1.464
N—O(1)	1.237	1.233	1.236	1.194
N—O(2)	1.237	1.234	1.236	1.194
C(10)—R	—	1.420	1.554	—

The C(9)—C(1a) and C(9)—C(8a) bond lengths are close to the average value[19] for the C(Ar)—C(sp^2) bonds. However, these bonds are noticeably longer than those in the anionic σ-complexes of trinitrobenzene.[7—11] Therefore, the effect of conjugation along these bonds in the compounds under study should be weaker than in other Meisenheimer complexes.

Nonsubstituted anion **1** is nonplanar. The central ring of the anthracene fragment adopts an asymmetrical boat conformation. The deviations of the C(9) and C(10) atoms from the plane through the C(1a), C(4a), C(5a), and C(8a) atoms are 0.34 and 0.50 Å, respectively. A flattening of the portion of the ring containing the C(9) atom is also indicative of the presence of conjugation between the π-systems of the C(9)—NO_2 fragment and the benzene rings.

As in the case of other anionic σ-complexes, the nitro group in anion **1** deviates from the plane of the adjacent unsaturated fragment (the C(4a)—C(1a)—C(9)—N torsion angle is 155.8°). Apparently, this is due to repulsion between the O atoms of the substituent and the C atoms at the *peri* positions of the benzene rings. These interactions can be also weakened due to the twist of the nitro group as is the case in 9-nitroanthracene in which the C(1a)—C(9)—N—O(1) torsion angle is −59.3° (Table 2). However, in anions **1**—**3** this substituent is virtually coplanar with the C(1a), C(9), C(8a) fragment. The C(1a)—C(9)—N—O(1) torsion angle in these structure is less than 4° (Table 2). This orientation of the nitro group can be considered as another argument in favor of the partially double character of the C(9)—N bond. Anion **1** as a whole has a symmetry plane passing through the C(9) and C(10) atoms.

When one H atom at the saturated C atom is replaced by the methoxy or acetonyl group, the conformation of the anthracene fragment of the anion remains virtually unchanged and only a slight decrease in the degree of puckering is observed (Table 3). The methoxy

Table 2. Bond angles (ω) and torsion angles (φ) in compounds **1—4** according to the data of *ab initio* HF/6-31G** calculations

Angle	1	2	3	4
		ω/deg		
C(4a)—C(10)—C(5a)	111.2	110.6	110.1	122.1
C(8a)—C(9)—C(1a)	117.1	117.4	117.0	124.0
		φ/deg		
C(1a)—C(4a)—C(10)—C(5a)	41.3	39.1	40.9	0.7
C(4a)—C(10)—C(5a)—C(8a)	−41.3	−39.6	−41.2	0.7
C(10)—C(5a)—C(8a)—C(9)	6.9	8.6	7.8	−1.3
C(5a)—C(8a)—C(9)—C(1a)	29.6	25.3	28.7	−0.7
C(8a)—C(9)—C(1a)—C(4a)	−29.6	−25.8	−29.0	0.7
C(9)—C(1a)—C(4a)—C(10)	−6.9	−7.0	−7.2	−1.3
C(4a)—C(1a)—C(9)—N	155.8	157.8	155.4	−179.3
C(1a)—C(9)—N—O(1)	−3.8	−2.1	−2.9	−59.3
C(1a)—C(4a)—C(10)—R	—	−84.3	−82.3	—

Table 3. Puckering parameters for compounds **1—4**

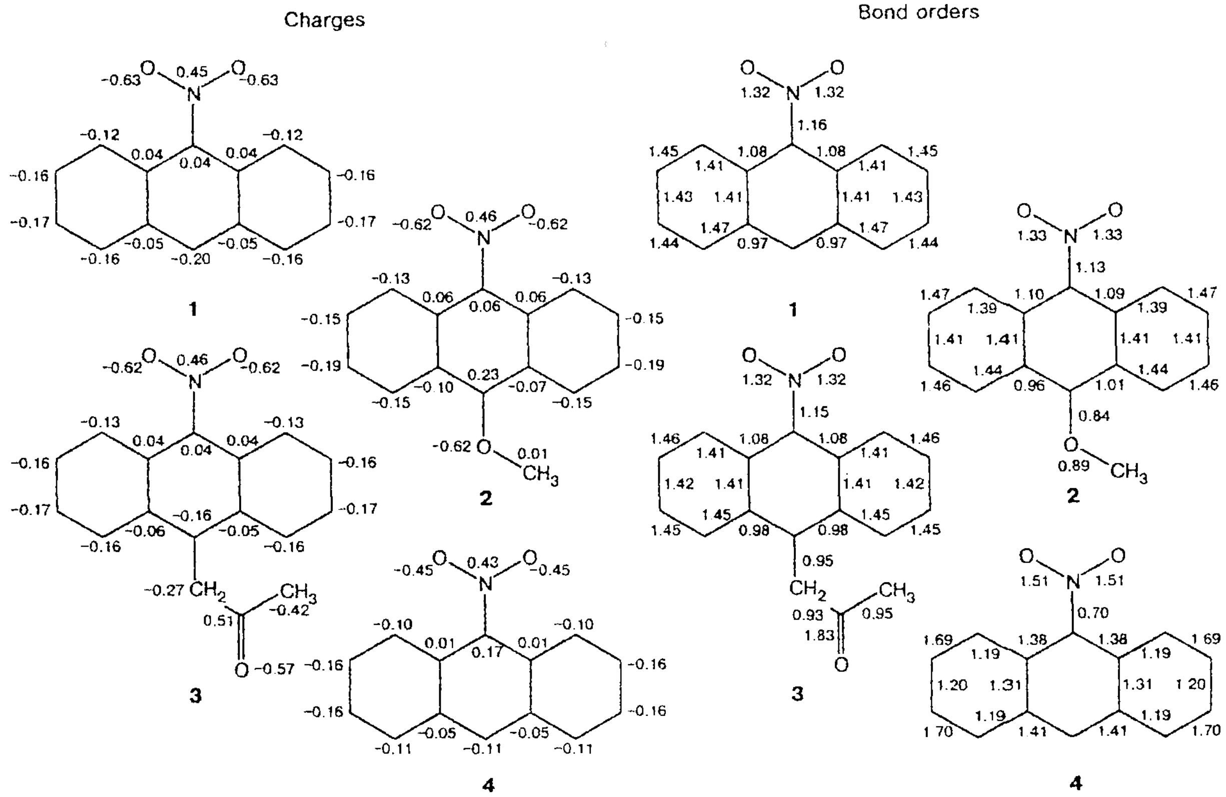
Parameter	1	2	3	4
S	0.62	0.58	0.62	0
θ	78.1	75.0	77.2	—
ψ	0	1.1	0.4	—

group is in the pseudoaxial orientation, which agrees with the data of X-ray diffraction analysis.[3] This orientation of the substituent causes the repulsion between the negatively charged O atoms of the MeO and NO_2 groups, which apparently leads to flattening of the anthracene fragment. The bond lengths in anions **2** and **1** are virtually identical, except for the slight shortening of the C(9)—C(Ar) bonds (Δd = 0.008 and 0.005 Å) and the elongation of the C(9)—N bond (Δd= 0.006 Å) in anion **2**. The nitroanthracene fragment in structure **2** has no symmetry plane.

The presence of the bulky substituent in anion **3** has no effect on the conformation of the ring (see Table 1). However, the steric repulsion between the acetonyl group and the anthracene fragment leads to the elongation of the C(10)—C(Ar) bonds (Δd = 0.005 and 0.006 Å) in derivative **3** compared to those in **1**. The C(10)—C(sp^3) bond lengths are also larger than the average value (1.532 Å)[19] typical of the C(sp^3)—C(sp^3) bonds. The acetonyl substituent is in the pseudoaxial orientation, which is in agreement with the general rules for 9,10-dihydroanthracene derivatives.[20]

The partially double character of the C(9)—N bond in anions **1—3** is also confirmed by its order (1.16) (Scheme 1), which is substantially larger than that in 9-nitroanthracene. The orders of the C(9)—C(1a) and C(9)—C(8a) bonds are indicative of the presence of

Scheme 1



conjugation between the C(9)—NO_2 fragment and the benzene rings. Of special note is the substantial decrease in the orders of the N—O bonds in structures **1—3** compared to those in compound **4**.

A comparison of the bond orders in the benzene rings of anions **1** and **4** suggests that the electron density is essentially delocalized (Scheme 1). The substituents at the saturated C atom have virtually no effect on the bond orders in the anthracene fragment. The slight decrease in the C(9)—N bond order is observed only in the case of anion **2**.

The results of calculations demonstrated that in complex **1** the negative charge is localized primarily on the O atoms of the nitro group and on the C(10) atom of the anthracene fragment (Scheme 1). Therefore, these atoms are the most probable reaction centers in the reactions of σ-complexes with electrophiles, for example, with protons or alkylating agents. Actually, the reactions of sodium and potassium salts of 9-nitroanthracene σ-complexes with alkyl halides afforded 10-substituted 9-anthrone oximes[21,22] as a result of decomposition of intermediate nitrone ethers. However, the latter were not isolated.

The O atom (more electronegative than C) of the methoxy group in anion **2** has a very strong effect on the charge of the C(10) atom (Scheme 1). In this case, the anthracene fragment is also slightly polarized. The acetonyl group also decreases the negative charge of the C(10) atom. However, this effect in anion **3** is weaker than in anion **2**.

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