1056 Russian Chemical Bulletin, International Edition, Vol. 50, No. 6, pp. 1056—1063, June, 2001

Regioselectivity in the reactions of the acetonate ion with electron-deficient arenes

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The reactions of the acetonate ion with 1,3-dinitro-5-X-, 1,3-X_2-5-nitro- (X = NO_2, CN, $COOCH_3$, $CONH_2$, COO^-, and H), and 1,3,5-tricyanobenzenes were studied by ^1H NMR and electronic absorption spectroscopy and by quantum-chemical methods. The kinetic factor is decisive for the initial attack of the carbanion on the C(2) atom of unsymmetrical arenes. However, σ-adducts in which a nucleophile is added to the C(4) atom are more stable thermodynamically. In the case of 1,3-X_2-5-nitrobenzenes (X = CN, $COOCH_3$, or $CONH_2$), the σ-adducts with the acetonate group in *para*-position to the X group unexpectedly proved to be very stable. The structures of the σ-adducts based on trinitro- and 1,3-dinitro-5-cyanobenzenes were determined by X-ray diffraction analysis. Quantum-chemical calculations (the AM1 and PM3 semiempirical methods and the density functional method) were used to interpret the reaction regioselectivity and the molecular and electronic structures of the σ-adducts.

Key words: anionic σ-adducts of arenes, regioselectivity, reaction mechanism, quantum-chemical calculation, molecular spectroscopy, X-ray diffraction analysis, Meisenheimer complexes.

Nucleophilic substitution in arenes is an important area of chemistry from the viewpoint of both practical applications and the development of the theory of reaction mechanisms. The most common mechanism of activated nucleophilic substitution in arenes is an ionic stepwise addition—elimination (S_NAr), with the formation of a negatively charged σ-adduct as the key stage.[1—3] Such anionic σ-adducts of arenes are highly reactive toward electrophilic agents and oxidants. Because of this, they seem to be attractive synthons for the preparative synthesis of a wide range of polyfunctional arenes, hetarenes, and alicyclic compounds.[4—5] However, the use of σ-adducts for these purposes is sometimes inconvenient owing to the formation of a mixture of isomers differing in the position at which a nucleophile is added to arenes containing different electron-withdrawing substituents. This process has been extensively studied for the reactions of 1-X-2,4-dinitro- and 1-X-2,4,6-trinitrobenzene derivatives with O- and N-nucleophiles,[6] so-called Meisenheimer complexes, and, to a lesser degree, for the reactions of arenes with C-nucleophiles, which yield more stable Yanovsky σ-adducts.[7]

The goal of the present work was to study the regioselectivity of the Yanovsky reaction for benzene derivatives (**1a**—**k**) depending on the reaction conditions and carry out quantum-chemical calculations by semiempirical (AM1 and PM3) and nonempirical methods (DFT/BLYP), as well as X-ray diffraction analysis of compounds **2b** (the $N(C_4H_9)_4^+$ cation) and **2c** (the K^+ cation), in order to establish the structures of such σ-adducts and the regularities of their formation. It should be noted that the structure of the Yanovsky adducts is studied insufficiently. Our recent papers[8—14] and previous investigations[15—20] have mainly been concerned with different aspects of the molecular structure of and electron-density distribution in the conventional Meisenheimer complexes, namely, 9-nitroanthracene, 5,7-dinitroquinoline, and 2,4,6-trinitrobenzene derivatives. Actually, there is only one study devoted to the X-ray diffraction analysis of the Yanovsky adduct.[21] However, these X-ray diffraction data are very inaccu-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1012—1019, June, 2001.

Table 1. Ratio of the product contents in the reactions of arenes **1a,c—i** with the acetonate ion according to the ^{1}H NMR data at 25 °C

Arene	Reaction mixture	Isolated product, **2** : **3**		Factors
		KOH	MeOK	
1a	**2** → **3**	0 : 1	0 : 1	3S, 3T, 3OK > 2CK
1c—e	**2**, **3**	1 : 1.2	1 : 1.2	3S, 3T, 3OK ≈ 2CK
1f	**2** → **3**	0 : 1	1 : 1.8	3S, 3T, 3OK > 2CK
1g—i	**2** → **3**	1 : 10	1 : 5.7	3S, 3CK, 3T > 2OK

Note. S, T, OK, and CK designate statistical, thermodynamic, orbital kinetic, and charge kinetic factors, respectively.

rate, thus preventing reliable analysis of the molecular structure of the compounds we are interested in.

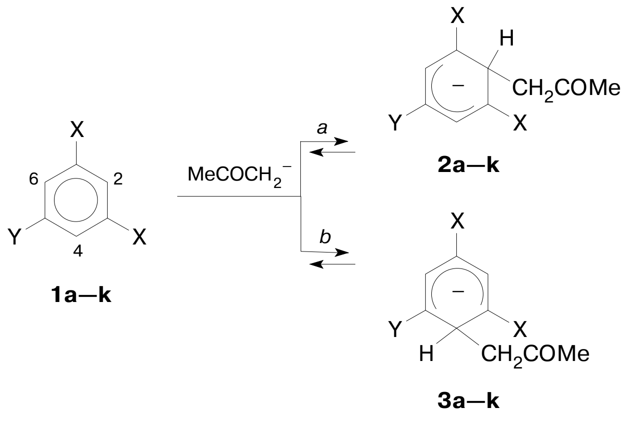
σ-Adducts were synthesized in acetone. A suspension of KOH or a solution of MeOK in MeOH were used as bases (B$^-$) to generate carbanions:

$$\mathrm{MeCOMe} + \mathrm{B}^- \rightleftharpoons \mathrm{CH_2COMe}^- + \mathrm{HB}. \qquad (1)$$

The course of the process was monitored by recording electronic and ^{1}H NMR spectra; the appearance of characteristic absorption bands and ^{1}H signals for the ring protons indicated the formation of σ-adducts. The relative content of isomers in the reaction mixture and in the product isolated therefrom was determined from a ratio of the integrated intensities of the corresponding signals in the ^{1}H NMR spectra (Table 1).

The electronic spectra of the reaction mixture of **1a—f** contain new absorption bands at 16000 and 18500 cm^{-1} for two isomeric adducts **2** and **3**, respectively (Scheme 1).

Scheme 1



1	X	Y	1	X	Y
a	NO$_2$	H	**f**	NO$_2$	COO$^-$
b	NO$_2$	NO$_2$	**g**	CN	NO$_2$
c	NO$_2$	CN	**h**	COOMe	NO$_2$
d	NO$_2$	COOMe	**i**	CONH$_2$	NO$_2$
e	NO$_2$	CONH$_2$	**k**	CN	CN

In the cases of dinitrobenzene **1a** and potassium dinitrobenzoate **1f**, a long-wave band from isomer **2** rapidly diminishes because of its transformation into more stable isomer **3**. The reactions of compounds **1c—e** with the acetonate ion yield equilibrium mixtures of isomers, whose compositions are independent of whether KOH or MeOK was used or whether the reaction was carried out in acetone—water (30 : 1, by volume).

The electronic spectra of the reaction mixture of 1,3-X$_2$-5-nitrobenzenes **1g—i** contain a characteristic absorption band at 18300 cm^{-1} for σ-adduct **3** (Scheme 1). In this case, isomer **2** was not detected. 1,3,5-Trinitro- (**1b**) and 1,3,5-tricyanobenzenes (**1k**) give σ-adducts **2b,k**.

An ^{1}H NMR study of the reaction of the corresponding arene in DMSO-d$_6$—Me$_2$CO in the presence of a suspension of KOH showed that the attack of the acetonate ions on arenes **1c—e** results in the simultaneous formation of isomers **2** and **3** in a ratio of 1 : 1.2 (see Table). Interestingly, the content of symmetrical isomers (**2c—e**) in the mixture is twice as high as that randomly expected from the number of nonequivalent C atoms of the arenes (n(**2**) : n(**3**) = 1 : 2). In the reaction mixtures of compounds **1g** and **1h** with the acetonate ion, the initial content of adduct **2** is 25 and 10%, respectively, but it rapidly decreases so that adduct **3** remains the sole product after 4 h. This unusual fact is in conflict with the conventional opinion that σ-adducts in which the nitro group is *para* to the C(1) atom in sp^3-hybridization are more stable.[22] ^{1}H NMR spectroscopy revealed no products of *ipso*-addition of the nucleophile to the C atoms bound to the substituents.

When isolated in the crystalline form, a mixture of adducts obtained from compounds **1c—e** retains the same composition as that in solution (1 : 1.2), whereas the ratio of isomers for **1f** and **1g** depends on the way of generating of the acetonate ion (see Table 1). With MeOK as a base, the concentration of MeCOCH$_2^-$ is higher than that in the case of the heterophase reaction with KOH. For this reason, the former reaction proceeds more rapidly, but it becomes less selective, which increases the relative number of unstable isomers.

The formation of σ-adducts is determined by the kinetic and thermodynamic factors. Based on them, we analyzed the data on the relative content of isomers in the reaction mixture. Earlier,[23,24] the enthalpy of formation of σ-adducts (ΔH_f) and the enthalpy of reaction (ΔH_r) in the gas phase were proposed as a measure of regioselectivity for the reactions of benzene, nitrobenzene, 4-fluoronitrobenzene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, and 2,4,6-trinitroanisole with the OH$^-$, OCH$_3^-$, and CH$_3^-$ ions. It was also shown[24] that the stability of isomers both in the gas phase and in solution obeys the same regularity.

In the present work, the AM1 and PM3 semiempirical methods and the *ab initio* DFT/BLYP method based on density functional theory with full optimization of the

Table 2. Quantum-chemical results for σ-adducts **2** and **3** by the density functional method (DFT/BLYP)

Compound	$-E$ /kcal mol^{-1}	E_{HOMO} /eV	ΔH_{P} /kcal mol^{-1}
2a	523356.89	−0.93	−37.15
3a	523357.26	−0.96	−37.53
2b	651751.87	−1.86	−58.55
2c	581266.76	−1.60	−53.97
3c	581267.01	−1.59	−54.22
2d	666382.30	−1.62	−50.19
3d	666382.55	−1.63	−50.44
2e	629246.82	−1.56	−39.42
3e	629245.44	−1.59	−38.04
2f	641325.51	2.08	38.21
3f	641337.93	2.16	25.79
2g	510780.45	−1.25	−48.19
3g	510780.70	−1.29	−48.44
2h	681020.07	−1.23	−26.79
3h	681031.53	−1.23	−38.25
2i	606757.27	−1.11	−37.35
3i	606757.45	−1.11	−37.53
2k	440292.25	−0.89	−40.53

geometry were used to calculate charges on the atoms, total energy (E), the enthalpies of formation (ΔH_f), and the energies of boundary orbitals (E_{HOMO} and E_{LUMO}) for the starting arenes, the acetonate ion, and isomeric σ-adducts. Based on the ΔH_f values, we determined the enthalpies of formation (ΔH_r) of σ-adducts **2a,c—i** and **3a—k** (Table 2).

The charge and orbital factors are responsible for the kinetic control of the direction of nucleophilic attack. The formation of isomers **2a,c—f** is favored by a greater charge on the C(2) atom positioned between two nitro groups in compounds **1a,c—f**. In the case of mononitroarenes **1g—i**, the charges of the reagents interact in such a way that the nucleophile adds to the C(4)(C(6)) atom. At the same time, the orbital factor, which considers the contribution from the p_z-orbitals of the C atoms to the LUMO of nitroarene as an acceptor of an electron pair, acts in an opposite way. In dinitro compounds **1a,c—f**, the C(4) and C(6) atoms contribute most considerably, which correlates with the predominant formation of adducts **3**, while in mononitroarenes **1g—i**, the greatest contribution is provided by the C(2) atom, thus giving isomers **2**. Taking into account the content of the isomers in the mixture (see Table 1), one can conclude that for this ion-molecular reaction the site of the initial acetonate attack on arenes is mainly determined by the charge factor; this correlates with a rather large difference between the energies of the reagent boundary orbitals, for which reasons their overlapping is hindered.

Analysis of ΔH_f, E_{HOMO} of σ-adducts, and the enthalpy of addition reaction ΔH_r showed that by and large all the methods correctly predict a higher thermodynamic stability of σ-adducts **3a,c—f** isolated from the reaction mixture (see Table 2). However, the semiempirical methods for adducts based on **1g—i** failed, predicting that isomers **2g—i** with the *para*-nitro group relative to the tetrahedral node of a σ-adduct should be more stable, though their content in the isolated product is low. Only the use of the density functional method proved that adducts **3g—i** are really more stable than their isomers **2g—i**.

Note that the steric effects influence this process insignificantly, because the ratio of isomers is independent of the bulkiness of the electron-withdrawing group (*e.g.*, CN and COOMe).

It can be seen from the energy parameters of formation of σ-adducts **2a—k** and **3a—k** that the reaction enthalpy and the stability of these adducts is determined by the number and nature of electron-withdrawing groups.

Thus, the most considerable contribution to the formation of σ-adducts based on compounds **1a,f** is provided by the statistical probability of the attack and by the thermodynamic stability of adducts (3S, 3T > 2K). When σ-adducts are obtained from compounds **1c—e**, these factors compete with the kinetic factor determined by the charge on the C(2) atom (3S, 3T ≈ 2K). Finally, in the case of arenes **1g—i**, the statistical probability of the attack on the C(4) atom and the charge-controlled kinetic factor prevail over the thermodynamic factor (3S, 3K > 2T).

The quantum-chemical results were confirmed by X-ray diffraction analysis of adducts **2b** ($\text{Kt}^+ = \text{N}^+(\text{C}_4\text{H}_9)_4$) (Fig. 1) and **2c** ($\text{Kt}^+ = \text{K}^+$) (Fig. 2, Tables 3—5).

The X-ray diffraction study of compound **2c** showed that the organic anion and the potassium cation are in the special position on a plane of symmetry *m* passing through the C(1), C(4), C(5), C(6), C(7), and N(2) atoms. According to both the X-ray data and quantum-

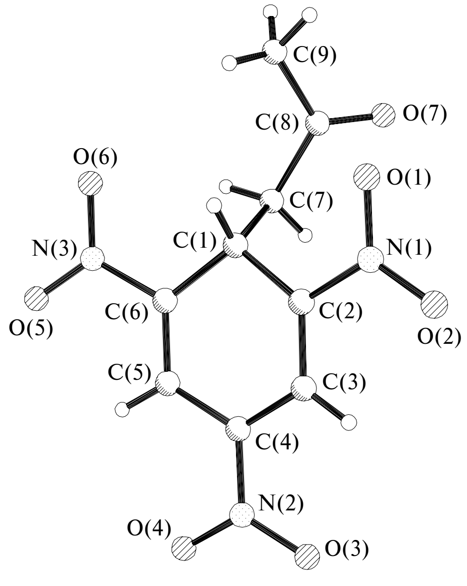


Fig. 1. General view of anionic σ-adduct **2b**.

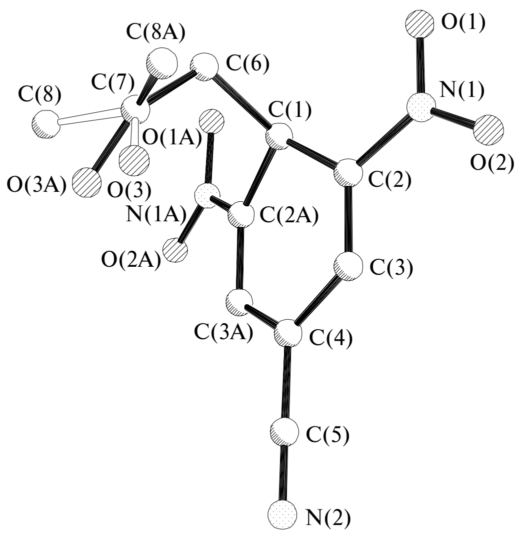


Fig. 2. General view of anionic σ-adduct **2c**. The coordinates of the C(2A), C(3A), C(8A), N(1A), O(1A), O(2A), and O(3A) atoms were obtained by the symmetry operation x, $-y - 0.5$, z.

chemical results (see Table 5), the conformation of the six-membered ring in adducts **2b,c** is a nonuniformly flattened boat (the C(1) and C(4) atoms deviate from the plane of the other ring atoms by 0.195(2) Å and 0.069(2) Å in **2b** and by −0.263(8) Å and −0.057(8) Å in **2c**) rather than it is virtually planar as in the previously studied[8] spirocyclic anionic σ-adducts. Apparently, this is due to the presence of the bulky acetonyl substituent at the C(sp^3) atom, which eliminates the symmetry of nonbonding interactions along the C(sp^2)—C(sp^3) bonds about the mean plane of the ring. As was illustrated earlier[9] with the Meisenheimer complexes (5,7-dinitroquinoline derivatives), this makes the dihydro ring in anionic σ-adducts nonplanar.

The bonds in the conjugated part of the six-membered ring of adducts **2b,c** are largely alternated (see Table 3). For example, the C(2)—C(3) (1.352(2) Å) and C(5)—C(6) bonds (1.348(2) Å) in complex **2b** are markedly shorter than the C(3)—C(4) (1.400(2) Å) and C(4)—C(5) bonds (1.417(2) Å). According to our quantum-chemical results, the same situation is observed in all of the anionic σ-adducts studied in this work. The largest deviation of the calculated C(2)—C(3) and C(5)—C(6) bond lengths from the experimental values is equal to 0.025 Å (see Table 3).

The C—N bond lengths for the *ortho*-nitro groups in anion **2b** (C(2)—N(1) 1.426(2) Å and C(6)—N(3) 1.437(2) Å), as in the previously[8,16] studied adducts (1,3,5-trinitrobenzene derivatives) are significantly longer than the C(4)—N(2) bond (1.399(2) Å) for the *para*-nitro group. However, the latter bond is shorter than that in the Meisenheimer adducts of this series and close in length to the corresponding bond in anionic σ-adducts,[9,10] namely, 5,7-dinitroquinoline derivatives. When the nitro group in anion **2c** is replaced by the cyano group, the C—N bonds for the *ortho*-nitro group become substantially shorter (1.412(5) Å) (see Table 3). At the same time, the C—N bond lengths in anion **2c** are close to the C—N bond length for the *ortho*-nitro group

Table 3. Selected bond lengths (d/Å) in anionic σ-adducts **2b,c** according to the X-ray data and quantum-chemical results

Bond	Complex **2b**				Complex **2c**			
	PM3	AM1	DFT	PCA	PM3	AM1	DFT	PCA[a]
C(1)—C(2)	1.511	1.502	1.528	1.515(2)	1.509	1.502	1.529	1.501(5)
C(2)—C(3)	1.370	1.375	1.373	1.352(2)	1.379	1.381	1.376	1.361(5)
C(3)—C(4)	1.416	1.416	1.414	1.400(2)	1.402	1.406	1.420	1.418(5)
C(4)—C(5)	1.416	1.415	1.413	1.417(2)	1.403	1.407	1.420	1.418(5)
C(5)—C(6)	1.371	1.376	1.373	1.348(2)	1.379	1.380	1.377	1.361(5)
C(6)—C(1)	1.508	1.502	1.528	1.510(2)	1.508	1.502	1.529	1.501(5)
C(2)—N(1)	1.460	1.461	1.440	1.426(2)	1.449	1.454	1.433	1.412(5)
C(4)—N(2)	1.449	1.450	1.440	1.399(2)	—	—	—	—
C(4)—C(11)	—	—	—	—	1.412	1.409	1.423	1.423(9)[b]
C(6)—N(3)	1.462	1.461	1.440	1.437(2)	1.450	1.455	1.433	1.412(5)
N(1)—O(1)	1.228	1.210	1.274	1.237(2)	1.227	1.212	1.276	1.251(4)
N(1)—O(2)	1.223	1.210	1.264	1.244(2)	1.229	1.213	1.268	1.245(5)
N(2)—O(3)	1.225	1.210	1.266	1.259(2)	—	—	—	—
N(2)—O(4)	1.225	1.211	1.266	1.247(2)	—	—	—	—
N(3)—O(5)	1.225	1.210	1.263	1.240(2)	1.229	1.212	1.269	1.245(5)
N(3)—O(6)	1.224	1.210	1.274	1.236(2)	1.227	1.211	1.276	1.251(4)
C(1)—C(7)	1.544	1.528	1.568	1.557(2)	1.541	1.529	1.567	1.553(8)

[a] The C(5), C(6), C(7), N(3), O(5), and O(6) atoms correspond to the C(3A), C(2A), C(6), N(1A), O(2A), and O(1A) atoms in structure **2b** according to the X-ray diffraction data (see Fig. 2).
[b] The C(4)—C(5) bond (see Fig. 2).

Table 4. Selected bond angles (ω/deg) in anionic σ-adducts **2b,c** according to the X-ray data and quantum-chemical results

Angle	Complex **2b**				Complex **2c**			
	PM3	AM1	DFT	X-ray data	PM3	AM1	DFT	X-ray data[a]
C(2)—C(1)—C(6)	110.0	110.6	109.1	107.2(1)	112.5	110.7	109.0	108.3(5)
C(1)—C(2)—C(3)	121.5	124.0	124.0	124.9(1)	121.3	123.4	123.8	124.1(4)
C(2)—C(3)—C(4)	121.5	120.4	120.3	120.6(1)	121.4	121.2	121.4	120.4(4)
C(3)—C(4)—C(5)	118.1	119.9	120.4	119.6(1)	120.2	119.5	118.8	118.7(5)
C(4)—C(5)—C(6)	120.2	120.4	120.4	119.6(1)	121.4	121.1	121.4	120.4(4)
C(1)—C(6)—C(5)	121.6	123.9	123.9	125.8(1)	121.3	123.5	123.7	124.1(4)
N(1)—C(2)—C(1)	118.6	117.0	117.4	116.7(1)	119.0	117.4	117.6	117.0(3)
N(1)—C(2)—C(3)	120.0	119.1	118.6	118.4(1)	119.8	119.2	118.6	118.9(4)
N(2)—C(4)—C(3)	120.9	120.0	119.7	120.0(1)	119.9[b]	120.3[b]	120.5[b]	120.6(2)[c]
N(2)—C(4)—C(5)	120.1	120.0	119.7	120.2(1)	—	—	—	—
N(3)—C(6)—C(1)	118.5	117.0	117.4	115.8(1)	118.9	117.3	117.7	117.0(3)
N(3)—C(6)—C(5)	120.2	119.1	118.6	118.4(1)	119.8	119.2	118.6	118.9(4)

[a] The C(5), C(6), C(7), N(3), O(5), and O(6) atoms in structure **7** correspond to the C(3A), C(2A), C(6), N(1A), O(2A), and O(1A) atoms in structure **2b** (see Figs. 1 and 2).

[b] The N(2)—C(11)—C(4) bond angle.

[c] The N(2)—C(5)—C(4) bond angle (see Fig. 2).

Table 5. Selected torsion angles (ω/deg) in anionic σ-complexes **2b,c** according to the X-ray data and quantum-chemical results

Angle	Complex **2b**				Complex **2c**			
	AM1	PM3	DFT	X-ray data	AM1	PM3	DFT	X-ray data[a]
C(6)—C(1)—C(2)—C(3)	20.22	13.56	13.81	15.5(2)	19.39	13.39	14.21	21.2(6)
C(1)—C(2)—C(3)—C(4)	−6.51	−4.26	−5.57	−6.0(2)	−6.63	−4.39	−5.95	−9.6(6)
C(2)—C(3)—C(4)—C(5)	−9.15	−6.24	−5.22	−6.4(2)	−7.72	−5.62	−4.78	−5.2(7)
C(3)—C(4)—C(5)—C(6)	9.02	5.59	5.39	6.5(2)	7.23	4.84	4.85	5.2(7)
C(4)—C(5)—C(6)—C(1)	6.80	5.60	4.97	5.7(2)	7.62	6.00	5.45	9.6(6)
C(2)—C(1)—C(6)—C(5)	−20.38	−14.25	−13.69	−15.4(2)	−19.91	−14.22	−14.12	−21.2(6)
O(2)—N(1)—C(2)—C(3)	2.47	3.47	3.50	0.8(2)	3.63	3.20	3.09	−2.8(5)
O(3)—N(2)—C(4)—C(3)	−6.17	−2.79	−2.33	−4.9(2)	—	—	—	—
O(5)—N(3)—C(6)—C(5)	−0.67	−2.62	−3.12	−0.1(2)	−1.42	−2.37	−2.62	2.8(5)
C(7)—C(1)—C(2)—C(3)	112.00	105.03	114.71	−105.5(2)	112.08	105.59	114.09	−107.4(4)
C(8)—C(7)—C(1)—C(2)	−57.39	−54.91	−65.30	−83.5(2)	−58.09	−54.53	−66.02	62.7(3)
C(9)—C(8)—C(7)—C(1)	−80.24	−83.28	−170.56	−57.1(2)	−79.69	−81.78	−169.68	106.1(5) −106.1(5)[b]
O(7)—C(8)—C(7)—C(1)	102.78	99.12	9.24	128.3(2)	103.71	100.60	10.34	−47.0(9) 47.0(9)[c]

[a] The C(5), C(6), C(7), C(8), C(9), N(3), O(5), O(6), and O(7) atoms in structure **7** correspond to the C(3A), C(2A), C(6), C(7), C(8), N(1A), O(2A), O(1A), and O(3) atoms in structure **2b** (see Fig. 2).

[b] The C(8A)—C(7)—C(6)—C(1) torsion angle.

[c] The O(3A)—C(7)—C(6)—C(1) torsion angle.

in the Meisenheimer adducts of the 5,7-dinitroquinoline series.[9,10] The AM1 and PM3 calculations markedly overestimate the C—N bond lengths for the nitro groups in complexes **2b,c** (see Table 3). However, this situation seems to be typical of semiempirical calculations of anionic σ-adducts and was noted earlier.[9,25] The DFT-calculated lengths of the C(4)—N(2) bond (1.440 Å) in ion **2b** and the C—N bonds for the *ortho*-nitro groups in ion **2c** are also substantially greater than the experimental values (see Table 3). Almost all of the C—N bonds in anion **2b** prove to be equalized according to nonempirical calculations. The X-ray diffraction data suggest that the C—N bond lengths for the nitro groups tend to become equal only in intramolecular (zwitterionic) Meisenheimer adducts.[11—14] It was shown both theoretically and experimentally that the nitro groups in anions **2b,c** are nearly coplanar with the ring planes (see Table 5).

The acetonyl substituent in anionic σ-complexes **2b,c** is axial (the torsion C(7)—C(1)—C(2)—C(3) angle is −105.5(2)° and −107.4(4)°) and perpendicular (**2b**) to or has the +*sc*-orientation (**2c**) relative to the C(1)—C(2) bond (the torsion C(8)—C(7)—C(1)—C(2) angle is −83.5(2)° and 62.7(3)°, see Table 5). In anion **2b**, the methyl group has the −*sc*-orientation (the torsion C(9)—C(8)—C(7)—C(1) angle is −57.1(2)°), while the carbonyl group has the *ac*-orientation (the torsion O(7)—C(8)—C(7)—C(1) angle is 128.3(2)°) relative to the C(7)—C(8) bond. The carbonyl O(3) atom and the methyl group are disordered in anion **2c** over two equally probable positions, in which these groups are oriented differently relative to the C(6)—C(7) bond (see Fig. 2, Table 5). Unlike ion **2b**, the methyl group in anion **2c** has the ±*ac*-orientation, while the carbonyl group has the ±*sc*-orientation.

On the whole, the quantum-chemical results satisfactorily correlate with the X-ray diffraction data. Some discrepancies are probably due to the effect of the cation on the anion geometry, since the adduct structure in crystal is known to largely depend on the nature of the counterion.[9]

The calculation of the charges on the anionic atoms using different methods demonstrated that they generally tend to change compared to the starting arenes, namely, a considerable increase in the total negative charge in the ring and on the atoms of substituents X. The degree of anionic charge delocalization correlates with the enthalpy of formation of σ-adducts (ΔH_r) and depends on the capability of substituent X for conjugation with the π system of the six-membered ring, increasing for compounds of the same type in the order: $COO^- < H < CN < CONH_2 < COOMe < NO_2$.

Experimental

Electronic spectra were recorded on Specord M-40 spectrophotometer in 0.2—1.0-cm quartz cells. IR spectra were recorded on Specord IR-75 and M-80 spectrophotometers (KBr). All spectroscopic instruments were connected to an analog-to-digital converter and controlled by a personal computer.

^1H NMR spectra were recorded on Jeol FX-90Q (90 MHz) and Bruker (300 MHz) spectrometers for solutions in acetone-d_6 and DMSO-d_6 with Me_4Si as the internal standard.

Elemental analysis was carried out on a Carlo Erba 1100 gas-chromatography elemental analyzer. The flow rate of a carrier gas (He) was 30 mL min^{-1}, a katharometer was used as a detector. A batch of the substance to be analyzed was 0.4—0.6 mg. The samples were burned in the presence of $AgMnO_4$ as an oxidant in aluminum containers in an atmosphere of helium and oxygen (20% He and 80% O_2). The combustion products were further oxidized in the presence of Cr_2O_3 and then CuO, whereupon they were passed through a layer of metallic copper (620 °C) and then through a chromatograph column with Chromosorb 102 as a stationary phase. Cyclohexanone 2,4-dinitrophenylhydrazone was used as a standard. The content of C, H, and N was calculated from the relative peak heights. To determine the content of potassium, a mixture of a σ-adduct and conc. H_2SO_4 was calcined at 600 °C, with subsequent weighing of the resulting K_2SO_4.

Quantum-chemical AM1 and PM3 calculations were performed using the HyperChem 5.02 program package; the density functional (DFT-BLYP) calculations used the known PC program.[26] The basis sets of contracted Gaussian functions included {311/1} for H and {61111/411/11} for C, N, and O. The electron density was represented with the use of auxiliary basis sets composed of nongrouped Gaussian functions with the dimension of (5s 1p) for H and (10s 3p 3d 1f) for C, N, and O.

The solvents used were purified according to the known procedure.[27]

The starting compounds **1a,b,d,f,h** (Aldrich) were used without additional purification; nitroarenes **1c,e,g,i,k** were synthesized as described in Ref. 28.

Anionic σ-adducts 2a—k and 3a—k were prepared by spectrophotometrically controlled Yanovsky reaction[29] and by the methylation method.[30] σ-Adducts **2b—e,k** and **3a,c—i** were precipitated from the reaction solution with diethyl ether, reprecipitated from acetone with ether, and dried *in vacuo* to a constant weight. Isomers **2c—e** and **3c—e** were separated by fractional precipitation. Isomers **2a,f—i** were not isolated in the individual state because of their high lability and low content in the reaction mixture. The structures of σ-adducts **2a—k** and **3a—k** were proved by electronic absorption, ^1H NMR, and IR spectroscopy.

Potassium 1-acetonyl-4-cyano-2,6-dinitrocyclohexa-2,5-dienide (2c). Yield 8%. Found (%): C, 42.35; H, 2.46; K, 14.32; N, 14.03. $C_{10}H_8KN_3O_5$. Calculated (%): C, 41.52; H, 2.79; K, 13.52; N, 14.53; O, 27.65. ^1H NMR (DMSO-d_6), δ: 5.04 (tt, 1 H, H(1), $J_{1,3(1,5)}$ = 0.9 Hz); 7.60 (d, 2 H, H(3), H(5)); 2.40 (d, 2 H, CH_2, $J_{1,\alpha}$ = 5.5 Hz); 2.10 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 25160, 15520. IR (KBr), ν/cm^{-1}: 2200 (ν(CN)), 1707 (ν(CO)), 1610 (ν(CC)), 1509 ($\nu_{as}(NO_2)$), 1122 ($\nu_{as}(NO_2)$).

Potassium 1-acetonyl-6-cyano-2,4-dinitrocyclohexa-2,5-dienide (3c). Yield 47%. Found (%): C, 42.30; H, 2.51; K, 14.22; N, 14.13. $C_{10}H_8KN_3O_5$. Calculated (%): C, 41.52; H, 2.79; K, 13.52; N, 14.53; O, 27.65. ^1H NMR (DMSO-d_6), δ: 4.47 (ddd, 1 H, H(1), $J_{1,3}$ = 0.7 Hz, $J_{1,\alpha}$ = 6.6 Hz, $J_{1,\alpha'}$ = 4.1 Hz); 8.38 (dd, 1 H, H(3), $J_{3,5}$ = 1.8 Hz); 7.42 (d, 1 H, H(5)); 2.71 (dd, H, $CH_{\alpha'}$, $J_{\alpha',\alpha''}$ = 15.7 Hz); 2.57 (dd, H, $CH_{\alpha''}$); 2.13 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 24850, 18540. IR (KBr), ν/cm^{-1}: 2208 (ν(CN)), 1705 (ν(CO)), 1633 (ν(CC)), 1563 ($\nu_{as}(NO_2)$), 1248, 1153 ($\nu_{as}(NO_2)$).

Potassium 1-acetonyl-4-methoxycarbonyl-2,6-dinitrocyclohexa-2,5-dienide (2d). Found (%): C, 41.81; H, 3.22; K, 12.75; N, 8.27. $C_{11}H_{11}KN_2O_7$. Calculated (%): C, 40.99; H, 3.44; K, 12.13; N, 8.69; O, 34.75. ^1H NMR (DMSO-d_6), δ: 5.19 (tt, 1 H, H(1), $J_{1,3(1,5)}$ = 0.9 Hz, $J_{1,\alpha}$ = 5.6 Hz); 8.15 (d, 2 H, H(3), H(5)); 2.43 (d, 2 H, CH_2); 2.16 (s, 3 H, Me); 3.66 (s, 3 H, OMe). UV (Me_2CO), ν/cm^{-1}: 24360, 16200.

Potassium 1-acetonyl-6-methoxycarbonyl-2,4-dinitrocyclohexa-2,5-dienide (3d). Yield 40%. Found (%): C, 42.01; H, 3.24; K, 12.50; N, 8.35. $C_{11}H_{11}KN_2O_7$. Calculated (%): C, 40.99; H, 3.44; K, 12.13; N, 8.69; O, 34.75. ^1H NMR (DMSO-d_6), δ: 4.72 (td, 1 H, H(1), $J_{1,3}$ = 0.9 Hz, $J_{1,\alpha}$ = 5.9 Hz); 8.42 (dd, 1 H, H(3), $J_{3,5}$ = 1.0 Hz); 7.92 (d, 1 H, H(5)); 2.47 (d, 2 H, CH_2); 2.13 (s, 3 H, Me); 3.68 (s, 3 H, OMe). UV (Me_2CO), ν/cm^{-1}: 24160, 18040.

Potassium 1-acetonyl-4-carbamoyl-2,6-dinitrocyclohexa-2,5-dienide (2e). Found (%): C, 39.59; H, 3.14; K, 12.80; N, 13.44. $C_{10}H_{10}KN_3O_6$. Calculated (%): C, 39.09; H, 3.28; K, 12.72; N, 13.67; O, 31.24. ^1H NMR (DMSO-d_6), δ: 5.05 (t, 1 H, H(1), $J_{1,3}$ = 0.9 Hz, $J_{1,\alpha}$ = 5.6 Hz); 8.10 (s, 1 H, H(3)); 2.36 (d, 2 H, CH_2); 2.14 (s, 3 H, Me); 8.70 (s, 2 H, NH_2). UV (Me_2CO), ν/cm^{-1}: 24600, 15280.

Potassium 1-acetonyl-6-carbamoyl-2,4-dinitrocyclohexa-2,5-dienide (3e). UV (Me_2CO), ν/cm^{-1}: 24760, 17480. Found (%): C, 39.59; H, 3.14; K, 12.80; N, 13.44. $C_{10}H_{10}KN_3O_6$. Calculated (%): C, 39.09; H, 3.28; K, 12.72; N, 13.67; O, 31.24.

Potassium 1-acetonyl-4-carboxylato-2,6-dinitrocyclohexa-2,5-dienide (2f). ^{1}H NMR (DMSO-d$_6$), δ: 5.02 (tt, 1 H, H(1), $J_{1,3(1,5)}$ = 0.8 Hz, $J_{1,\alpha}$ = 5.6 Hz); 8.10 (d, 2 H, H(3), H(5)); 2.30 (d, 2 H, CH_2); 2.09 (s, 3 H, Me).

Potassium 1-acetonyl-6-carboxylato-2,4-dinitrocyclohexa-2,5-dienide (3f). Yield 74%. Found (%): C, 34.96; H, 2.32; K, 23.01; N, 7.84. $C_{10}H_8KN_2O_7$. Calculated (%): C, 34.68; H, 2.33; K, 22.58; N, 8.09; O, 32.33. ^{1}H NMR (DMSO-d$_6$), δ: 4.62 (td, 1 H, H(1), $J_{1,3(1,5)}$ = 0.9 Hz, $J_{1,\alpha}$ = 5.7 Hz); 8.22 (dd, 1 H, H(3)); 7.38 (d, 1 H, H(5)); 2.10 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 24970, 17920. IR (Vaseline oil), ν/cm^{-1}: 1707 (ν(CO)), 1633 (ν(CC)), 1540 ($\nu_{as}(NO_2)$), 1180, 1120 ($\nu_{as}(NO_2)$).

Potassium 1-acetonyl-2,6-dicyano-4-nitrocyclohexa-2,5-dienide (2g). ^{1}H NMR (DMSO-d$_6$), δ: 6.76 (t, 1 H, H(1), $J_{1,\alpha}$ = 5.6 Hz); 7.32 (s, 2 H, H(3), H(5)); 2.52 (d, 2 H, CH_2); 2.08 (s, 3 H, Me).

Potassium 1-acetonyl-2,4-dicyano-6-nitrocyclohexa-2,5-dienide (3g). Yield 51%. Found (%): C, 50.13; H, 2.91; K, 14.20; N, 15.45. $C_{11}H_8KN_3O_3$. Calculated (%): C, 49.06; H, 2.99; K, 14.52; N, 15.60; O, 17.82. ^{1}H NMR (DMSO-d$_6$), δ: 4.37 (ddd, 1 H, H(1), $J_{1,5}$ = 1.0 Hz, $J_{1,\alpha'}$ = 6.6 Hz, $J_{1,\alpha''}$ = 4.7 Hz); 6.75 (d, 1 H, H(3), $J_{3,5}$ = 1.5 Hz); 7.50 (dd, 1 H, H(5)); 2.58 (dd, H, $CH_{\alpha'}$, $J_{\alpha',\alpha''}$ = 17.0 Hz); 2.41 (dd, H, $CH_{\alpha''}$); 2.09 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 18340. IR (KBr), ν/cm^{-1}: 2202 (ν(CN)), 1704 (ν(CO)), 1610 (ν(CC)), 1534 ($\nu_{as}(NO_2)$), 1194 ($\nu_s(NO_2)$).

Potassium 1-acetonyl-2,6-di(methoxycarbonyl)-4-nitrocyclohexa-2,5-dienide (2h). ^{1}H NMR (DMSO-d$_6$), δ: 4.17 (t, 1 H, H(1)); 7.82 (s, 2 H, H(3), H(5)).

Potassium 1-acetonyl-2,4-di(methoxycarbonyl)-6-nitrocyclohexa-2,5-dienide (3h). Yield 18%. Found (%): C, 42.28; H, 4.59; K, 11.99; N, 4.42. $C_{11}H_{14}KNO_7$. Calculated (%): C, 42.44; H, 4.53; K, 12.56; N, 4.50; O, 35.97. ^{1}H NMR (DMSO-d$_6$), δ: 4.63 (td, 1 H, H(1)); 7.97 (dd, 1 H, H(3)); 7.47 (d, 1 H, H(5)); 2.65 (d, 2 H, CH_2); 2.11 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 28240, 18040.

Potassium 1-acetonyl-2,4-dicarbamoyl-6-nitrocyclohexa-2,5-dienide (3i). Found (%): C, 41.68; H, 4.74; K, 12.53; N, 4.48. $C_{11}H_{14}KNO_7$. Calculated (%): C, 42.44; H, 4.53; K, 12.56; N, 4.50; O, 35.97. UV (Me_2CO), ν/cm^{-1}: 18250.

Potassium 1-acetonyl-2,4,6-tricyanocyclohexa-2,5-dienide (2k). Yield 8%. Found (%): C, 58.31; H, 3.02; K, 15.45; N, 17.02. $C_{12}H_8KN_3O$. Calculated (%): C, 57.81; H, 3.23; K, 15.68; N, 16.85; O, 6.42. ^{1}H NMR (DMSO-d$_6$), δ: 3.64 (t, 1 H, H(1)); 6.54 (s, 2 H, H(3), H(5)); 2.42 (d, 2 H, CH_2); 2.13 (s, 3 H, Me). UV (Me_2CO), ν/cm^{-1}: 22400. IR (KBr), ν/cm^{-1}: 2162, 2135 (ν(CN)), 1680 (ν(CO)), 1608 (ν(CC)).

X-ray diffraction analysis of compounds 2b,c. The crystallographic parameters and a summary of data collection for structures **2b,c** are presented in Table 6. The reflection intensities were measured on Siemens P3/PC and Syntex P2$_1$/PC automated four-circle diffractometers (graphite monochromator, Mo-Kα radiation, θ/2θ scan mode).

The structures were solved by the direct method with the use of the SHELXTL-97 program package.[31] All H atoms in adducts **2b,c** were located from the electron density difference map. The non-hydrogen atoms were refined by the full-matrix least-squares method on F^2 in the anisotropic approximation. For structure **2b**, the H atoms of the organic cation were refined isotropically. The H atoms in the $N^+(C_4H_9)_4$ cation were refined in the "rider" model with the fixed $U_{iso} = nU_{eq}$ for the non-hydrogen atom bound to the given H atom (n = 1.5 for

Table 6. Crystallographic data for compounds **2b,c**

Parameter	2b	2c
Empirical formula	$C_{25}H_{44}O_7N_4$	$C_{10}H_8O_5N_3K$
Crystal system	Triclinic	Rhombic
Space group	$P\bar{1}$	*Pnma*
a/Å	9.797(4)	7.979(2)
b/Å	12.111(4)	10.196(3)
c/Å	13.187(5)	14.453(6)
α/deg	112.31(3)	90
β/deg	90.70(3)	90
γ/deg	104.43(3)	90
V/Å^3	1391.8(9)	1175.8(7)
Z	2	4
D_{calc}/g cm^{-3}	1.223	1.634
μ/mm^{-1}	0.089	0.473
F(000)	556	592
T/K	153(2)	193(2)
Crystal size (mm)	0.5×0.4×0.2	0.4×0.2×0.2
Diffractometer	Siemens P3/PC	Syntex P2$_1$/PC
Scan range, 2θ/deg	2< 2θ < 50	2< 2θ < 50
No. of measured reflections	5181	2093
No. of independent reflections	4872	1074
R_{int}	0.022	0.046
No. of reflections in LSM	4872	1074
No. of reflections with $F > 4\sigma(F)$	3855	712
No. of parameters	361	117
wR_2	0.119	0.158
R_1 (for reflections with $F > 4\sigma(F)$)	0.044	0.056
S	0.99	0.95

the methyl group and $n = 1.2$ for the other H atoms). In adduct **2c**, all H atoms were refined isotropically, except for the H atoms of the disordered Me group. The latter were refined in the "rider" model with the fixed $U_{iso} = 1.5U_{eq}$ for the C atom bound to the given hydrogen atom. In addition, restrictions were imposed on the following bond lengths in the disordered part of the molecule: C(6)—C(7) 1.500(2) Å, C(7)—C(8) 1.500(2) Å, C(7)—O(3) 1.210(2) Å.

Atomic coordinates in structures **2b,c** and complete tables of bond lengths and angles were deposited with the Cambridge Crystallographic Database; the selected bond lengths and bond and torsion angles in compounds **2b,c** are given in Tables 3—5.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-15-97359 and 00-03-32807a).

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Received June 30, 2000;
in revised form March 12, 2001