Heteroatom Chemistry
Volume 18, Number 1, 2007

Reactions of Carbanions with 2,4-Dinitrofluorobenzene Leading to Stable Heptatrienide Moieties

Yuri G. Gololobov, Olesya A. Linchenko, Pavel V. Petrovskii, Zoija A. Starikova, and Irina A. Garbuzova

A.N.Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, 119991 M-334, Vavilov Str. 28, Moscow, Russia

Received 21 December 2005; revised 13 February 2006

ABSTRACT: *Reactions of NCCH$_2$COOMe* **1a** *and CH$_2$(CN)$_2$* **1b** *with 2,4-dinitrofluorobenzene* **2** *at the presence of Et$_3$ N result in deeply colored crystalline stable salts* **4a,4b** *with anions that contain a system of conjugated bonds. Similar reaction of* **2** *with phosphorus-containing zwitterion* **6** *bearing ethoxy- and cyano-groups at the carbanion center is the first example of the reaction leading to the formation of P-zwitterion* **9** *with a negatively charged heptatriene moiety. This reaction proceeds via a new route of decomposition of the intermediate σ-complex* **7** *occurring with formation of ethylfluoroformate.*

INTRODUCTION

Stable salts or zwitterion conjugates, i.e., negatively charged moieties, for example, **4a,b** and **9**, have not been described. Formation of the intermediate possessing the structure similar to that of the anion in salts **4a,b** was suggested solely from the IR spectroscopy data for the reaction of malonic ester with **2** at the presence of triethylamine [1].

The development of new methods to synthesize highly conjugated, deeply colored stable organic salts and phosphonio heptatrienide zwitterion may be of interest to build electron conductive materials and new reagents for analytical chemistry.

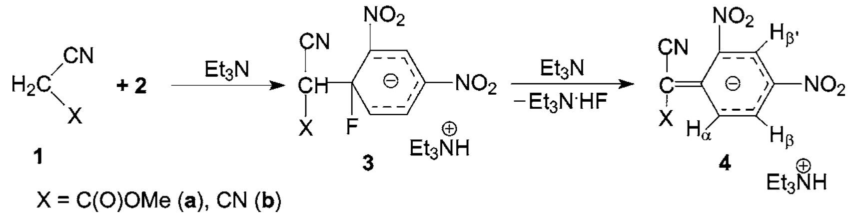
In this work, we report new reactions of carbanions with 2,4-dinitrofluorobenzene that lead to new stable salts with the system of conjugated bonds and the first synthesis of phosphorus-containing zwitterion with heptatriene moiety.

RESULTS AND DISCUSSION

Interaction of methylcyanoacetate and malononitrile with **2** at the presence of triethylamine in CH$_3$CN proceeded very smoothly with the formation of almost black powder. Crystallization of the latter in appropriate solvent resulted in compounds **4a,b**. Apparently, at the first stage of the reaction (Scheme 1), σ-complex **3** was formed. At the second stage, the triethylamine molecule promoted decomposition of σ-complex **3** resulting in the formation of the stable ion pairs **4a,b**.

The composition and the structure of compounds **4a,b** was established by the C, H, N analysis, IR, NMR spectra. For **4a**, X-ray diffraction study and chemical transformations were performed. Compound **4a** was found to be a salt consisting of [NHEt$_3$]$^+$ cations and organic anions.

Correspondence to: Yuri G. Gololobov; e-mail: Yugol@ineos.ac.ru.
Contract grant sponsor: Russian Foundation for Basic Research.
Contract grant sponsor: 04-03-32489.



SCHEME 1

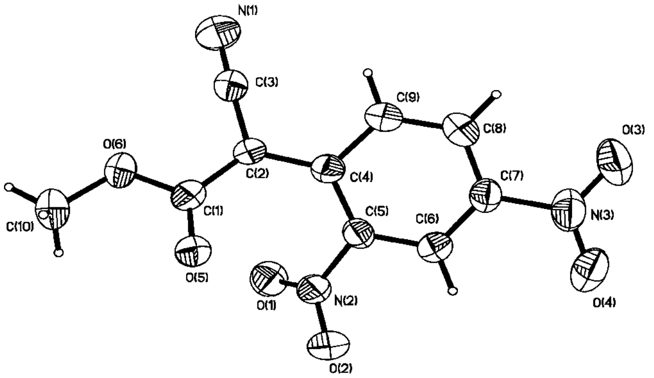


FIGURE 1 Structure and atom labeling of the anion of compound **4a**.

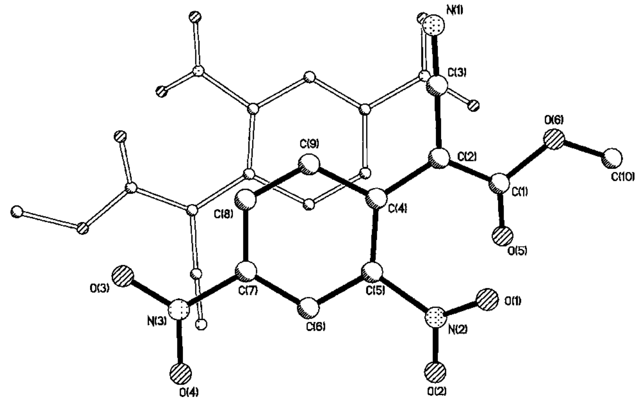


FIGURE 2 The dimeric crystal packing of the anions in compound **4a**.

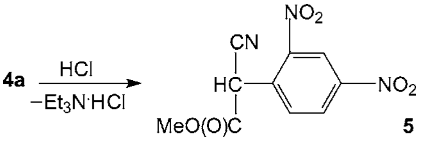
Molecular structure of these anions is presented in Fig. 1. The anions possess a nonplanar structure with the dihedral angle between the ring and the C(1)–C(2)–C(4) plane of 25.1°. The torsion angles C(4)–C(2)–C(1)–O(5) and C(9)–C(4)–C(2)–C(3) are equal to 9.9(6)° and 15.0(4)°, respectively. Although one of the NO_2 groups [N(3)O_2] is coplanar with the ring, other group [N(2)O_2] is rotated around the C(5)–N(2) bond. The dihedral angles between the NO_2 and the ring planes are equal to 1.9° and 40.5°, respectively. In the anion, the negative charge on atom C(4) as is evidenced from that fact that the length of all C(4) bonds was found to exceed the standard bond length including the olefin C(4)=C(2) bond. In the ring, the lengths of the other four C–C bonds [C(5)–C(6), C(6)–C(7), C(7)–C(8), and C(8)–C(9)] are nearly identical (av. 1.371 Å). The C–N and N=O bond lengths are also standard (Table 2).

The mode of the packing of anions and cations in the crystals of salt **4a** is of certain interest. We found that the cation–anion pairs in salt **4a** were assembled in the discrete fashion. This can be explained by the hydrogen bond between the cation Et_3N^+–H and the carbonyl O(5) atom of the anion (the interatomic distances: N···O 2.822(4) Å, H···O 1.88 Å; the angle: N–H···O 158°). Moreover, the rings were found to form the centrosymmetrical dimers (Fig. 2); most likely due to weak attractive π–π stacking interactions between them. The shortest distance between parallel rings was found to be of 3.51 Å.

We found that salt **4a** was a stable compound (cf. [1]). The most reasonable explanation of this fact is the relatively high acidity of the conjugated CH-acid **5** that was formed upon acidification of the triethylammonium salt **4a** (Scheme 2).

In addition to **1a, b**, other methyleneactive compounds with sufficient CH-acidity (e.g., 3-methyl-1-phenyl-2-pyrazoline-5-on, etc.) may form polyconjugated compounds similar to compounds **4a, 4b** upon their reaction with **2** at the presence of triethylamine. A detailed discussion of this topic will be presented in our upcoming publications.

Transformation of σ-complex **3** into **4** discussed above occurs due to relatively high mobility of the H-atom attached to the α-C atom in **3**. It would be interesting to know what might happen to



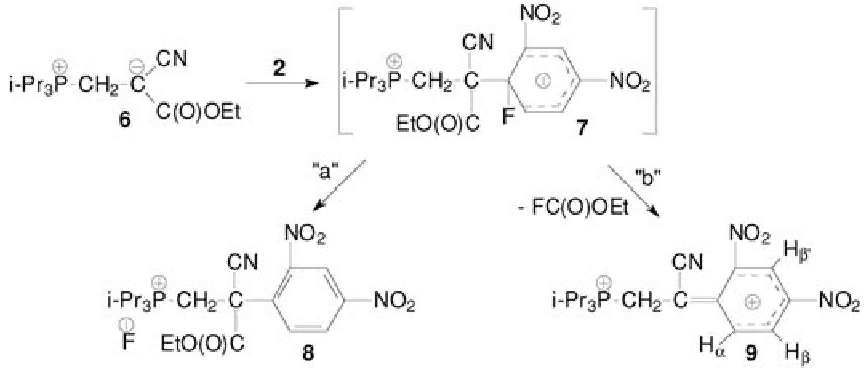
SCHEME 2

σ-complex like **3**, if instead of labile C—H bond, the α-C atom bore loosely bound C(O)OEt group (cf. [2]). To construct such σ-complex, we reacted **2** with zwitterion **6**. We assumed that **6** would react with **2** in dual way: according to the traditional scheme with the formation of the new aromatic system **8** (direction “a”); and with the rupture of the weak C—C bond between the α-C atom and the —C(O)OEt moiety (the CN group weakens the C—C(O)OEt bond in σ-complex **7**) (direction “b”). The latter should yield ethylfluoroformate and zwitterion of a new type **9**. Our experiments showed that at 10–20° and a 20% solution of the starting materials in CH_3CN or CH_2Cl_2, direction “b” became dominant, resulting in almost black crystals of zwitterion **9** (preliminary information [3]) (Scheme 3). Formation of phosphonio heptatrienide zwitterion **9** seems to include intramolecular or intermolecular attack of the —C(O)OEt group by the fluorine atom. Structure of ethylfluoroformate was established by IR and NMR (^1H, ^{19}F) spectroscopy. The lengthening of the conjugation chain due to the attachment of the CN-group to the carbon atom bearing the double bond is, most likely, the driving force of the process.

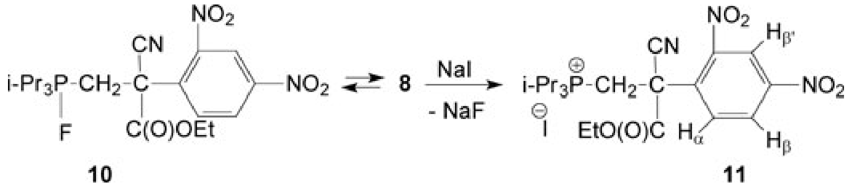
At a reduced temperature (−15 to −20°C) and concentration of the reagents of 3–5%, σ-complex **7** formed in the reaction was transformed mostly according to the traditional scheme of aromatic substitution, i.e., according to direction “a”. This resulted in the formation of the phosphonium fluoride **8** that was in equilibrium with isomeric fluorophosphorane **10** (Scheme 4). Low melting **8** was transformed into crystalline compound **11** by substitution of the fluoride ion to the iodide ion.

Physicochemical methods confirmed the composition of compound **9**. The structure of zwitterion **9** was established by X-ray diffraction. UV/Vis spectroscopy in acetone showed $\lambda_{max} = 478$ nm and $\varepsilon = 34,000$. The IR spectrum showed the intensive band at 2158 cm^{-1}. This suggests a high degree of interactions between the CN group and the negative charge. The IR spectrum also contained the intensive band at 1589 cm^{-1}, which can be the result of the formations of a system of the conjugated bonds. In the proton-NMR spectra, the ring protons of zwitterion **9** were shifted upfield in comparison with aromatic protons of compound **11** due to the negatively charged heptatriene fragment.

X-ray studies of compound **9** confirmed the zwitterionic nature of this compound (Fig. 3). The molecule was found to contain a planar moiety that consisted of the ring and the C(2)—C(4) bond. The angle between this moiety and the CN-group is 10.9°. The dihedral angle between the *ortho*-NO_2 group [N(2)—O(1)—O(2)] and C(4)—C(9) planes is equal to 52.4°. In contrast to the *ortho*-NO_2 group, the *para*-NO_2 group [N(3)—O(4)—O(5)] and the ring were found to be at the same plane. The C(5)—C(6) and C(8)—C(9) bonds are shorter than the other four (av. 1.370 and 1.418 Å, respectively). In other words, the C—C bond length distribution in the ring (Table 2) showed a considerable contribution of the quinoid



SCHEME 3



SCHEME 4

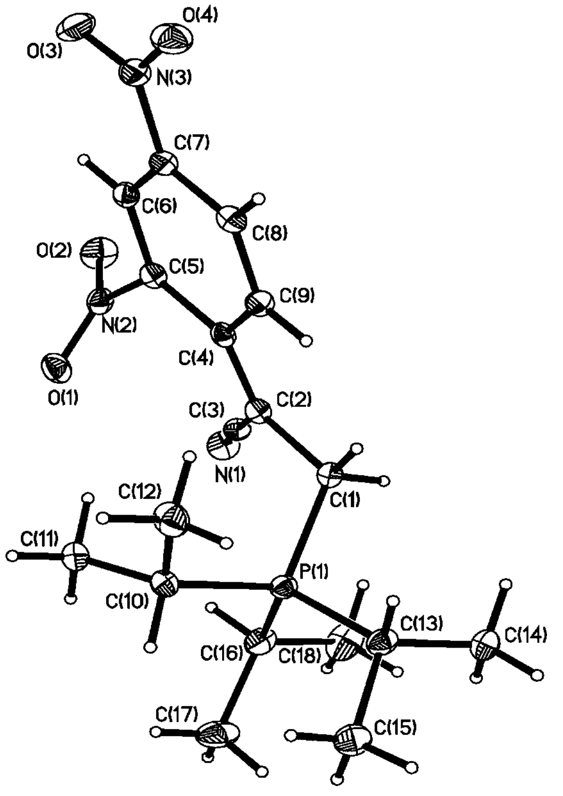


FIGURE 3 X-ray structure and atom labeling of the anion of compound **9**.

form. The C(7)—N(3) (1.421(2) Å) bond is shorter than the C(5)—N(2) (1.456(2) Å) bond. On the contrary, the N(3)—O bond is shorter than the N(2)—O bond (av. 1.229 and 1.240 Å, respectively). According to the literature data [4], in 1,3-dinitrobenzene both the nitro groups are coplanar with the phenyl ring and there is no contribution of the quinoid form to the geometry of the phenyl ring. The length of all the C—N bonds in 1,3-dinitrobenzene is 1.475 Å. In **9**, the P—C bond lengths (av. 1.827(2) Å) are close to the bond lengths [5] in cation Pr^i_4P^+.

Thus, the data obtained unequivocally point out to a bipolar character of the molecule **9**: negative charge is delocalized over the C(6)—C(7)(NO_2)C(8) fragment. The role of the *para*-NO_2 group in such a delocalization was confirmed by the formation of the intermolecular hydrogen bonds O(3)· · ·H—C(1) (the O(3)· · ·H and O(3)· · ·C(1) interatomic distances are equal to 2.17 and 3.055(2) Å, respectively, the O(3)· · ·H—C(1) angle is 150°) (Fig. 4).

NMR spectra showed that in DMSO-d_6, acetone-d_6, or the $CDCl_3$/DMSO-d_6 mixture, zwitterion **9** existed as a mixture of geometrical isomers (Scheme 6); the isomer ratio depended on the nature of the solvent (Table 3).

In view of the fact that, according to our RCA data, in the crystalline state phosphonio

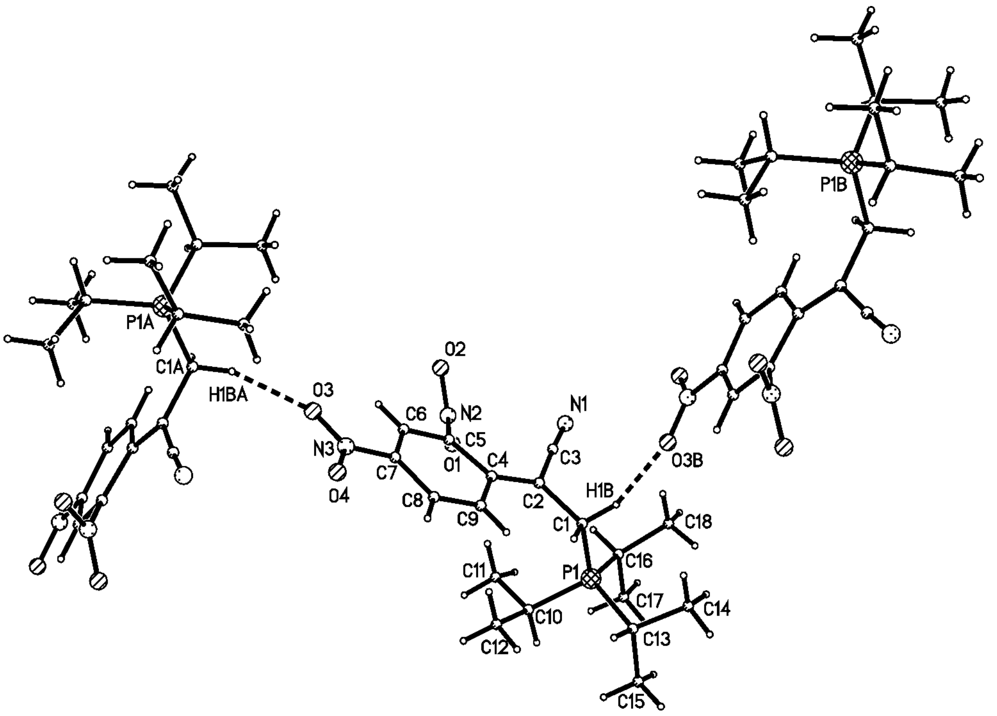
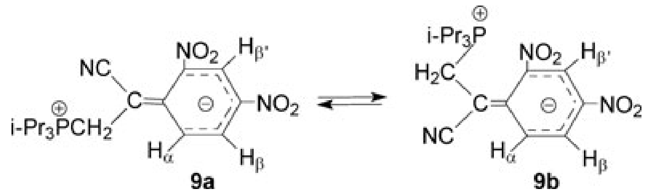


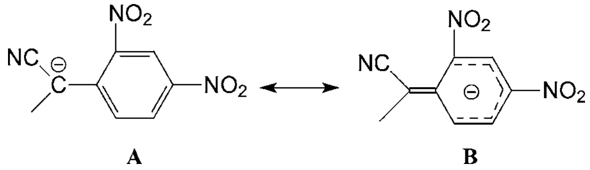
FIGURE 4 The intermolecular hydrogen bonds in crystals of compound **9**.



SCHEME 5 Geometrical isomers of zwitterion **9**.

heptatrienide zwitterion **9** existed in the *cis*-form, we may assume that in the solution the *cis*-form of **9** also prevails. Most likely, isomer **9b** is less stable due to steric effects of a bulky *i*-Pr_3P^+ group (Scheme 5).

The structure of the anion in **9** resembles the structure of a similar fragment in compound **4** (Table 1), but the heptatriene structure is not observed in **4**. The term "heptatriene form" is rather subjective. Negatively charged moieties of compounds **4** and **9** can be presented as superposition of two extreme mesomeric forms **A** and **B**.



At this moment, it is difficult to say what contribution of forms **A** and **B** exists in real electron states of compounds **4** and **9**. The IR and UV spectra suggest that **4** and **11** possess similar delocalization of negative charges (for **4a**: $\nu_{CN} = 2178$ cm^{-1}, $\lambda_{max} = 487$ nm, $\varepsilon = 34{,}300$; for **9**: $\nu_{CN} = 2160$ cm^{-1}, $\lambda_{max} = 478$, $\varepsilon = 34{,}000$). However, RCA data suggest much more pronounced contribution of the heptatriene form in compound **9** (see lengths of the bonds in Table 2).

Dark-cherry solution of zwitterion **9** in acetone was instantaneously decolorized by hydrogen chloride in ether. Under basic conditions, CH-acid **12** again turned into colored zwitterion **9** (Scheme 6).

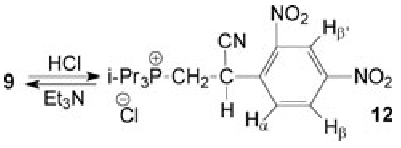
In this paper, we report the first examples of nucleophilic aromatic substitution reactions of fluorine atom in a highly electron deficient arenes, giving stable organic salts or zwitterions with conjugated

TABLE 1 Crystal Data and Structure Refinement Parameters for **4** and **9**

	4	**9**
Formula	$C_{16}H_{22}N_4O_6$	$C_{18}H_{26}N_3O_4P$
Molecular weight	366.38	379.39
Crystal color, habit	Red plate	Black prism
Crystal size (mm)	0.30 × 0.25 × 0.20	0.35 × 0.40 × 0.50
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
a (Å)	7.915(2)	8.511(2)
b (Å)	10.344(3)	16.185(3)
c (Å)	12.135(4)	13.806(3)
α (°)	96.21(3)	90
β (°)	102.87(2)	99.268(4)
γ (°)	106.47(2)	90
V (Å^3)	1413.2(9)	1876.9(6)
Z	2	4
D_{calcd} (g cm^{-3})	1.331	1.343
$2\theta_{max}$ (°)	54	58
Absorption coefficient μ (Mo Kα) (cm^{-1})	1.03	1.75
No. of reflections collect	4282	15475
No. of independent reflections	3876 ($R_{int} = 0.0622$)	4838 ($R_{int} = 0.0470$)
No. of observed reflections ($I > 2\sigma(I)$)	1619	3065
No. of parameters	254	235
R_1 (on *F* for observed reflections)	0.0569	0.0519
WR_2 (on F^2 for all reflections)	0.1332	0.0995
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP,\ P = (1/3)(F_o^2 + 2F_c^2)$	
a	0.0025	0.0117
b	1.3250	1.5015
F (0 0 0)	388	808
Goodness-of-fit	0.986	0.996
Largest differential peak and hole (e Å^{-3})	0.248 and −0.256	0.386 and −0.224

TABLE 2 Selected Bond Lengths (Å), Bond Angles, and Dihedral Angles α (°) of Anion **4** and Molecule **9**

	4	**11**
C(2)—C(4)	1.429(4)	1.398(3)
C(4)—C(5)	1.410(4)	1.447(3)
C(5)—C(6)	1.377(4)	1.370(3)
C(6)—C(7)	1.364(5)	1.387(3)
C(7)—C(8)	1.373(5)	1.402(3)
C(8)—C(9)	1.369(5)	1.371(3)
C(9)—C(4)	1.428(4)	1.436(3)
C(5)—N(2)	1.470(4)	1.456(2)
C(7)—N(3)	1.460(4)	1.421(2)
C(2)—C(3)	1.410(5)	1.417(3)
C(3)—N(1)	1.149(5)	1.145(2)
N(2)—O(1)	1.219(4)	1.226(2)
N(2)—O(2)	1.231(3)	1.232(2)
N(3)—O(3)	1.227(4)	1.237(2)
N(3)—O(4)	1.229(4)	1.244(2)
C(1)—C(2)	1.430(4)	1.516(2)
C(1)—P(1)	–	1.824(2)
P(1)—C(Et)	–	1.821(2), 1.822(2), 1.836(2)
C(4)—C(2)—C(3)	118.5(3)	122.1(2)
C(5)—C(4)—C(9)	113.7(3)	113.2(2)
C(6)—C(7)—C(8)	121.3(3)	120.5(2)
α_1(N(2)O_2)	40.5	54.5
α_2(N(3)O_2)	1.9	2.4



SCHEME 6

anions. This extends our knowledge of the properties of σ-complexes, and enables us to synthesize new perspective synthones. Formation of ethylfluoroformate (Scheme 3) allows us to suggest that this reaction is a special case of a new class of transformations, i.e., such transformations in which the development of the heptatriene systems is the result of the formation of a new olefin bond because of ethylfluoroformate elimination. Most likely, the fluorine atom can be combined not only with the —C(O)OEt group during σ-complex decomposition (e.g., complex **7**), but also with other electrophilic moieties having considerable affinity to the fluorine atoms, for example, Me_3Si—, $Ph_2P(O)$—, etc. This suggests that the formation of highly conjugated systems in **4** and **9** are special cases of novel general reactions involving, on the one hand, various electrophilic fluoroaromatic compounds and, on the other hand, methyleneactive compounds and phosphorus-containing zwitterions. Our preliminary experiments have confirmed this key conclusion. In details, we will discuss them in the follow-up publications.

EXPERIMENTAL

The NMR spectra were obtained on a Bruker spectrometers Avance AMX-400 (400.1 MHz (^1H), 162.0 MHz (^{31}P)) and Avance AMX-300 (282.4 MHz (^{19}F) relative to $CFCl_3$, 121.5 MHz (^{31}P)), δ (ppm), multiplicity, number of protons, reference of protons, J (Hz). The IR spectra were recorded on a Nicolet IR-Fourier spectrometer Magna-IR-750 (ν/cm^{-1}). UV/Vis spectra were recorded on a Carl Zeiss spectrometer Specord M-40 (nm). The reactions were carried out under dry N_2.

Triethylammonium (Cyano-methoxycarbonyl-methylidine)-2, 4-dinitrocyclo-hexadienide **4a**

Triethylamine (0.69 mL, 5.0 mmol) was added dropwise, with stirring, to the mixture of methylcyanoacetate (0.5 g, 5.0 mmol), **2** (0.93 g, 5.0 mmol), and CH_3CN (1 mL). After 3 days, ether was added and the crystalline powder was filtered off. Yield 1.10 g (60%), m.p. 103–105°C (ether–acetone 1:1). Calcd. for $C_{16}H_{22}N_4O_6$: C, 52.46; H, 6.01; N, 15.30. Found: C, 52.21; H, 6.00; N, 15.17. ^1H NMR ($CDCl_3$): 1.12 (t, 9H, $C\underline{H}_3CH_2N$, $^3J_{HH} = 7.3$ Hz), 3.00 (q, 6H, $CH_3C\underline{H}_2N$, $^3J_{HH} = 7.3$ Hz), 3.47 (s, 3H, $\underline{CH}_3O$), 7.59 (d, 1H, H_α, $^3J_{H\alpha H\beta} = 9.3$ Hz), 7.97 (dd, 1H, H_β, $^3J_{H\beta H\alpha} = 9.3$ Hz, $^4J_{H\beta H\beta'} = 2.5$ Hz), 8.27 (d, 1H, $H_{\beta'}$, $^4J_{H\beta' H\beta} = 2.5$ Hz), 9.10–11.10 (s broad, 1H, $^+$NH). IR ($CDCl_3$): 1305 (NO_2), 1658 (C(O)OMe), 2178 (CN), 2702 ($^+$NH). UV (acetone): 487 ($\varepsilon = 34$, 300). ^{13}C NMR ($CDCl_3$): 8.53 ($\underline{C}H_3CH_2N$), 46.52 ($\underline{C}H_3CH_2N$), 50.34 (MeO), 60.94 (C_{1Ar}), 121.78, 125.02, 126.72 (CH_{Ar}), 125.39 (CN), 138.15, 138.18 (C—NO_2), 141.86 (C=C_{1Ar}), 169.01 (CO).

Triethylammonium (Dicyanomethylidine)-2,4-dinitrocyclohexadienide **4b**

Triethylamine (0.60 mL, 4.3 mmol) in ether (10 mL) was added dropwise, with stirring, to the mixture of malononitrile (0.3 g, 4.5 mmol), **2** (0.84 g, 4.5 mmol), and ether (20 mL). After 10 min, ether was removed in vacuo and the crystalline powder was crystallized from toluene. Yield 0.35 g (23%), m.p. 84–86°C. Calcd for $C_{15}H_{19}N_5O_4$: C, 54.05; H, 5.70; N, 21.02. Found: C, 54.03; H, 5.75; N, 20.90. ^1H NMR ($CDCl_3$): 1.39 (t, 9H, $C\underline{H}_3CH_2N$, $^3J_{HH} = 7.3$ Hz), 3.18 (dq, 6H, $CH_3C\underline{H}_2N$, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 2.4$ Hz), 7.34 (d, 1H, H_α, $^3J_{H\alpha H\beta} = 8.5$ Hz), 7.94 (d, 1H, H_β, $^3J_{HH} = 8.5$ Hz), 8.49 (s, 1H, $H_{\beta'}$), 8.92 (s, 1H, $^+$NH). IR ($CDCl_3$): 1321 (NO_2), 2160, 2194 (CN), 2736 ($^+$NH). UV (acetone): 464 ($\varepsilon = 33$, 400).

TABLE 3 NMR Spectra of the Geometrical Isomers of Zwitterion **9** in DMSO-d$_6^a$

Isomers	*cis-isomer **9a**, 83.5%*	*trans-isomer **9b**, 16.5%*
^{31}P	44.52	44.68
(C$\underline{H}_3$)$_2$CH	1.38 (dd, 18H, $^3J_{PH} = 15.6$ Hz, $^3J_{HH} = 7.2$ Hz)	1.45 (dd, 18H, $^3J_{PH} = 17.6$ Hz, $^3J_{HH} = 7.2$ Hz)
(C$\underline{H}_3$)$_2$C$\underline{H}$	2.88 (dsept, 3H, $^2J_{PH} = 12.4$ Hz, $^3J_{HH} = 7.2$ Hz)	3.38 (m, 3H)
CH$_2$P$^+$	3.74 (d, 2H, $^2J_{PH} = 12.1$ Hz)	3.20 (d, 2H, $^2J_{PH} = 12.8$ Hz)
H$_\alpha$	7.12 (d, 1H, $^3J_{H_\alpha H_\beta} = 7.5$ Hz)	7.72 (d, 1H, $^3J_{H_\alpha H_\beta} = 6.9$ Hz)
H$_\beta$	7.54 (dd, 1H, $^3J_{H_\beta H_\alpha} = 7.5$ Hz, $^4J_{H_\beta H_{\beta'}} = 2.1$ Hz)	7.97 (dd, 1H, $^3J_{H_\beta H_\alpha} = 6.9$ Hz, $^4J_{H_\beta H_{\beta'}} = 1.8$ Hz)
H$_{\beta'}$	8.32 (d, 1H, $^4J_{H_{\beta'} H_\beta} = 2.1$ Hz)	8.59 (d, 1H, $^4J_{H_{\beta'} H_\beta} = 1.8$ Hz)

[a] Ratio of **9a**:**9b** in acetone-d$_6$ 7:4, in the 1:1 mixture of CDCl$_3$–DMSO-d$_6$ 1.5:1.

Methyl [Cyano-(2,4-dinitrophenyl)]ethanoate **5**

The solution of hydrogen chloride in dry ether was added dropwise, with stirring, to the suspension of salt **4** (0.05 g, 0.14 mmol) in ether. Light crude product formed upon stirring was reprecipitated twice with petroleum ether from acetone solution. Removal of the solvent under vacuo produced an oil product. Yield 0.03 g (81%). IR (CDCl$_3$): 1354, 1541 (NO$_2$), 1758 (C(O)OMe), 2253 (CN). ^{1}H NMR (CDCl$_3$): 3.84 (s, 3H, CH$_3$O), 5.76 (s, 1H, CH), 8.02–8.96 (m, 3H, H$_{Ar}$).

(1-Cyano-2-triisopropylphosphonioethylidene)-2, 4-dinitrocyclohexadienide **9**

Compound **2** (3.26 g, 17.5 mmol) in CH$_2$Cl$_2$ (25 mL) was added dropwise, with stirring, to the solution of zwitterion **6** (5.0 g, 17.5 mmol) in CH$_2$Cl$_2$ (75 mL) at 3°C. The reaction mixture was left for 2 days and then petroleum ether (100 mL) was added. The residue was filtered off and washed with CCl$_4$. Dark crystals (2.27 g) were rinsed with cold acetone several times. Yield 36%, m.p. 158–159°C. Calcd. for C$_{18}$H$_{26}$N$_3$O$_4$P: C, 56.99; H, 6.86; N, 11.08. Found: C, 56.97; H, 6.98; N, 11.07. IR (Nujol mull): 1320 (NO$_2^-$), 1592 (conjugated heptatriene system), 2160 (CN). UV (acetone): 478 ($\varepsilon = 34,000$). For the NMR spectra of compound **9** see Table 3.

The filtrate was distilled off. The presence of ethylfluoroformate in the filtrate was proven by the NMR and IR spectra. ^{19}F NMR (CDCl$_3$): −17.02, s (broad). ^{1}H NMR (CDCl$_3$): 1.33 (dt, 3H, C$\underline{H}_3$CH$_2$O, $^3J_{HH} = 9.2$ Hz, $^5J_{HF} = 1.2$ Hz), 4.29 (dq, 2H, C$\underline{H}_2$O,$^3J_{HH} = 9.2$ Hz, $^4J_{HF} = 0.8$ Hz). IR (CH$_2$Cl$_2$): 1824 (COOEt).

Reaction of **2** *with Zwitterion* **6**

Compound **2** (0.65 g, 3.5 mmol) in CH$_2$Cl$_2$ (25 mL) was added dropwise, with stirring, to the solution of **6** (1.0 g, 3.5 mmol) in CH$_2$Cl$_2$ (75 mL) at −15°C. After 2 days, the solvent was removed in vacuo. The residue (oil) represented a mixture of **8**, 90% (^{31}P NMR (CDCl$_3$): 46.16; ^{19}F NMR (CDCl$_3$): −106.07) and **10**, 5% (^{31}P NMR (CDCl$_3$): −15.66 (d, $J_{PF} = 646$ Hz); ^{19}F NMR (CDCl$_3$): −62.13 (d, $J_{PF} = 646$ Hz)) and uncertain compounds (5%).

[2-Cyano-2-ethoxycarbonyl-2-(2,4-dinitrophenyl)ethyl]triisopropylphosphonium Iodide **11**

The solution of NaI (0.52 g, 3.5 mmol) in acetone was added to the solution of **8** in acetone (1.65 g, 3.5 mmol). After filtration, the solvent was removed in vacuo. The residue was crystallized from acetone. Yield 0.45 g (22%), m.p. 132–133°C. Calcd. for C$_{21}$H$_{31}$N$_3$PO$_6$I: C, 43.52; H, 5.35; N, 7.25; P, 5.35. Found: C, 43.68; H, 5.35; N, 7.27; P, 5.22. ^{31}P NMR (CDCl$_3$): 46.89 ppm. ^{1}H NMR (CDCl$_3$): 1.20 (t, 3H, C$\underline{H}_3$CH$_2$, $^3J_{HH} = 7.2$ Hz), 1.59 (dd, 18H, (C$\underline{H}_3$)$_2$CH, $^3J_{HH} = 7.2$ Hz), 3.51 (m, 4H, (CH$_3$)$_2$C$\underline{H}$, C$\underline{H}_A$H$_B$), 4.26 (q, 2H, CH$_3$C$\underline{H}_2$O, $^3J_{HH} = 7.2$ Hz), 4.81 (dd, 1H, CH$_A\underline{H}_B$, $^2J_{HP} = 11.8$ Hz, $^2J_{HH} = 4.1$ Hz), 8.73 (dd, 1H, H$_\beta$, $^3J_{H_\beta H_\alpha} = 7.2$ Hz,$^4J_{H_\beta H_{\beta'}} = 2.8$ Hz), 8.91 (d, 1H, H$_{\beta'}$, $^4J_{H_\beta H_{\beta'}} = 2.8$ Hz), 9.01 (d, 1H, H$_\alpha$, $^3J_{H_\alpha H_\beta} = 7.2$ Hz). IR (CDCl$_3$, ν/cm^{-1}): 1348, 1542 (NO$_2$), 1752 (COOEt), 2206 (CN).

[2-Cyano-2-(2,4-dinitrophenyl) ethyl]-triisopropylphosphonium Chloride **12**

The solution of hydrogen chloride in dry ether was added to a dark-cherry solution of zwitterion **9** (0.05 g, 0.13 mmol) in CH$_2$Cl$_2$ (30 mL) until acid reaction of the reaction mixture. Immediate discoloration of the reaction solution was observed. The solvent was distilled off and the obtained crude product was crystallized from petroleum ether–acetone (2:1) mixture. Product **12** was obtained as a powder (0.04 g).

Yield 83%, m.p. 167–169°C. ^{1}H NMR ($CDCl_3$): 1.57 (dd, 18H, $(C\underline{H}_3)_2CH$, $^3J_{PH} = 23.9$ Hz, $^3J_{HH} = 7.0$ Hz), 3.44 (dsept, 3H, $(CH_3)_2C\underline{H}$, $^2J_{PH} = 13.4$ Hz, $^3J_{HH} = 7.0$ Hz), 3.60 (m, 1H, $C\underline{H}_AH_BP^+$), 3.87 (dd, 1H, $CH_A\underline{H}_BP^+$, $^2J_{PH} = 25.3$ Hz, $^3J_{HH} = 11.4$ Hz), 5.67 (d, 1H, $C\underline{H}CH_2P^+$, $^3J_{HH} = 11.4$ Hz), 8.57 (d, 1H, H_α, $^3J_{H_\alpha H_\beta} = 7.2$ Hz), 8.85 (d, 1H, $H_{\beta'}$, $^4J_{H_{\beta'}H_\beta} = 1.7$ Hz), 9.20 (d, 1H, H_β, $^3J_{H_\beta H_\alpha} = 7.2$ Hz). ^{31}P NMR ($CDCl_3$): 43.74.

Single-Crystal X-ray Structure Determination of **4a, 9**

Single-crystal X-ray diffraction experiments were carried out with a CAD4 Enraf-Nonius diffractometer at 293 K for **4a** and a Bruker SMART 1000 CCD area detector at 120 K for **9** using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) and isotropic (for H atoms) approximation. The H(C) atom positions were calculated, the H(N) hydrogen atom in **4a** was located from the difference Fourier synthesis. All hydrogen atoms were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to $1.2U_{eq}$(X), for methyl groups equal to $1.5U_{eq}$(Ci), where U(X) and U(Ci) are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded.

Crystal data and structure refinement parameters for **4a** and **9** are given in Table 1. All calculations were performed on using the SHELXTL software [6]. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition numbers CCDC 297193 (**4a**), CCDC 270207 (**9**). These data can be obtained free of charge via http://www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-335-033; or e-mail: deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers.

ACKNOWLEDGMENT

We thank Dr. Mikhail Gololobov for his advice and helpful discussions.

REFERENCES

[1] Leffek, K. T.; Tremaine, P. H. Can J Chem 1971, 49, 1979.

[2] Gololobov, Yu. G.; Galkina, M. A.; Kuzmintseva, I. Yu.; Petrovskii, P. V. Russ Chem Bull 1998, 47(9), 1878.

[3] Gololobov, Yu.; Linchenko, O. A.; Petrovskii, P. V.; Starikova, Z. A.; Garbuzova, I. A. Russ Chem Bull 2005, 54(10), 2471–2472.

[4] Wojcik, G.; Mossakowska, I.; Holband, J.; Bartkowiak, W. Acta Crystallogr, Sect B: Struct Sci 2002, 58, 998.

[5] Schmidbaur, H.; Schier, A.; Frazao, C. M. F.; Muller, G. J Am Chem Soc 1986, 108, 976.

[6] Sheldrick, G. M. SHELXTL-97, Version 5.10; Bruker AXS Inc.: Madison, WI, USA.