Synthesis and structures of the CH acid salts obtained in the reactions of malonic acid esters and malononitriles with 2,4,6-trinitrohalobenzenes in the presence of triethylamine

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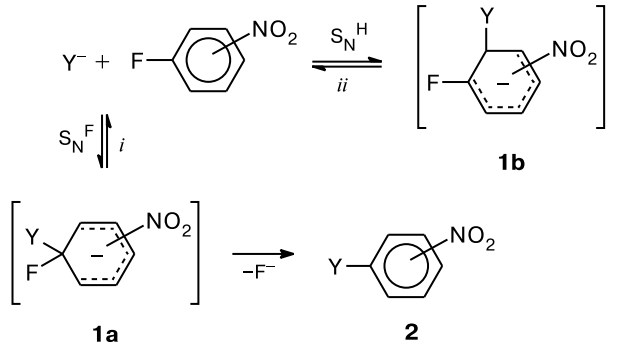
Reactions of dimethyl malonate, diphenyl malonate, methyl cyanoacetate, and malononitrile with 1-chloro-2,4,6-trinitrobenzene or 1-fluoro-2,4,6-trinitrobenzene in the presence of triethylamine in organic solvents gave stable brightly colored crystalline triethylammonium salts of the corresponding 2,4,6-trinitrophenylmalonic acid derivatives.

Key words: 2,4,6-trinitrohalobenzenes, active methylene compounds, triethylammonium salts, CH acids, malonates.

Most nucleophilic aromatic substitution reactions involving halonitrobenzenes usually follow a two-step addition—elimination mechanism.[1] The first step leads to unstable, intensely colored cyclohexadienylide adducts (σ-complexes **1a**,**b**), which undergo *in situ* transformations into new aromatic compounds **2** (Scheme 1).

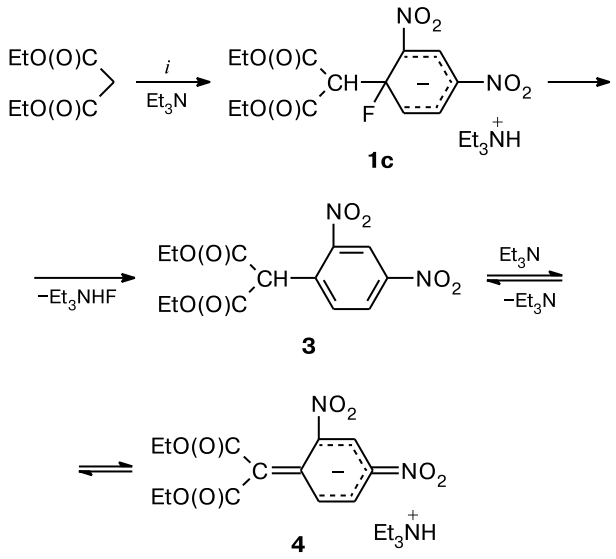
Scheme 1



i. Slow. *ii*. Rapid.

The basic reaction mixture is usually neutralized with an acid solution, whereupon aromatic compounds are isolated in common ways. The possible formation of reaction intermediates other than σ-complexes **1a** and **1b** during S_NAr reactions was first discussed, to the best of our knowledge, by Leffek *et al.*[2] When analyzing the results obtained in the study[3] of a reaction of ethyl malonate with 1-fluoro-2,4-dinitrobenzene (FDNB) in the presence of triethylamine, Leffek *et al.*[2] have disproved, using spectroscopic methods, the conclusions[3] about the formation of stable σ^F-complex **1c** (Scheme 2).

Scheme 2



i. FDNB.

They have found[2] that the reaction of ethyl malonate with FDNB actually gives, apart from σ^F-complex **1c**, unstable triethylammonium salt **4** in equilibrium with a mixture of CH acid **3** and triethylamine. We replicated the synthesis[2] according to Scheme 2 and ascertained that, in fact, salt **4** decomposes to CH acid **3** on attempted

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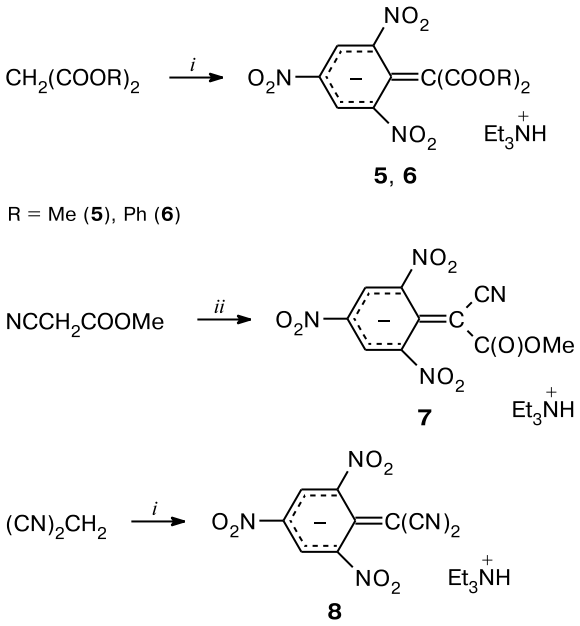
isolation from the solution. In another study,[4] a similar reaction of a substituted CH acid produces a mixture containing, apart from triethylamine hydrochloride, the corresponding triethylammonium salt with the 2,4,6-trinitrophenyl substituent at the carbanion center. The formation of stable triethylammonium salts of CH acids in reactions of active methylene compounds with polynitrohalobenzenes (with FDNB as an example) in the presence of organic bases was first mentioned in our previous paper.[5] Using physicochemical methods (including X-ray diffraction) for investigation of the reaction products, we also demonstrated[5] that methyl cyanoacetate arylated with FDNB is a nonaromatic compound and that all functional groups in the anionic fragment of the salt are highly conjugated. Earlier,[6] we have described brightly colored triethylammonium salts of 2,4-dinitrophenylcyanoacetamides, whose anions are also characterized by a system of highly conjugated bonds. Apparently, such compounds can change their properties when exposed to external factors (temperature, electromagnetic radiation, *etc.*),[7] which may be of interest for the design of practically useful electronic devices. In addition, one can believe that the triethylammonium salts of nitroarylated CH acids under discussion can possess unusual biological properties since these are organic salts containing nitro groups, which often impart a high biological activity to organic compounds.[8] In connection with this, we continued to study the synthesis and properties of new stable triethylammonium salts with a highly conjugated anion.

The instability of triethylammonium salt **4** in THF is probably due to the relatively low acidity of the corresponding CH acid **3**. Obviously, triethylammonium salts of the type **4** will be more stable if (1) stronger starting CH acids are used (*e.g.*, alkyl cyanoacetates instead of alkyl malonates)[5,6] and (2) the CH acid is arylated with a stronger electron acceptor than the 2,4-dinitrophenyl fragment. Here we offer a synthetic route to stable triethylammonium salts of CH acids *via* reactions of malonic and cyanoacetic acid esters and malononitrile with 1-fluoro-2,4,6-trinitrobenzene (FTNB) in the presence of triethylamine.

Triethylammonium salts **5**—**8** were obtained in satisfactory yields from active methylene compounds and 1-chloro-2,4,6-trinitrobenzene (CTNB) or FTNB in the presence of triethylamine (Scheme 3). The reaction rate is sufficiently high, regardless of the solvents used. The N-arylation of the cyano-containing carbanions with FTNB, which has been noted earlier,[9—12] does not occur in these reactions.

The mechanism of the formation of salts **5**—**8** according to Scheme 3 is unclear. Apparently, the first step involves deprotonation of the active methylene compounds under the action of triethylamine. The carbanion generated in this equilibrium process (Scheme 4) reacts with 1-halotrinitrobenzene to give σ-complex **M**. The latter gives up the fluoride ion to the triethylammonium cation

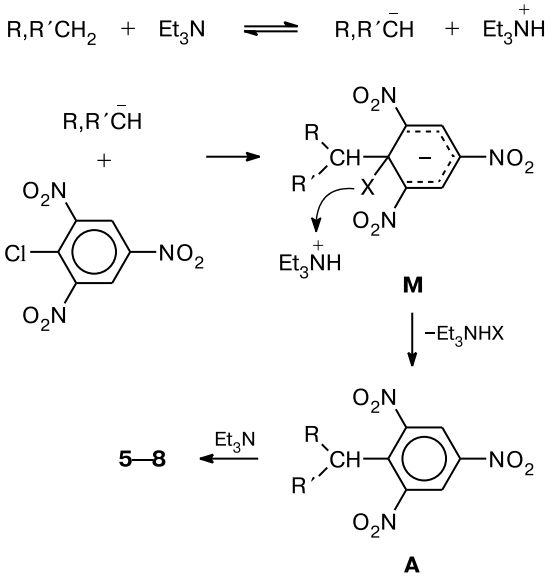
Scheme 3



i. CTNB, Et_3N. *ii*. FTNB, Et_3N.

and the resulting CH acid **A** is deprotonated by triethylamine to the corresponding salt **5**—**8**.

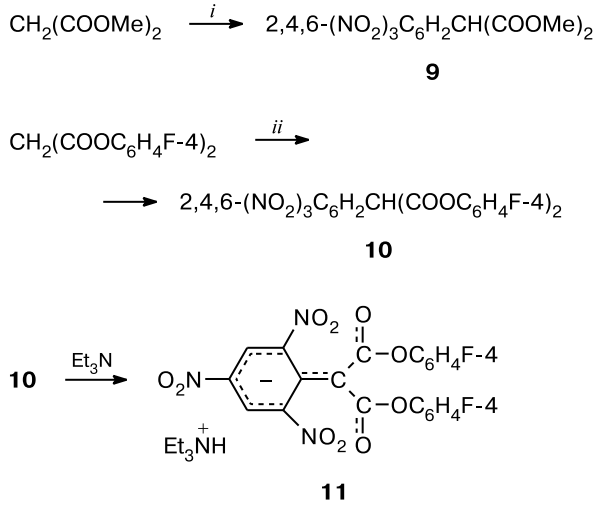
Scheme 4



R,R′ = CN, COOMe, COOAr
X = Cl, F

Free CH acid **9** was obtained by arylation of active methylene compounds as shown in Scheme 5. The same scheme was used to obtain CH acid **10**, which was transformed into salt **11** by deprotonation with triethylamine.

Scheme 5



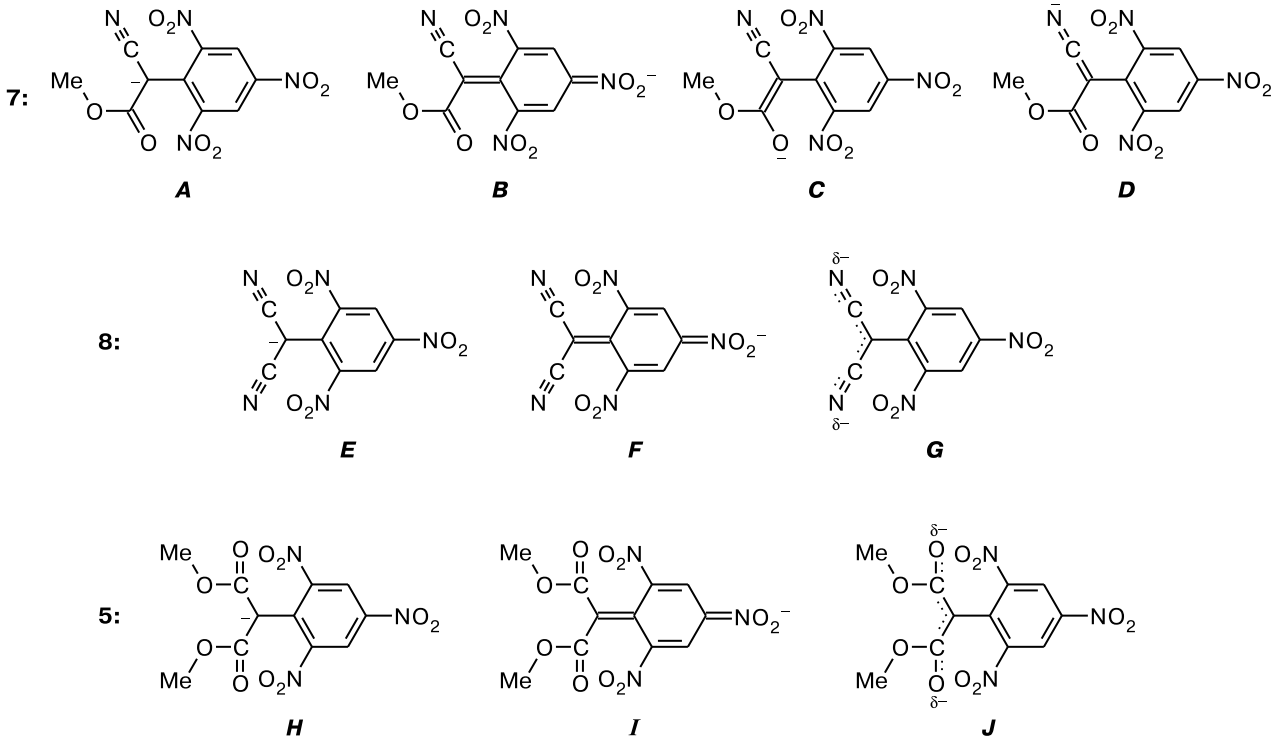
i. 1) Et_3N; 2) CTNB; 3) HCl. *ii*. 1) NaH; 2) CTNB; 3) HCl.

The compositions and structures of triethylammonium salts **5**—**8** and **11** and CH acids **9** and **10** were confirmed by elemental analysis, IR spectroscopy, and NMR spectroscopy; compounds **5**—**9** were additionally examined by X-ray diffraction.

In salts **5**—**8** and **11**, the negative charge of the anion is delocalized over a system of conjugated double bonds. The anions of these salts can be represented by resonance structures ***A***, ***B***, ***C***, and ***D*** (for **7**), ***E***, ***F***, and ***G*** (for **8**), and ***H***, ***I***, and ***J*** (for **5**) with different locations of the negative charge.

The IR spectrum of CH acid **9** contains bands at 3096, 1606, and 758 cm^{-1} (benzene ring) and at 1746 and 1724 cm^{-1} (standard values for carboxylate groups). At the same time, the IR spectra of salts **5**, **7**, and **8** show no bands characteristic of the aromatic system; the bands of the C=O groups in salts **5**—**7** are shifted by 60—150 cm^{-1} to the lower frequencies, which suggests the involvement of the carboxylate groups in the chain of conjugation. Apparently, some contribution from resonance structure ***J*** provides sufficiently strong hydrogen bonds between the O atoms of the C=O groups and the proton of the Et_3NH^+ group (see below). Analogous changes in position and intensity are experienced by the absorption bands due to the CN groups. In the IR spectrum of salt **7**, the band of the cyano group is much more intense and appears at a substantially lower frequency (2173 cm^{-1}) compared to the standard values for the CN groups in the starting active methylene compounds (2215—2230 cm^{-1}). It should be noted that salt **8** has a strong hydrogen bond between the proton of the Et_3NH^+ group and the N atom of the cyano group (X-ray diffraction data, see below), which can be attributed to some contribution of resonance structure **G** (*cf.* Ref. 6). Solutions of salts **5**—**8** in acetone are colored deep cherry-red because of their absorption at 500—540 nm.

Comparison of the ^1H NMR spectra of CH acids **9** and **10** with those of their salts **5** and **11** showed that the negative charge acquired by a molecule causes an upfield shift of the signals for the protons of all functional groups,



much as in other similar cases.[5,6,13] For instance, the protons of the MeO group and the *meta*-protons of the benzene ring in CH acid **9** resonate at δ 3.79 and 9.04, respectively (against δ 3.59 and 8.50 for analogous protons in the anion of salt **5**). Thus, the IR, UV-Vis, and NMR spectra of the salts under study suggest that the negative charge in their anions is delocalized over all the functional groups, although the contribution from each functional group in this delocalization can be estimated only qualitatively so far.

Valuable information on the electronic structures of salts **5**, **7**, and **8** and free CH acid **9** was obtained by X-ray diffraction (Figs 1—3; Table 1). It can be seen in Table 1 that the geometrical parameters of the central framework in salts **5**, **7**, and **8** are equal. The characteristic features include (a) the shorter C_{carb}—C_{Ar} bond (C(4)—C(1), av. 1.434 Å) compared to a single C_{sp3}—C_{Ar} bond; (b) the longer C(4)—C(5) and C(4)—C(9) ring bonds compared to the aromatic bonds in the benzene ring; (c) the shorter N(3)—C(7) bond (av. 1.454 Å) and the nearly coplanar arrangement of the *para*-nitro group and the benzene ring (the dihedral angle $\varphi_2 < 15°$); the C—N bonds involving the *ortho*-nitro groups are on average 1.474 Å, which approximates to the bond lengths in CH acid **9**; (d) equalization of the bond lengths in the fragment C(5)—C(6)—C(7)—C(8) as in structure **9**, (e) the smaller exocyclic angle C(5)—C(4)—C(9) (av. 111.8°) compared to this angle in structure **9**.

One can infer from X-ray diffraction data that, to a first approximation, resonance structures ***A*** and ***B*** (for **7**), ***E*** and ***F*** (for **8**), and ***H*** and ***I*** (for **5**) are most favorable. The C_{carb}—C_{Ar} bond in the anions is intermediate between single and double bonds[14] and the C_{Ar}—*p*-NO_2 bond is substantially shorter than the chemically related C_{Ar}—*o*-NO_2 bonds. In addition, the *para*-nitro group is virtually coplanar with the phenyl ring, while the *ortho*-nitro groups are noticeably rotated about the C_{Ar}—N bond (see Table 1).

Shortening of the C_{carb}—C(CN) and C_{carb}—C(COOMe) bonds and lengthening of the C≡N bonds in the anions, which are possible in resonance structures ***C***, ***D***, ***G***, and ***J***, are not very pronounced. Lengthening of the C=O bond in compounds **5** and **7** (1.235(1) and 1.225(2) Å) is greatly

Table 1. Selected geometrical parameters of the central fragment in compounds **5** and **7**—**9***

Parameter	**5**	**7**	**8**	**9**	
				A	**B**
Bond			*d*/Å		
C(2)—C(1)	1.444(2)	1.430(2)	1.409(1)	1.527(2)	1.530(2)
C(3)—C(1)	1.445(2)	1.415(2)	1.418(1)	1.527(2)	1.524(2)
C(4)—C(1)	1.436(2)	1.437(2)	1.428(1)	1.518(2)	1.515(2)
C(4)—C(5)	1.436(2)	1.420(2)	1.426(1)	1.399(2)	1.397(2)
C(5)—C(6)	1.372(2)	1.383(2)	1.379(1)	1.382(2)	1.382(2)
C(6)—C(7)	1.386(2)	1.382(2)	1.382(1)	1.375(2)	1.382(2)
C(7)—C(8)	1.380(2)	1.387(2)	1.382(1)	1.376(2)	1.377(2)
C(8)—C(9)	1.378(2)	1.382(2)	1.383(1)	1.382(2)	1.384(2)
C(9)—C(4)	1.428(2)	1.417(2)	1.424(1)	1.401(2)	1.403(2)
C(5)—N(2)	1.478(2)	1.473(1)	1.473(1)	1.472(2)	1.479(2)
C(7)—N(3)	1.450(2)	1.457(1)	1.454(1)	1.472(2)	1.468(2)
C(9)—N(4)	1.475(2)	1.473(1)	1.471(1)	1.483(2)	1.487(2)
N(2)—O	1.224(2), 1.230(2)	1.227(1), 1.232(1)	1.226(1), 1.225(1)	1.230(2), 1.217(2)	1.231(2), 1.218(2)
N(3)—O	1.231(2), 1.232(2)	1.226(1), 1.235(1)	1.228(1), 1.228(1)	1.215(2), 1.224(2)	1.215(2), 1.229(2)
N(4)—O	1.225(2), 1.228(2)	1.228(1), 1.221(1)	1.231(1), 1.226(1)	1.213(2), 1.215(2)	1.213(2), 1.216(2)
Angle			ω/deg		
$\varphi_1(N(2)O_2)$	41.1(1)	38.6(1)	56.0(1)	52.4(2)	52.3(2)
$\varphi_2(N(3)O_2)$	15.3(2)	6.1(1)	1.3(1)	27.2(2)	19.0(2)
$\varphi_3(N(4)O_2)$	51.1(1)	67.3(1)	42.5(1)	12.2(2)	19.1(2)
C(5)—C(4)—C(9)	110.7(1)	112.6(1)	112.0(1)	114.1(2)	114.3(2)
C(4)—C(5)—C(6)	125.5(1)	124.2(1)	125.1(1)	124.9(2)	125.2(2)
C(6)—C(7)—C(8)	120.7(1)	121.4(1)	120.8(1)	122.7(2)	122.9(2)
C(8)—C(9)—C(4)	125.6(1)	125.1(1)	124.6(1)	123.7(2)	123.4(2)

*The atomic numbering for the central fragment is shown in Fig. 3.

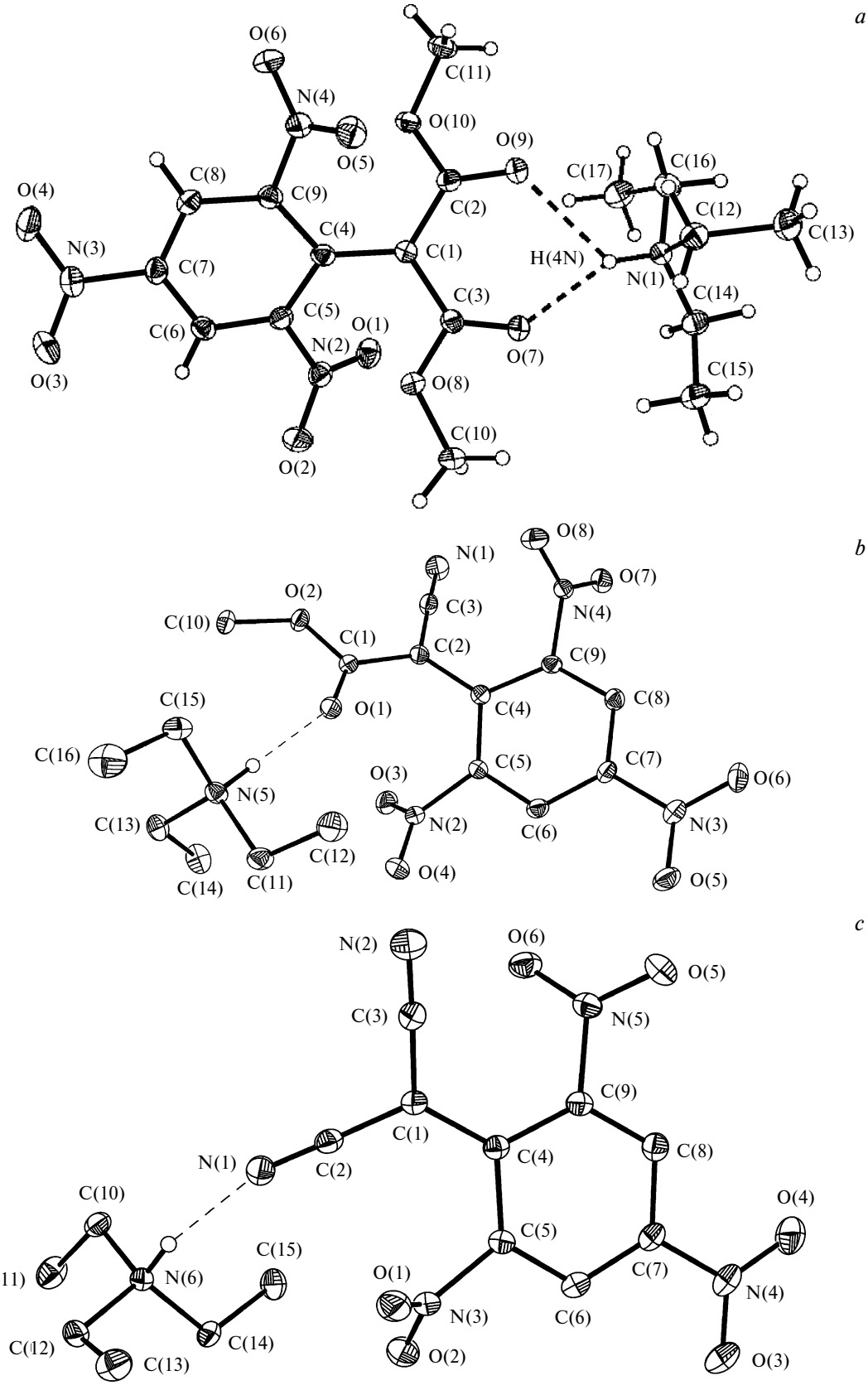


Fig. 1. Crystal structures of compounds **5** (*a*), **7** (*b*), and **8** (*c*) with atomic thermal displacement ellipsoids ($p = 50\%$). The hydrogen atoms in structures **7** (*b*) and **8** (*c*) are omitted, except for those involved in the hydrogen bonding (indicated with dashed lines).

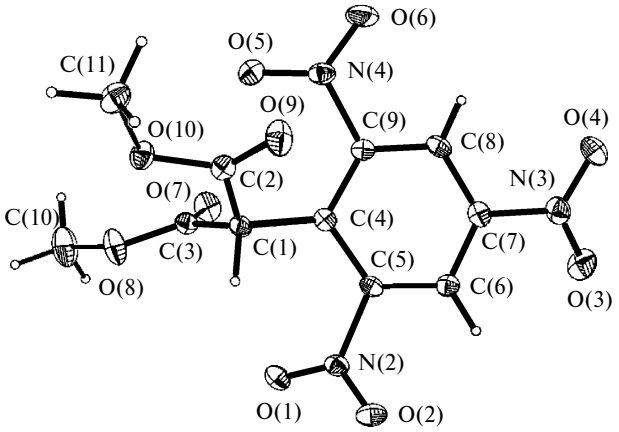


Fig. 2. One of the crystallographically independent molecules in the crystal structure of compound **9** with atomic thermal displacement ellipsoids (p = 50%).

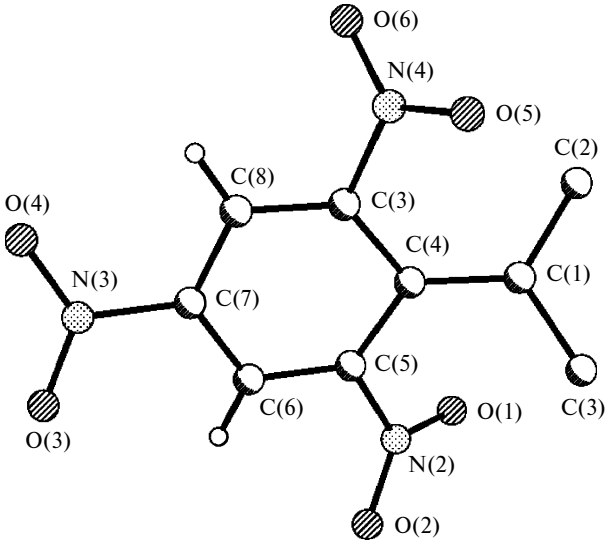


Fig. 3. Central fragment of compounds **5** and **7**—**9**.

due to the intermolecular hydrogen bond N^+—H...O=C (Table 2).

Interestingly, we have found earlier[6] that resonance structures like ***A*** and ***B*** are preferred in related amides as well. Note that the conjugation between the carbenoid and trinitrophenyl fragments in the salts under discussion is obvious, although steric repulsions between the cyano and ester groups of the carbenoid fragment and the *ortho*-nitro groups of the trinitrophenyl substituent give rise to a *twist*-conformation of the anions because of the rotation about the C_{carb}—C_{Ar} bond (the angles between the corresponding planes are 36.54(2)°, 26.73(3)°, and 20.02(3)° in compounds **7**, **8**, and **5**, respectively). The above steric repulsions are also responsible for the deviations of the N atoms of the *ortho*-nitro groups from the plane of the benzene ring (−0.326 and 0.095 Å in **7**, −0.193 and 0.178 Å in **8**, and −0.259 and 0.139 Å in **5**). A similar effect has been discovered earlier for related amides.[6] The bond equalization in the fragment C(5)—C(6)—C(7)—C(8) of the benzene rings of the anions is probably due to the electronic and steric effects of the *ortho*-nitro groups, which is more pronounced in dinitrophenyl amides.[6]

It is known that the size of the endocyclic bond angles in 1-substituted benzene largely depends on the substituent: the endocyclic bond angles at the C atoms in positions 1, 3, and 5 are reduced by σ-electron donors but increased by σ-electron acceptors, as compared to an idealized value of 120°.[15,16] The endocyclic bond angles in the benzene fragments of the anions of compounds **5**, **7**, and **8** is consistent well with this concept (see Table 1). However, it should be noted that the endocyclic bond angle at the carbenoid C(4) atom in the anions of salts **5**, **7**, and **8** (110.7(1)°, 112.62(9)°, and 112.01(7)°, respectively is much smaller than an analogous angle in related amides (114.4(2)° and 114.4(3)° (see Ref. 6) and CH acid **9** (see Table 1). These facts provide further evidence that the cyano and ester groups are more powerful σ-electron acceptors than the amido group.

The triethylammonium cations and the anions in structures **5**, **7**, and **8** form ionic pairs through the strong hydrogen bonds N^+—H...O=C and N^+—H...N≡C (see Fig. 1). In the crystals of these compounds, the ionic pairs are stacked.

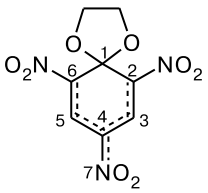
It is interesting to compare the bond length distribution in the cyclic fragment of the anion of salt **5** with the corresponding characteristics of the cyclic fragment in the stable Meisenheimer σ-complex **12** (Table 3).[17]

When comparing the X-ray diffraction and spectroscopic (IR and NMR) data for Meisenheimer σ-com-

Table 2. Parameters of the hydrogen bonds in compounds **7**—**9**

Compound	Type of the H bond	H...A*	D...A
7	N(5)—H(5N)...O(1)	1.88	2.7896(14)
8	N(6)—H(6N)...N(1)	1.98	2.8943(11)
9	N(4)—H(4N)...O(7)	1.97	2.797(2)
	N(4)—H(4N)...O(9)	2.28	2.910(2)

* D is the proton donor and A is the proton acceptor.



12

Table 3. Bond lengths d in the stable Meisenheimer complex **12** containing the 2,4,6-trinitrocyclohexadienylide anion[17]

Bond	d/Å
C(1)—C(2)	1.497
C(2)—C(3)	1.355(6)
C(3)—C(4)	1.396(6)
C(4)—C(5)	1.369(6)
C(5)—C(6)	1.378(6)
C(4)—C(7)	1.427(6)

plexes[17] with those for the anionic part of salts **5**, **7**, and **8**, one can conclude that they have closely related electronic configurations. Analogous conclusions can be drawn from comparison of the structures of Meisenheimer complexes with the structures of the anions of the salts and zwitterions described earlier.[5,6,9–12] Note, however, that the ring C(4) atom in mesomeric ions **5**, **7**, and **8** has a near-sp^2 configuration, while the spiro C atom in Meisenheimer complex **12** is sp^3-hybridized. Because the C(1)—C(4) bond in the anions of salts **5**, **7**, and **8** is partially double, their negative charge is delocalized over a longer chain (compared to Meisenheimer complexes) including not only the *p*-NO_2 group of the benzene ring but also the exocyclic ester and cyano groups.

When summing up the results obtained in this study and previous data,[3] one can conclude that attachment of the 2,4,6-trinitrophenyl (instead of 2,4-dinitrophenyl) moiety to the central C atom of active methylene compounds makes the corresponding triethylammonium salts more stable and allows their synthesis from not only malonates but also less reactive CH acids. Development of the latter approach will be useful for practical applications of the discussed concept of designing stable monomeric, dimeric, and polymeric triethylammonium salts with a highly conjugated anion.

According to the spectroscopic (IR, UV-Vis, and NMR) and X-ray diffraction data, the anionic charge in the salts of the CH acids under study is delocalized more strongly than that in salts containing the 2,4-dinitrophenyl substituent at the carbanionic center.[5,6]

Experimental

NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.1 (^{1}H) and 282.4 MHz (^{19}F)). IR spectra were recorded on a Magna-IR-750 FTIR spectrometer (Nicolet). UV-Vis spectra were recorded on a Specord M-40 spectrometer in acetone. Reactions were carried out under dry nitrogen.

Methyl 2-cyano-2-(2,4,6-trinitrophenyl)acetate, triethylammonium salt 7. ***A.*** Triethylamine (1.2 mL, 8.6 mmol) was added to a stirred solution of methyl cyanoacetate (0.42 g, 4.3 mmol) and FTNB (0.1 g, 4.3 mmol) in benzene (5 mL). The solution turned colored immediately, with gradual segregation of a dark mass. After 2 h, the solution was separated, the segregated dark mass was washed three times with diethyl ether and mixed with a minimum amount of acetone. The resulting solution was added to a fivefold amount of light petroleum. The mass that formed was kept *in vacuo* and dissolved in ethyl acetate. The resulting solution was kept at −15 °C for 24 h. The black crystals that formed were filtered off. The yield of salt **7** was 62.5%, m.p. 130—132 °C. Found (%): C, 46.75; H, 5.04; N, 16.91. $C_{10}H_5N_4O_8 \cdot C_6H_{16}N$. Calculated (%): C, 46.71; H, 5.11; N, 17.03. ^{1}H NMR ($CDCl_3$), δ: 1.39 (t, 9 H, $C\underline{H}_3CH_2N$, $^3J_{H,H}$ = 7.3 Hz); 3.19 (q, 6 H, $MeC\underline{H}_2N$, $^3J_{H,H}$ = 7.3 Hz); 3.59 (s, 3 H, Me); 8.50 (s, 2 H, H_{Ar}); 9.75 (s, 1 H, NH). IR (Nujol), ν/cm^{-1}: 2173 (CN), 1630 (CO), 1597 (system of the conjugated bonds), 1334 (NO_2). UV-Vis (acetone), λ/nm: 536 (ε 41 400).

B. Triethylamine (0.55 mL, 4.00 mmol) was added to a solution of methyl cyanoacetate (0.20 g, 2.00 mmol) and CTNB (0.50 g, 2.00 mmol) in DMF (5 mL). The solution turned dark cherry instantaneously; the reaction was exothermic. After 24 h, triethylamine hydrochloride (180 mg, 65%) was separated. The residue was crystallized from diethyl ether—acetone (1 : 1). The yield of the product was 0.50 g (60%), m.p. 130—132 °C. Found (%): C, 46.75; H, 5.04; N, 16.91. $C_{10}H_5N_4O_8 \cdot C_6H_{16}N$. Calculated (%): C, 46.71; H, 5.11; N, 17.03. ^{1}H NMR ($CDCl_3$), δ: 1.39 (t, 9 H, $C\underline{H}_3CH_2N$, $^3J_{H,H}$ = 7.3 Hz); 3.19 (q, 6 H, $MeC\underline{H}_2N$, $^3J_{H,H}$ = 7.3 Hz); 3.59 (s, 3 H, Me); 8.50 (s, 2 H, H_{Ar}); 9.75 (s, 1 H, NH). IR (Nujol), ν/cm^{-1}: 2173 (CN), 1630 (CO), 1597 (system of the conjugated bonds), 1334 (NO_2). UV-Vis (acetone), λ/nm: 536 (ε 41 400).

Diphenyl 2,4,6-trinitrophenylmalonate, triethylammonium salt (6). A solution of triethylamine (0.39 g, 4.0 mmol) in diethyl ether (5 mL) was added dropwise at 5 °C to a stirred solution of diphenyl malonate (0.5 g, 2.0 mmol) and CTNB (0.58 g, 2.3 mmol) in diethyl ether (10 mL). After 24 h, the precipitate of triethylamine hydrochloride that formed was filtered off and the mother liquor was placed in a refrigerator. After 72 h, product **6** (61%) was isolated as bright dark red crystals, m.p. 125—127 °C. Found (%): C, 56,89; H, 4.96; N, 9.78. $C_{27}H_{28}N_4O_{10}$. Calculated (%): C, 57,04; H, 4.93; N, 9.86. IR (KBr pellets), ν/cm^{-1}: 1712, 1594 (CO), 1335, 1191 (NO_2). ^{1}H NMR ($CDCl_3$, 600.220 MHz), δ: 1.18 (t, 9 H, $C\underline{H}_3CH_2N$, $^3J_{H,H}$ = 7.32 Hz); 2.96 (q, 6 H, $MeC\underline{H}_2N$, $^3J_{H,H}$ = 7.32 Hz); 6.98 (m, 4 H, *o*-H_{Ph}); 7.15 (m, 2 H, *p*-H_{Ph}); 7.28 (m, 4 H *m*-H_{Ph}); 8.77 (s, 2 H, $C_6H_2(NO_2)_3$). UV-Vis (acetone), λ/nm: 517 (ε 21 150).

Bis(4-fluorophenyl) 2,4,6-trinitrophenylmalonate (10). Sodium hydride (0.32 g, 6.0 mmol) was added in small portions to a solution of bis(4-fluorophenyl) malonate (1 g, 3.0 mmol) in THF (5 mL). After 10 min, CTNB (0.85 g, 3.0 mmol) in THF (5 mL) was added under nitrogen. The solution turned intense red instantaneously, the color intensity increasing with time. After 24 h, the solvent was removed *in vacuo* and the residue was washed with benzene and acidified with a solution of CF_3COOH in benzene. The precipitate that formed was filtered off, the mother liquor was concentrated, and the residue was recrystallized from diethyl ether—acetone. The yield of compound **10** was 80—90%, light yellow fibrous crystals, m.p. 89—91 °C. Found (%): C, 50.41; H, 2.51; N, 8.05; F, 7.13. $C_{21}H_{11}N_3O_{10}F_2$. Calculated (%): C, 50.10; H, 2.19; N, 8.35; F, 7.13. IR (KBr pellets), ν/cm^{-1}: 1767, 1741 (CO), 1545, 1356 (NO_2). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 5.91 (s, 1 H, CH); 7.09 (m, 8 H, FC_6H_4); 9.13 (s, 2 H, $C_6H_2(NO_2)_3$). ^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −115.04 (s, FC_6H_4).

Bis(4-fluorophenyl) 2,4,6-trinitrophenylmalonate, triethylammonium salt (11). Triethylamine (0.26 g, 2.5 mmol) was added to a solution of CH acid **10** (0.65 g, 1.3 mmol) in a mixture of light petroleum (1 mL), acetone (2 mL), and toluene (2 mL). The solution turned intense red instantaneously. The reaction mixture was kept at −15 °C for 24 h. The precipitate that formed was recrystallized from the above system of solvents. Storage at −15 °C for 10 days produced dark red crystals. The yield of product **11** was 70%, m.p. 110—112 °C. Found (%): C, 53.95; H, 4.56; N, 8.91; F, 6.65. $C_{27}H_{26}N_4O_{10}$. Calculated (%): C, 53.64; H, 4.30; N, 9.27; F, 6.29. IR (KBr pellets), ν/cm^{-1}: 1715, 1601 (CO), 1335, 1175 (NO_2). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.15 (t, 9 H, $C\underline{H}_3CH_2N$, $^3J_{H,H}$ = 8.0 Hz); 2.92 (q, 6 H, $MeC\underline{H}_2N$, $^3J_{H,H}$ = 8.0 Hz); 6.92 (m, 8 H, $FC_6\underline{H}_4$); 8.74 (s, 2 H, $C_6H_2(NO_2)_3$).

^{19}F NMR ($CDCl_3$, 282.4 MHz), δ: −115.24 (s, FC_6H_4). UV-Vis (acetone), λ/nm: 521 (ε 18 800).

Dimethyl 2,4,6-trinitrophenylmalonate, triethylammonium salt (5). Triethylamine (1.5 mL, 10 mmol) was added at 5 °C to a stirred mixture of dimethyl malonate (0.57 g, 5 mmol) and CTNB (1.23 g, 5 mmol) in diethyl ether (10 mL). The resulting mixture was left for 12 h. The precipitate (2.4 g) that formed was washed with acetone—diethyl ether (1 : 1). Triethylamine hydrochloride (1.4 g) was filtered off. The solution was kept at −15 °C for 24 h. The black precipitate that formed was dissolved in acetone and the resulting solution was kept again at −15 °C for 24 h. The yield of product **5** was 1.0 g (45%), black crystalline solid, m.p. 133—135 °C. Found (%): C, 46.07; H, 5.44; N, 12.66. $C_{17}H_{24}N_4O_{10}$. Calculated (%): C, 45.94; H, 5.4; N, 12.61. IR, ν/cm^{-1}: 1689, 1597 (C=O), 1331 (NO_2), 2827 (NH^+). ^{1}H NMR ($CDCl_3$), δ: 1.31 (t, 9 H, $C\underline{H}_3CH_2N$, J = 7.24 Hz); 3.14 (q, 6 H, $MeC\underline{H}_2N$, J = 7.24 Hz); 8.58 (s, 2 H, H_{Ar}); 10.11 (br.s, 1 H, NH). ^{13}C NMR (acetone-d_6), δ: 8.19 ($C\underline{H}_3CH_2N$); 46.26 ($MeC\underline{H}_2N$); 48.22 (MeO); 74.8 (C^-); 122.54 (CH_{Ar}); 138.40 (C—NO_2-*p*). UV-Vis (acetone), λ/nm: 526 (ε 12 500).

Dimethyl 2,4,6-trinitrophenylmalonate (9). Triethylamine (1.5 mL, 10 mmol) was added dropwise to a stirred mixture of dimethyl malonate (0.66 g, 5.0 mmol) and CTNB (1.23 g, 5 mmol) in acetonitrile (2 mL). A slightly exothermic reaction produced a black precipitate. After 2 h, the mixture was diluted with acetone (20 mL) and mixed with water. The product was extracted with CH_2Cl_2 (3×15 mL). The combined extracts were dried with Na_2SO_4 and concentrated. The residue was dissolved in CH_2Cl_2—MeCN and the resulting solution was gradually acidified with 3% HCl. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was crystallized and recrystallized from acetone. The yield of compound **9** was 0.5 g (29%), light yellow crystals, m.p. 145—147 °C. Found (%): C, 38.33; H, 2.53; N, 12.11. $C_{11}H_9N_3O_{10}$. Calculated (%): C, 38.48; H, 2.62; N, 12.24. IR, ν/cm^{-1}: 1746, 1724 (C=O); 1545, 1356 (NO_2); 3096, 1606, 758 (arom. ring). ^{1}H NMR ($CDCl_3$), δ: 3.79 (s, 6 H, MeO); 9.04 (s, 2 H, H_{Ar}).

2,4,6-Trinitrophenylmalononitrile, triethylammonium salt (8). A solution of triethylamine (2.76 g, 20 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred ice-cooled mixture of malononitrile (0.66 g, 10 mmol) and CTNB (2.47 g, 10 mmol) in CH_2Cl_2 (5 mL). The reaction was exothermic. The reaction mixture was stirred for 2 h, kept at room temperature for 12 h, and poured into diethyl ether—light petroleum (1 : 1, 50 mL). The mass that segregated was mixed with acetone. The precipitate of triethylamine hydrochloride (1.4 g) was filtered off. The acetone was removed *in vacuo* and the residue was washed with toluene, light petroleum, and diethyl ether. The remaining dark mass was dissolved in acetone and the solution was poured into ethanol—water (1 : 1). The orange precipitate that formed was dried. The yield of salt **8** was 2.55 g (67%). Found (%): C, 47.41; H, 4.69; N, 22.11. $C_{15}H_{18}N_6O_6$. Calculated (%): C, 47.62;

Table 4. Crystallographic parameters and the data collection and refinement statistics for compounds **5** and **7**—**9**

Parameter	Value			
	5	**7**	**8**	**9**
Molecular formula	$C_{17}H_{24}N_4O_{10}$	$C_{16}H_{21}N_5O_8$	$C_{15}H_{18}N_6O_6$	$C_{11}H_{18}N_3O_{10}$
Molecular mass	444.40	411.38	378.35	686.42
T/K	120	100	100	100
Crystal color and shape	Red plate	Dark red prism	Dark red prism	Colorless plate
Crystal dimensions (mm)	0.55×0.35×0.25	0.30×0.15×0.10	0.25×0.20×0.20	0.50×0.35×0.25
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	9.0455(7)	7.9663(5)	7.9031(4)	8.9399(7)
b/Å	10.4472(8)	11.2277(7)	10.1588(5)	14.373(1)
c/Å	11.8088(9)	11.9043(7)	12.3014(6)	21.997(2)
α/deg	64.374(1)	104.975(1)	68.683(1)	90.0
β/deg	85.670(2)	99.672(1)	87.100(1)	100.183(2)
γ/deg	88.561(2)	107.652(1)	73.427(1)	90.0
V/Å^3	1003.3(1)	944.41(10)	880.28(8)	2781.9(4)
Z	2	2	2	4
d_{calc}/g cm^{-3}	1.471	1.447	1.427	1.639
F(000)	467	432	396	1408
μ/mm^{-1}	0.122	0.118	0.113	0.148
$2\theta_{max}$/deg	56	65	60	54
Number of reflections				
measured	10387	14173	11211	28002
independent	4825	6841	5072	6054
(R_{int})	(0.0216)	(0.0294)	(0.0155)	(0.03625)
with $I > 2\sigma(I)$	3717	5120	4462	4983
Number of parameters refined	282	266	247	433
R_1 ($I > 2\sigma(I)$)	0.0426	0.0452	0.0341	0.0417
wR_2 (all reflections)	0.0972	0.1125	0.0919	0.1056
GOOF	1.019	1.000	1.000	1.010

H, 4.76; N, 22.22. IR, ν/cm^{-1}: 1330, 1298 (NO_2); 2172, 2199 (CN); 2748 (NH^+). ^{1}H NMR (acetone-d_6), δ: 1.42 (t, 9 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.28 Hz); 3.48 (q, 6 H, $MeC\underline{H}_2$, $^3J_{H,H}$ = 7.28 Hz); 7.1 (br.s, 1 H, NH); 8.45 (s, 2 H_{Ar}).

X-ray diffraction studies of compounds **5** and **7—9**. The unit cell parameters and reflection intensities for compounds **7—9** were measured on a Bruker APEX II CCD automatic three-circle diffractometer (λMoKα radiation, graphite monochromator, φ and ω scan modes). For compound **5**, the experiment was carried out on a Bruker SMART 1000 CCD diffractometer. Selected crystallographic parameters and the data collection and refinement statistics are summarized in Tables 1—4. The structures of all the compounds were solved by the direct methods and refined anisotropically by the full-matrix least-squares method on F^2_{hkl} for non-hydrogen atoms. The hydrogen atoms of the amino groups of the cations were objectively located from electron-density difference maps and refined with fixed coordinates and thermal parameters. The other hydrogen atoms were located geometrically and refined with fixed coordinates (using a riding model) and thermal parameters ($U_{iso}(H) = 1.5U_{equiv}(C)$ for the Me groups and $U_{iso}(H) = 1.2U_{equiv}(C)$ for the other groups). All calculations were performed with the SHELXTL program package.[18]

The tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for compounds **5** and **7—9** have been deposited with the Cambridge Crystallographic Data Center (CCDC Nos 768508—768511).

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