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To the 100th anniversary of A.A. Petrov

Synthesis, Structural and Spectral Features of CH-Acids: Amides of 2,4-Dinitrophenylcyanoacetic Acid and Their Ammonium Salts

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Abstract—New *N*-methylmorpholinium and triethylammonium salts of 2,4-dinitrophenylcyanoacetic acid were obtained. Their electronic and spatial structure was studied by IR, NMR spectroscopy (including two-dimensional correlation spectra HMQC and HMBC), as well as by XRD analysis.

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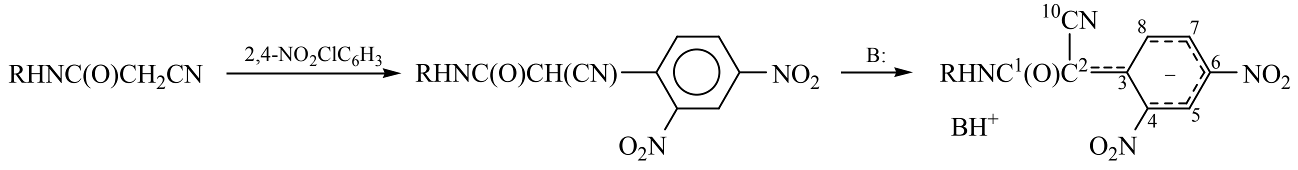
Cyanoacetamides are promising reagents for the synthesis of functionalized linear and heterocyclic compounds, including biologically active substances [1]. Cyanoacetamides undergo readily *C*-arylation with 2,4-di-nitrochlorobenzene in a MeCN–K_2CO_3 medium [2]. The introduction of nitrophenyl substituent to the active methylene group increases their CH-acidity by 6–8 orders of magnitude [3]. In the case of cyanoacetamides this provides formation of stable ammonium salts with triethylamine and *N*-methylmorpholine [2].

In continuation of research on the structural and spectral characteristics of organic salts of 2,4-dinitrophenylcyanoacetic acid and the corresponding CH-acids we obtained new specimens of these compounds and discussed the peculiarities of their structure. The structural differences of CH-acids **I** and the salts **II** and **III** were examined in detail using an X-ray diffraction analysis.

Compounds **I**–**III** used in this study were synthesized as described in [2] by reacting the corresponding cyanoacetic acid amides with 2,4-dinitrochlorobenzene in acetonitrile in the presence of potassium carbonate. The obtained CH-acids **I** react with triethylamine or *N*-methylmorpholine to form salts **II** or **III**. The structure and composition of CH-acids **I** and salts **II**, **III** were confirmed by elemental analysis data, IR, ^{1}H and ^{13}C NMR spectroscopy. Yields, melting points, and elemental analysis data of the compounds obtained are listed in Table 1.



I

II, III

R = methyl (**a**), allyl (**b**), cyclohexyl (**c**); B: = Et_3N (**II**), *N*-methylmorpholine (**III**).

As in other similar cases [2], in the IR spectra the absorption bands ν(CN), ν(CO), and ν(NO_2) are shifted to the low-frequency region by 100–50 cm^{-1} on passing from **I** to **II** and **III**, and the intensity of ν(CN) band increases strongly (Table 2). Previously, this phenomenon was observed for the salts of amides of

Table 1. Yields, melting points, and elemental analysis data of compounds **I**–**III**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIIa	84	105–106	49.26	5.21	19.26	$C_{15}H_{19}N_5O_6$	49.31	5.24	19.17
IIb	70	116–118	54.96	6.29	17.74	$C_{18}H_{25}N_5O_5$	55.23	6.44	17.89
IIIb	68	108–109	52.31	5.44	17.94	$C_{17}H_{21}N_5O_6$	52.17	5.41	17.89
Ic	67	160–162	54.29	4.92	16.95	$C_{15}H_{16}N_4O_5$	54.21	4.85	16.86
IIc	82	146–148 (decomp.)	58.07	7.24	16.11	$C_{21}H_{31}N_5O_5$	58.18	7.21	16.15
IIIc	72	140–142 (decomp.)	55.21	6.38	16.09	$C_{20}H_{27}N_5O_6$	55.42	6.28	16.16

Table 2. IR spectral parameters (ν, cm^{-1}) of compounds **I**–**III**

Comp. no.	C≡N	C=O	NO_2	NH	NH^+	Other
IIIa	2159	1599	1294, 1276	3413	2615	
IIb	2163	1608	1304, 1274	3335	2683	1642 (C=C, allyl)
IIIb	2158	1603	1304, 1281	3341	2724	1635 (C=C, allyl)
Ic	2240	1664	1531, 1346	3289		1601 (aromatic ring)
IIc	2152	1606	1299, 1269	3318	2673	
IIIc	2156	1601	1309, 1279	3348	2682	

the functionally substituted cyanoacetic acid [4], as well as for the salts of 2,4-dinitrocyanoacetates [5]. The signals of the ring protons in the ^{1}H NMR spectra are shifted upfield indicating the participation of the ring protons in the delocalization of the charge, and it is consistent with the data of [2]. The NMR spectra of anionic salts **II** and **III** (Table 3, 4) are almost independent of the substituents in the amide group. In the COSY spectrum of compound **IIa** in DMSO-d_6 a doublet at 2.58 ppm gives a correlation signal with a quartet at 6.87 ppm, confirming the assignment to the protons of NCH_3 and NHC(O) groups. At 295 K there are weak cross-peaks between the protons H^5 and H^7, and there is no correlation between the proton H^7 signals and broadened signal at 7.30 ppm. When the temperature rises to 343 K, this signal is narrowed, shifted downfield (7.49 ppm), and appears as a doublet with *J* 8.5 Hz, which gives a cross-peak with a doublet of doublets of H^5 atom. This allows the attribution of a broad signal to the protons H^8. The broadening of H^8 protons signal at 295 K is apparently due to the presence of a hindered in the NMR time scale rotation around the probable double C^1–N and C^2–C^3 bonds. The effect of an anisotropic C(CN)CONHMe substituent close to the *ortho*-proton H^8 averages as the rotation accelerates. Note also that in the EXSY spectrum of **IIa** there is a slow in the NMR time scale hydrogen exchange between H^8 and HDO from DMSO-d_6. At higher temperatures the remaining signals in the ^{1}H NMR spectrum undergo only a minor change in the chemical shifts values.

The assignment of the signals in the ^{13}C NMR spectrum was carried out on the basis of the correlation of two-dimensional HMQC and HMBC spectra of the same pair of model compounds **Ia**/**IIa** and compound **Ic** (Table 4). In the HMQC spectrum of compound **IIa** three from four closely arranged signals of the ^{13}C nuclei at 124.8–123.4 ppm have the correlation peaks with three CH-protons of the ring, whereas the remaining signal of lower intensity at 124.1 ppm belongs to the CN-group. In the HMBC spectra the signals at 133.3 (**Ia**) and 133.6 ppm (**Ib**) have intensive correlation peaks with a singlet of H^2 that can be attributed to the C^2 atom. The signal at 143.3 ppm in the spectrum of salt **IIa** has an intensive correlation

Table 3. ^{1}H NMR spectral parameters [δ, ppm (*J*, Hz)] of compounds **I**–**III**[a]

№	H^5	H^7	H^8	$N\underline{H}$
IIIa	8.24 d (1H, *J* 2.5)	7.79 d. d (1H, *J* 2.5, 9.5)	7.33 br.s	6.85 q (1H, *J* 4.2)
IIb	8.25 d (1H, *J* 2.5)	7.80 d. d (1H, *J* 2.5, 9.3)	7.35 br.s	6.97 t (1H, *J* 5.3)
IIIb	8.25 d (1H, *J* 2.6)	7.81 d. d (1H, *J* 2.6, 9.5)	7.35 br.s	6.96 br.s
Ic	8.80 d (1H, *J* 2.3)	8.63 m (2H, H^7+NH)	8.03 d (1H, *J* 8.7)	
IIc	8.26 d (1H, *J* 2.3)	7.78 d. d (1H, *J* 2.3, 9.4)	7.30 br.s	6.50 d (1H, *J* 7.7)
IIIc	8.25 d (1H, *J* 2.3)	7.76 d. d (1H, *J* 2.3, 9.3)	7.31 br.s	6.51 d (1H, *J* 7.7)

[a] Other signals, δ, ppm (*J*, Hz): allyl: **IIb**, 3.69 t (2H, CH_2, *J* 5.3), 5.01 d (1H, *cis*-H, *J* 10.3), 5.11 d (1H, *trans*-H, *J* 17.3), 5.80 m (1H, CH=); **IIIb**, 3.76 br.s (2H, CH_2), 5.00 d (1H, *cis*-H, *J* 10.0), 5.11 d (1H, *trans*-H, *J* 17.6), 5.80 m (1H, CH=); cyclohexyl: **Ic**, 1.16–1.77 m (10H), 3.54 br.s (1H); **IIc**, **IIIc**, 1.17 m (5H), 1.56 m (1H), 1.70 m (4H), 3.12 br.s (1H); morpholine fragment: **IIIa**, 3.10 br.s (4H), 3.75 br.s (4H); **IIIb**, 3.11 br.s (4H), 3.69 br.s (4H); **IIIc**, 3.12 br.s (4H), 3.71 br.s (4H); CH_3N: **IIIa**, 2.73 s (3H); **IIIb**, 2.74 s (3H); **IIIc**, 2.73 s (3H); $CH_3C(O)$: **IIIa**, 2.59 d (3H, *J* 4.2); CH_3CH_2: **IIb**, 1.19 t (9H, CH_3, *J* 7.3), 3.09 q (6H, CH_2, *J* 7.3); **IIc**, 1.17 t (9H, CH_3, *J* 7.3), 3.08 q (6H, CH_2, *J* 7.3); H^2: **Ic**, 5.75 s (1H).

Table 4. ^{13}C NMR spectral parameters [δ_C, ppm (*J*, Hz)] of compounds **I**–**III**[a]

Comp. no.	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^{10}
Ia	162.6	41.5	133.3	148.22	121.4	148.12	128.9	133.9	115.9
IIa	166.9	70.8	143.2	139.0	123.4	133.3	124.4	124.8	124.1
IIIa	166.9	69.6	143.0	138.9	123.2	133.1	124.3	124.7	124.0
Ib	162.0	41.2	133.0	147.9	120.9	148.0	128.7	133.6	116.7
IIIb	165.9	69.3	142.8	138.8	123.7	133.2	124.2	124.4	122.9
Ic	161.3	49.3	133.6	148.2	121.1	148.0	128.8	133.5	117.0

[a] Other signals, δ_C, ppm (*J*, Hz): **Ia**, 26.6 ($\underline{C}H_3NH$); **IIa**, 26.5 ($\underline{C}H_3NH$), 8.9 ($\underline{C}H_3$), 46.2 ($\underline{C}H_2$, Et_3NH^+); **IIIa**, 26.5 ($\underline{C}H_3NH$), 43.1 ($\underline{C}H_3$, *N*-methylmorpholinium); **Ib**, 41.1 ($\underline{C}H_3NH$), 115.8 ($\underline{C}H_2$=), 134.3 ($\underline{C}H$=); **IIIb**, 41.3 ($\underline{C}H_2NH$), 42.9 ($\underline{C}H_3$, *N*-methylmorpholinium), 52.9 and 65.7 ($\underline{C}H_2$, morpholine), 114.4 ($\underline{C}H_2$=), 136.8 ($\underline{C}H$=); **Ic**, 24.6, 24.7, 25.5, 32.2, 32.4. 41.7 (cyclohexyl).

peak with the doublet of doublets of the H^7 atom and corresponds to the C^3 atom. The signal at 133.3 ppm in the spectrum of salt **IIa** gives two weak correlation peaks with the signals of H^5 and H^7 protons, and therefore it refers to the atom C^6. According to the data of Table 4, on passing from CH-acids **I** to their ammonium salts **II** and **III** the signals of C^4, C^6, C^7, and C^8 atoms in the ^{13}C NMR spectra undergo diamagnetic shift and the signals of C^1, C^2, C^3, and C^{10} atoms, paramagnetic shift.

The spectral data show significant differences in the electronic structure of CH-acids **I** and their deprotonated forms in ammonium salts **II** and **III** due to the delocalization of the negative charge in the anionic part of the salt. These structural differences were studied in detail using the X-ray diffraction analysis.

The structure of compounds **Ia**, **IIIa**, **IIIb** was also confirmed by X-ray diffraction (Figs. 1–3). The main crystallographic and geometric parameters are shown in Tables 5 and 6.

Compound **Ia** is a chiral CH-acid containing asymmetric C^2 carbon atom and crystallizing in a chiral monoclinic space group $P2_1$. However, in this case the determination of its absolute configuration by the X-ray diffraction analysis is not possible due to the lack of elements with $Z >$ Si in their structure. Some structural features of the molecule **Ia** worth mentioning are elongated ordinary C–C bonds involving the central carbon atom (Table 6) compared with the average values of the lengths of appropriate bonds C^3_{sp}–C^2_{sp} (1.50 Å), C^3_{sp}–C_{Ar} (1.51 Å) and C^3_{sp}–C_{sp} (1.47 Å). Apparently, this is due to the strong σ-

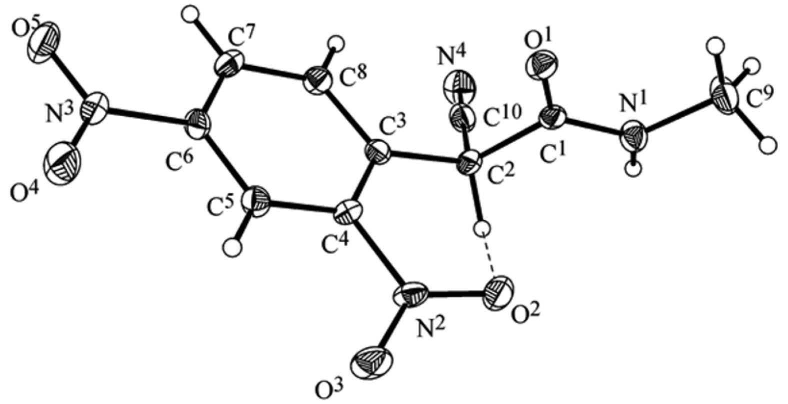


Fig. 1. The molecular structure of compound **Ia** in the non-hydrogen atoms presentation with 50% probability ellipsoids of anisotropic displacement. The *dashed line* shows the intramolecular hydrogen bond.

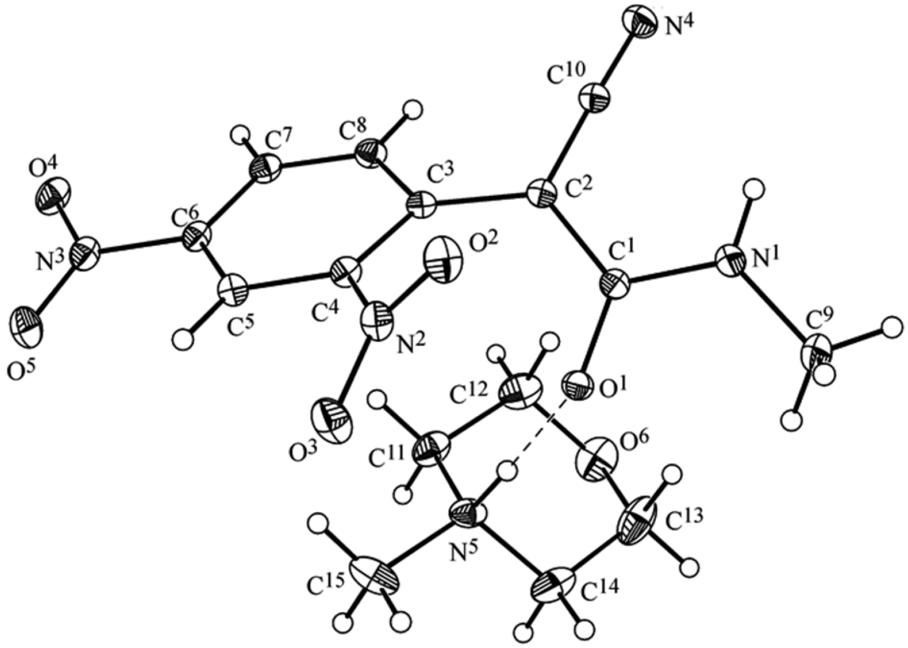


Fig. 2. The crystal structure of compound **IIIa** in the non-hydrogen atoms presentation with 40% probability ellipsoids of anisotropic displacement. The *dashed line* shows the intramolecular hydrogen bond.

electron-withdrawing substituents at the C^2 atom. For the same reason, the hydrogen atom H^{2A} at the same carbon atom possesses sufficient acidic character and participates in the formation of intramolecular hydrogen bond $C^2–H^{2A}\cdots O^2$ (Table 7, Fig. 1) with such a weak proton-acceptor as nitro group. In this case the *ortho*-nitro group involved into the above-described intramolecular hydrogen bond deviates slightly from the coplanar location with the plane of the benzene ring (the angle between the planes is 16.2°), while the *para*-nitro group is materially coplanar with this ring (interplanar angle equal to 3.2°).

It is known that the values of the endocyclic bond angles in the 1-substituted benzene are largely dependent on the substituent type, i. e., σ-electron-donating substituents tend to reduce, and σ-electron-withdrawing, on the contrary, to increase the values of the endocyclic bond angles at the carbon atoms at positions 1,3,5 in comparison with an ideal value of 120° [7, 8]. The distribution of the values of the endocyclic bond angles in the benzene moiety of the molecule **Ia** is consistent with this principle (Table 6). Among the exocyclic angles the angle $C^2C^3C^4$ can be distinguished, whose value is increased due to the steric effects.

The lengths of the C–C bonds in the benzene ring are nearly equal and close to the average value of 1.39 Å, although it is possible to note some of their differentiation [the bonds C^4–C^5, C^5–C^6, and C^6–C^7 are slightly shorter than the bonds C^3–C^4, C^3–C^8, and C^7–C^8 (Table 6)] which is more pronounced in the anions of the compounds **IIIa** and **IIIb**. The bond lengths of C^4–N^2 and C^6–N^3 are very close to each other despite of the varying degrees of conjugation of two nitro groups with the aromatic ring.

In the crystal, the molecules of **Ia** form an H-linked chains along the *b* axis through weak intermolecular hydrogen bonds N^1–$H^1N\cdots N^4$ (Table 7, Fig. 4). The formation of intermolecular hydrogen bond between an amine proton and cyano group is somewhat surprising, since the structure contains a free carbonyl group, which clearly is a stronger proton-acceptor.

Comparing the structure of the neutral **Ia** with that of its deprotonated form in the salt **IIIa** (Fig. 2) and the related anion of salt **IIIb** (Fig. 3) leads to some interesting observations. It should be said that compound **IIIb** crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent structural units per unit cell, which differ only in the conformations of the allyl fragments in the amide substituents of anions [torsion angles $C^1N^1C^9C^{10}$, $N^1C^9C^{10}C^{11}$ and $C^{18}N^6C^{26}C^7$, $N^6C^{26}C^{27}C^{28}$ equal –111.9(4) –120.0(4), and –81.5(4), –1.0(6)°, respectively (Fig. 3)]. Therefore, average values of the geometric parameters of the two crystallographically independent structural units of compound **IIIb** will be discussed below.

Due to the deprotonation the central carbon atom C^2 is carbenoid and acquires a negative charge, which is delocalized on the long chain of the conjugated double bonds. In accordance with this, the length of the ordinary C–C bonds with the carbon atom C^2 is considerably shortened (Table 6). Noteworthy is the fact that the C^2–C^3 bond in the anions of compounds **IIIa** and **IIIb** is intermediate between the ordinary and double bonds. Due to the delocalization of the negative charge there is of redistribution of values of the bond lengths in the dinitrophenyl substituent (Table 6). Thus, the bond lengths of C^4–C^5, C^5–C^6 and C^6–C^7 are the same, whereas the bonds C^3–C^4 and C^3–C^8 are significantly lengthened, and C^7–C^8 bond is considerably shortened compared with the same bonds in the neutral CH-acid **Ia**. Moreover, the bond lengths of C^4–N^2 and C^6–N^3 are different: the bond C^4–N^2 is lengthened, and the bond C^6–N^3 is shortened. As in the case of neutral CH-acid **Ia**, *para*-nitro group in the salts **IIIa** and **IIIb** deviates from the coplanar position with the plane of the benzene ring to a lesser extent

Table 5. Main crystallographic data and refinement parameters for compounds **Ia**, **IIIa**, **IIIb**

Parameter	**Ia**	**IIIa**	**IIIb**
Emptrical formula	$C_{10}H_8N_4O_5$	$C_{15}H_{19}N_5O_6$	$C_{17}H_{21}N_5O_6$
M	264.20	365.35	391.39
T, K	100	293	120
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$	$P2_1/n$	*P*-1
a, Å	6.8232(8)	9.8404(8)	7.9897(11)
b, Å	7.8680(9)	15.8427(13)	15.093(2)
c, Å	10.3606(11)	11.1728(9)	15.949(2)
α, deg	90	90	88.225(3)
β, deg	102.062(2)	93.424(2)	84.711(3)
γ, deg	90	90	79.703(3)
V, $Å^3$	543.93(11)	1738.7(2)	1884.0(4)
Z	2	4	4
d_{calc}, g cm^{-3}	1.613	1.396	1.380
F(000)	272	768	824
μ, mm^{-1}	0.133	0.110	0.106
$2\theta_{max}$, deg	56	56	54
Reflections collected	6013	17559	17957
Independent reflections	1384	4186	8203
Reflections with $I > 2\sigma(I)$	1147	2447	3573
Refined parameters	173	237	507
R_1 [$I > 2\sigma(I)$]	0.0411	0.0534	0.0632
wR_2 (all data)	0.1112	0.1593	0.2060
GOF	1.004	1.000	1.003

Table 6. Some geometric parameters of compounds **Ia**, **IIIa**, **IIIb**[a]

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Compound **Ia**							
O^1–C^1	1.216(2)	$C^1C^2C^3$	110.6(2)	C^2–C^{10}	1.493(3)	$C^5C^6C^7$	123.0(2)
N^1–C^1	1.332(2)	$C^1C^2C^{10}$	108.0(2)	C^3–C^4	1.394(3)	$C^6C^7C^8$	118.0(2)
N^2–C^4	1.474(3)	$C^3C^2C^{10}$	110.8(2)	C^3–C^8	1.397(3)	$C^3C^8C^7$	121.7(2)
N^3–C^6	1.468(2)	$C^2C^3C^4$	123.7(2)	C^4–C^5	1.389(3)		
N^4–C^{10}	1.137(3)	$C^4C^3C^8$	117.2(2)	C^5–C^6	1.384(3)		
C^1–C^2	1.550(3)	$C^3C^4C^5$	123.0(2)	C^6–C^7	1.382(3)		
C^2–C^3	1.523(2)	$C^4C^5C^6$	117.1(2)	C^7–C^8	1.396(3)		
Compound **IIIa**							
O^1–C^1	1.255(2)	$C^1C^2C^3$	123.1(2)	C^2–C^{10}	1.432(3)	$C^5C^6C^7$	120.5(2)
N^1–C^1	1.352(3)	$C^1C^2C^{10}$	117.7(2)	C^3–C^4	1.410(3)	$C^6C^7C^8$	119.7(2)
N^2–C^4	1.470(2)	$C^3C^2C^{10}$	118.7(2)	C^3–C^8	1.421(3)	$C^3C^8C^7$	123.0(2)
N^3–C^6	1.444(3)	$C^2C^3C^4$	125.6(2)	C^4–C^5	1.380(3)		
N^4–C^{10}	1.154(3)	$C^4C^3C^8$	114.4(2)	C^5–C^6	1.379(3)		
C^1–C^2	1.440(3)	$C^3C^4C^5$	123.2(2)	C^6–C^7	1.383(3)		
C^2–C^3	1.411(3)	$C^4C^5C^6$	119.0(2)	C^7–C^8	1.363(3)		
Compound **IIIb**							
O^1–C^1	1.254(4)	$C^1C^2C^3$	124.8(3)	C^2–C^{12}	1.411(5)	$C^5C^6C^7$	120.5(3)
N^1–C^1	1.350(4)	$C^1C^2C^{12}$	117.1(3)	C^3–C^4	1.419(5)	$C^3C^2C^{12}$	117.4(3)
N^2–C^4	1.460(4)	$C^6C^7C^8$	119.5(4)	C^3–C^8	1.416(5)	$C^2C^3C^4$	125.6(3)
N^3–C^6	1.449(5)	$C^3C^8C^7$	123.1(4)	C^4–C^5	1.390(5)		
N^4–C^{12}	1.159(4)	$C^4C^3C^8$	114.4(3)	C^5–C^6	1.380(5)		
C^1–C^2	1.450(5)	$C^3C^4C^5$	122.9(3)	C^6–C^7	1.393(5)		
C^2–C^3	1.429(5)	$C^4C^5C^6$	118.8(3)	C^7–C^8	1.366(5)		

[a] For **IIIb** average values for two crystallographically independent anions are given.

[interplanar angles are 10.6 (**IIIa**) and 7.1° (**IIIb**)] than the *ortho*-nitro groups [interplanar angles are 39.0 (**IIIa**) and 35.9° (**IIIb**)]. Importantly, due to the absence of hydrogen atom at the carbenoid carbon atom C^2 and the impossibility of formation of an intramolecular hydrogen bond with the *ortho*-nitro group the repulsive interaction between these moieties in the salts **IIIa** and **IIIb** leads both to a substantial increase in the angle of rotation of the *ortho*-nitro group relative to the ring and to a significant deviation of its nitrogen atom from the plane of phenyl substituent [0.257 (**IIIa**) and 0.327 Å (**IIIb**)]. In this case, the flat conformation of the ring is slightly distorted in the direction of a *boat* conformation. The carbon atoms C^3 and C^6 are out of the mean square plane passing through the remaining ring atoms [at

Table 7. Parameters of hydrogen bonds (Å, deg) in compounds **Ia**, **IIIa**, **IIIb**[a]

Bond	D–H	H···A	D···A	∠(D–H···A)
Compound **Ia**				
$C^2–H^{2A}\cdots O^2$	1.00	2.45	2.666(2)	104
$N^1–H^1N\cdots N^4$ [$-x, ½ + y, -z$]	0.94	2.61	3.297(2)	131
Compound **IIIa**				
$N^5–H^5N\cdots O^1$	0.96	1.78	2.744(2)	177
$N^1–H^1N\cdots O^5$ [$x - ½, -y + ½, z + ½$]	0.92	2.51	3.295(3)	143
Compound **IIIb**				
$N^1–H^1N\cdots N^4$ [$-x + 1, -y + 1, -z$]	0.91	2.24	3.058(4)	150
$N^5–H^5N\cdots O^1$ [$-x, -y + 1, -z + 1$]	0.97	1.78	2.700(4)	157
$N^6–H^6N\cdots N^9$ [$-x, -y, -z + 1$]	0.91	2.07	2.924(4)	156
$N^{10}–H^{10}N\cdots O^7$ [$-x + 1, -y + 1, -z + 1$]	0.98	1.68	2.650(4)	172

[a] D is proton-donor; A is proton-acceptor.

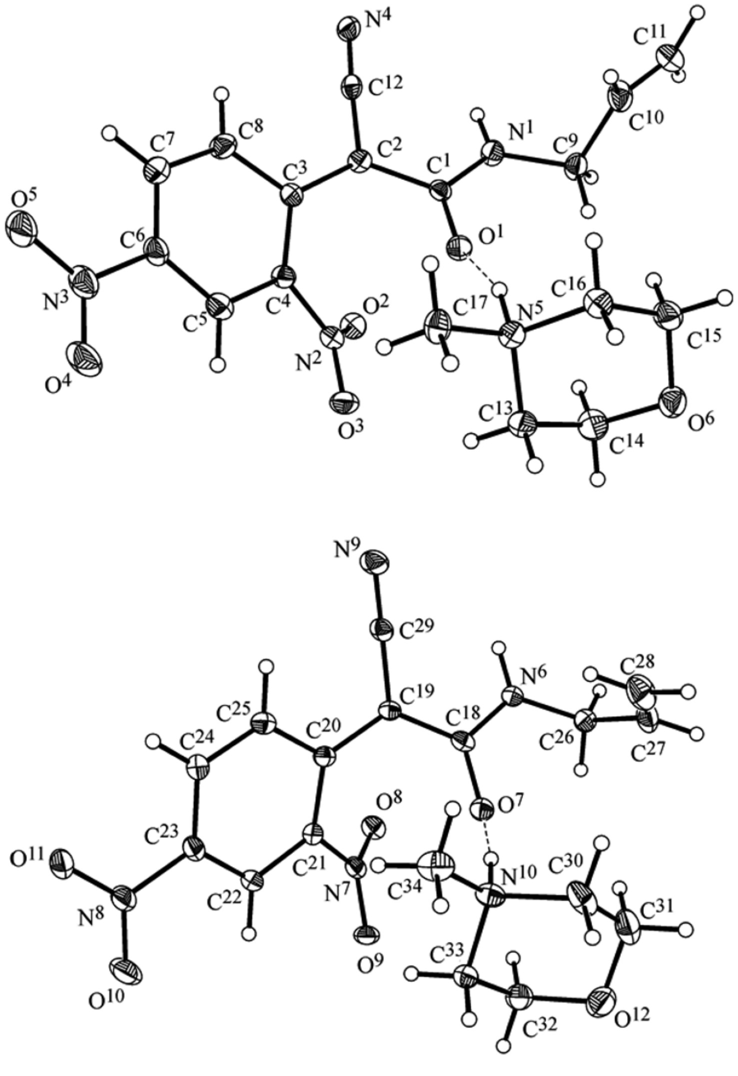


Fig. 3. The crystal structure of compound **IIIb** in the non-hydrogen atoms presentation with 50% probability ellipsoids of anisotropic displacement. Two crystallographically independent units are presented. The *dashed lines* show the intramolecular hydrogen bonds.

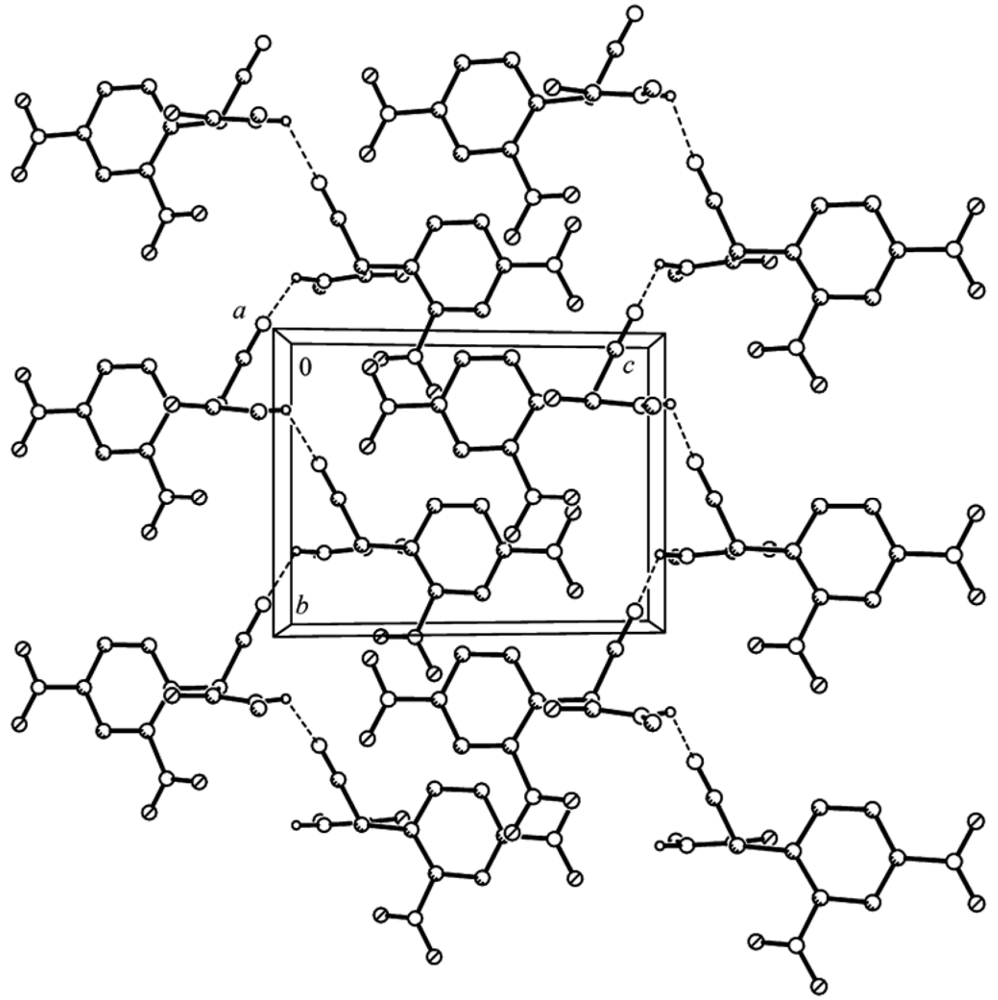
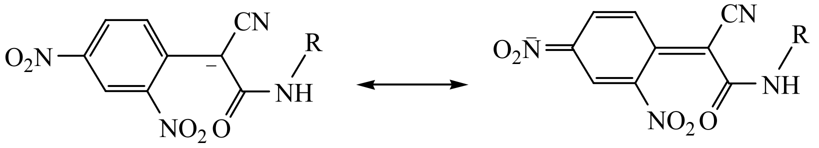


Fig. 4. Crystal packing of the molecules of **Ia** along the *a* axis. Only hydrogen atoms involved into the hydrogen bonding are represented. The *dashed lines* show the intermolecular hydrogen bonds.

0.044 and 0.020 Å (**IIIa**) and 0.093 and 0.042 Å (**IIIb**), respectively]. Furthermore, the value of the endocyclic angle $C^4C^3C^8$ in the ring is still more reduced, while the values of the endocyclic angles $C^4C^5C^6$, $C^5C^6C^7$, and $C^6C^7C^8$ are leveled and close to 120° (Table 6). Thus, the observed structural features of compounds **IIIa** and **IIIb** suggest clearly the existence of their anions as two main resonance forms. Apparently, larger value of the bond length of C^4–C^5 compared with the bond length of C^7–C^8 in the anions **IIIa** and **IIIb** is caused by the influence of electronic and steric effects of the *ortho*-nitro group at the carbon atom C^4. Cyano and amido substituents are also involved into delocalization of the negative charge which is manifested in the lengthening bonds C≡N, C=O, and C–N(H) (Table 6) and shifting the absorption bands of C≡N and C=O groups to the in low-frequency region by 50–100 cm^{-1} in the IR spectra.



N-Methylmorpholinium cations and anions in the structures **IIIa** and **IIIb** form the ion pairs by strong hydrogen bonds N^+–H···O=C (Table 7, Figs 2, 3). In the crystal of **IIIa** the described ion pairs form infinite chains along direction [101] due to intermolecular hydrogen bonds between the amide proton and the

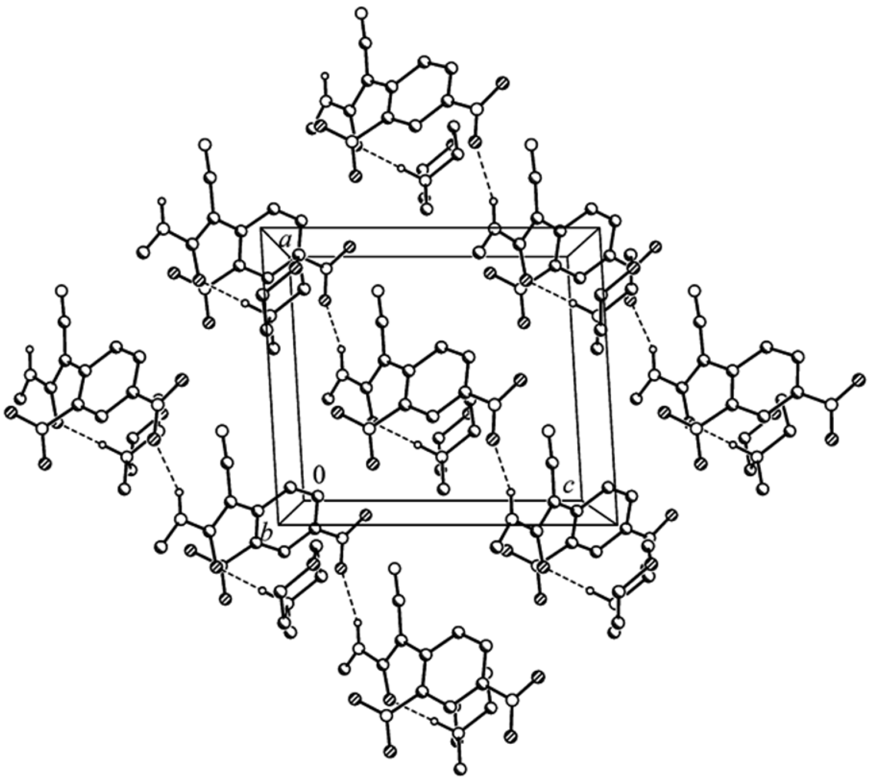


Fig. 5. Crystal packing of the molecules of **IIIa** along the *b* axis. Only hydrogen atoms involved into the hydrogen bonding are represented. The *dashed lines* show the intermolecular hydrogen bonds.

oxygen atom of *para*-nitro group N–H···O (*p*-NO_2) (Table 7, Fig. 5). In the crystal of **IIIb** they form separate centrosymmetric dimers by intermolecular hydrogen bonds between the amide proton and the nitrogen atom of the cyano group N–H···N≡C, which are packed into stacks along the *a* axis (Table 7, Fig. 6). Probably, a choice of proton acceptors between the amino and cyano groups to form a three-dimensional structure of compounds **IIIa** and **IIIb** is dictated by the steric features of anions in ionic pairs, i. e., by the presence of methyl or allyl groups in the amide substituent.

Therefore, the deprotonation of 2,4-dinitrophenylcyanoacetic acid amides with the tertiary amines results in the formation of salts in which the anion part undergoes great changes in geometric and electronic structure compared with the original CH-acids. In this case, the ^{13}C NMR signals of the ring of the salts are shifted upfield, and the exocyclic, downfield. In the structure of compounds **I–III** intra- and intermolecular hydrogen bonds of the amide proton and ammonium cations with *O*- and *N*-proton-acceptors play an important role.

EXPERIMENTAL

The NMR spectra were obtained on a spectrometer AvanceTM-400 [400.1 (^1H), 100.6 (^{13}C) MHz]. The IR spectra were recorded on a Magna-IR-750 Nicolet FTIR spectrometer.

Reactions were performed under dry nitrogen atmosphere.

Synthesis of compounds **Ia**, **Ib**, and **IIa** is described in [2]. Some characteristics of the new compounds are shown in Tables 1–4.

***N*-Cyclohexylamide of 2,4-dinitrophenylcyanoacetic acid (Ib).** To a solution of 2.49 g (15 mmol) of *N*-cyclohexylcyanoacetamide and 3.03 g of (15 mmol) of 2,4-dinitrochlorobenzene in 45 ml of anhydrous acetonitrile was added 9.0 g of finely-powdered potassium carbonate. The mixture was stirred at 20°C for 48 h, and the solvent was removed. To the residue 50 ml of water and 50 ml of $CHCl_3$ and diluted hydrochloric acid (1:5) were added in order to adjust pH to 2–3. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 × 50 ml).

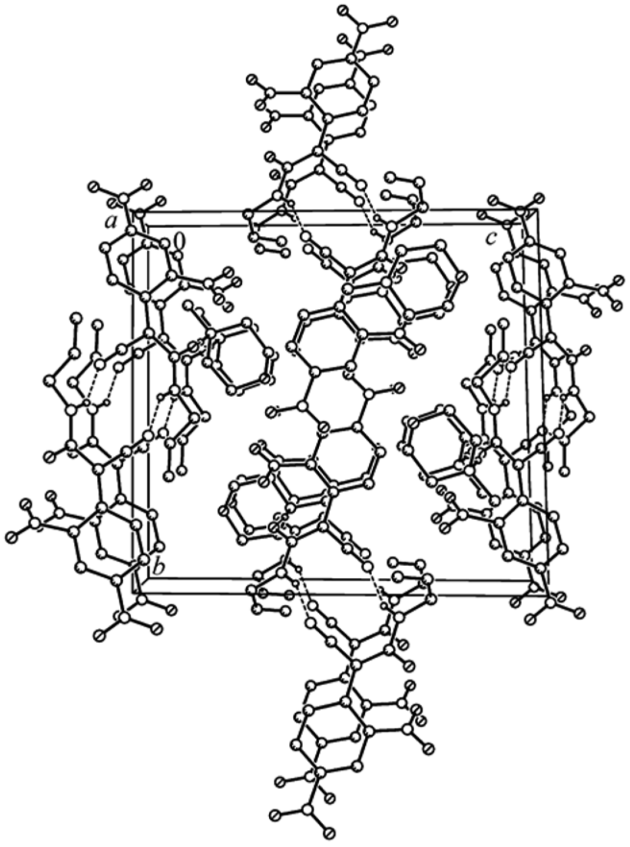


Fig. 6. Crystal packing of the molecules of **IIIb** along the *a* axis. Only hydrogen atoms involved into the hydrogen bonding are represented. The dashed lines show the intermolecular hydrogen bonds.

The combined extracts were dried over anhydrous sodium sulfate and potassium carbonate, and then filtered. The solvent was removed, and the residue was crystallized from a chloroform–petroleum ether mixture (2:1). Yield 3.34 g (67%).

***N*-Methylmorpholinium *N*-methylcarboxamido-2,4-dinitrocyclohexa-2,5-dienide (IIIa), triethylammonium and *N*-methylmorpholinium *N*-cyclohexylcarboxamido-2,4-dinitrocyclohexa-2,5-dienides (IIc, IIIc), triethylammonium and *N*-methylmorpholinium *N*-allylcarboxamido-2,4- dinitrocyclohexa-2,5-dienides (IIb, IIIb)** were obtained by the general procedure. To a solution of 1 mmol of the amide **I** in 8 ml of a diethyl ether–MeCN mixture (1:1) was added a solution of 0.2 g (2 mmol) of triethylamine or *N*-methylmorpholine in 4 ml of ether. The mixture was stirred for 5 h at 20°C. After adding 4 ml of petroleum ether, the mixture was kept overnight at –10°C. The carmine red precipitate was separated, washed with ether, and dried in vacuum.

X-ray diffraction analysis of compounds Ia, IIIa, IIIb. The unit cell parameters and the intensity of the reflections of compounds **Ia**, **IIIa**, **IIIb** were measured on an automatic three-circle diffractometers Bruker SMART APEX II CCD (λMoK_α-radiation, graphite monochromator, φ- and ω-scanning) (**Ia**) and Bruker SMART 1000 CCD (λMoK_α-radiation, graphite monochromator, φ- and ω-scanning) (**IIIa**, **IIIb**). The main crystallographic data are shown in Table 5. The structures of the compounds were solved by the direct method and refined by the full matrix least squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms of amino groups were objectively localized by Fourier syntheses and refined with the fixed positional and thermal parameters. Positions of the remaining hydrogen atoms were geometrically calculated and included into the refinement with fixed positional (*rider* model) and thermal parameters [$U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other groups]. All calculations were performed using SHELXTL software package [9]. Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for compounds **Ia**, **IIIa**, **IIIb** are deposited in the Cambridge Structural Database.

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REFERENCES

1. D’yachenko, V.D., Tkachev, R.P., and Bityukova, O.S., *Zh. Org. Khim.*, 2008, vol. 44, p. 1591.
2. Gololobov, Yu.G., Gol’ding, I.R., Ter’ye, F., Petrovskii, P.V., Lysenko, K.A., and Garbuzova, I.A., *Izv. Akad. Nauk., Ser. Khim.*, 2009, p. 2365.
3. Kavalec, F., Manacek, V., and Sterba, V., *Collect. Chech. Chem. Commun.*, 1976, vol. 41, p. 590.
4. Gololobov, Yu.G., Linchenko, O.A., Gol’ding, I.R., Galkina, M.A., Krasnova, I.A, Garbuzova, and I.A. Petrovskii, P.V., *Izv. Akad. Nauk., Ser. Khim.*, 2005, p. 2323.
5. Gololobov, Yu.G., Linchenko, O.A., Petrovskii, P.V., Starikova, Z.A., and Garbuzova, I.A., *Heteroatom Chem.*, 2007, vol. 18, p. 108.
6. *International Tables for Crystallography*, 2006, vol. C, ch. 9.5, p. 790.
7. Domenicano, A., Vaciago, A., and Coulson, C.A., *Acta Cryst. (B)*, 1975, vol. 31, p. 221.
8. Domenicano, A. and Vaciago, A., *Acta Crystallogr. (B)*, 1979, vol. 35, p. 1382.
9. Sheldrick, G.M., *Acta Crystallogr. (A)*, 2008, vol. 64, p. 112.