Synthesis and structure of 2,4-dinitrophenylcyanoacetamide derivatives as CH acids and their organic salts

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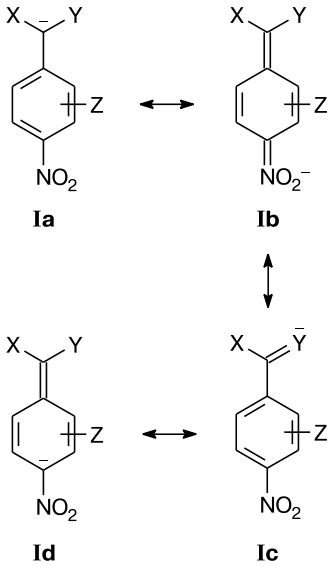
C-Arylation of cyanoacetamides with chloro-2,4-dinitrobenzene was performed in acetonitrile in presence of potassium carbonate. The CH acids obtained react with triethylamine or *N*-methylmorpholine to give salts that contain anions possessing highly conjugated system of unsaturated bonds.

Key words: 2,4-dinitrophenylacetamides, CH acids, triethylammonium and *N*-methylmorpholinium salts of CH acids, chloro-2,4-dinitrobenzene, X-ray diffraction analysis.

The specific features of proton transfer in CH acid—solvent—an organic base systems were discussed in papers,[1—4] the main attention being focused on the study of the resulting benzyl and benzylidene carbanions containing nitro groups in the ring. Usually, carbanions **I** were studied in the solution of deuterated dimethyl sulfoxide, the carbanions being obtained directly in solution by reaction of CH acids with bases. Using UV—Vis spectroscopy, NMR spectroscopy, and thermodinamics data, it was found that one of the shown resonance structures dominates depending on substituents X, Y, Z in anion **I** (Scheme 1). Attempts to isolate carbanions as crystalline salts of the corresponding CH acids are described in some publications, however either these attempts were unsuccesful,[5] or the obtained compounds have not been studied.[6] Only recently, methods for the preparation of stable crystalline organic salts and zwitterions with anions possesing highly conjugated system of delocalized bonds have been developed. However, cyanoacetamides have not previously been used in the synthesis of organic salts of the corresponding CH acids.

Scheme 1



X, Y, Z are electron-withdrawing groups.

The present paper is dedicated to the synthesis and structural studies of 2,4-dinitrophenylcyanoacetamide derivatives as CH acids and their organic salts.

Results and Discussion

Two methods are used for the synthesis of organic salts of type **I** carbanions. One of them is based on direct reaction of methylene-active compounds with halogenonitrobenzenes in presence of 2 equivs of an organic base[7] (usually triethylamine) according to Scheme 2. In this method, the reaction immediately results in the desired salts.

The second method assumes the preliminary synthesis of CH acids with subsequent transformation of the latter into salts under the action of organic bases.

It is the latter method that was used in the present study. The corresponding of cyanoacetamide **1** was treated with chloro-2,4-dinitrobenzene in the presence of dry potassium carbonate in acetonitrile. Then the reaction

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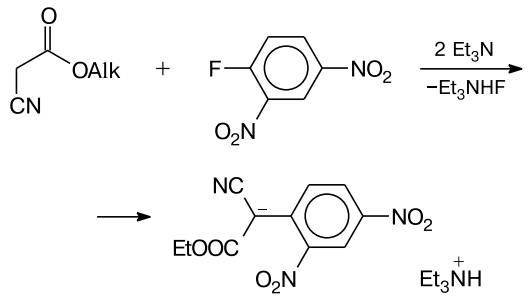
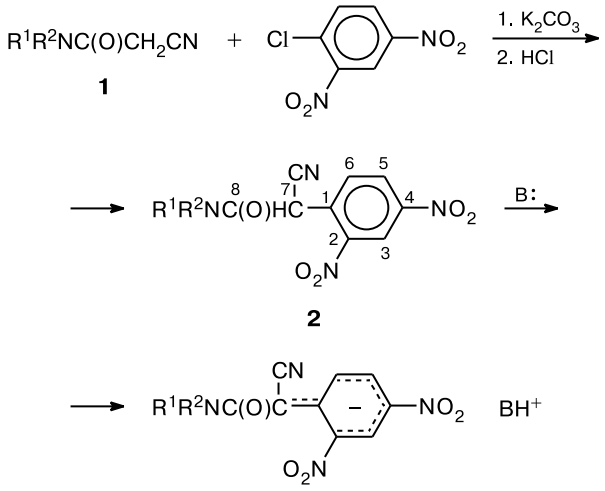
Scheme 2



mass was acidified with dilute hydrochloric acid, and CH acid **2** was isolated from the organic layer (Scheme 3). The thus obtained CH acids **2** by this method were converted to crystalline salts **3** and **4** by the reactions with triethylamine or *N*-methylmorpholine in a mixture acetonitrile — ether. Analytical and physicochemical characteristics of the synthesized compounds are shown in Tables 1—5.

Scheme 3



1—4: R^1R^2N = morpholino (**a**), piperidino (**b**); R^1 = *m*-tolyl, R^2 = H (**c**); $R^1 = R^2$ = H (**d**); R^1 = Me, R^2 = H (**e**); R^1 = allyl, R^2 = H (**f**); B = Et_3N (**3**), *N*-methylmorpholine (**4**)

The compositions and the structures of CH acids **2** and the corresponding salts **3**, **4** followed from the data of elemental analysis, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy. The X-ray structure analysis was performed for compound **4a**. In the IR spectra of CH acids **2** (see Table 3), the vibration frequencies (ν) of CN, $C(O)NR^1R^2$, NO_2 groups and the benzene ring have the standard values. However, these parameters substantially change for salts **3** and **4** (see Table 4). Deprotonation of CH acids **2** leads to decrease of vibration frequencies of the nitrile, carbonyl, and nitro groups by 50—100 cm^{-1} (*cf.* Ref. 7). The presence of the negative charge so much

Table 1. The yields and physicochemical characteristics of CH acids **2a—f**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula
2a	62	132—134	48.64 / 48.65	3.74 / 3.77	17.54 / 17.49	$C_{13}H_{12}N_4O_6$
2b	55	130—132	52.85 / 52.83	4.38 / 4.43	17.67 / 17.60	$C_{14}H_{14}N_4O_5$
2c	58	175—176	56.59 / 56.47	3.52 / 3.55	16.32 / 16.46	$C_{16}H_{12}N_4O_5$
2d	32	171—172	43.11 / 43.21	2.31 / 2.42	22.29 / 22.39	$C_9H_6N_4O_5$
2e	39	154—155	45.61 / 45.46	2.98 / 3.05	21.14 / 21.23	$C_{10}H_8N_4O_5$
2f	57	130—131	49.44 / 49.65	3.44 / 3.47	19.24 / 19.30	$C_{12}H_{10}N_4O_5$

Table 2. The yields and physicochemical characteristics of ammonium salts **3** and **4**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula
3a	93	96—97	54.01 / 54.15	6.49 / 6.45	16.41 / 16.62	$C_{19}H_{27}N_5O_6$
4a	92	104—106	51.30 / 51.30	5.59 / 5.50	16.74 / 16.62	$C_{18}H_{23}N_5O_7$
3b	95	95—96	57.25 / 57.27	7.01 / 6.97	16.58 / 16.69	$C_{20}H_{29}N_5O_5$
3c	93	108—109	59.92 / 59.85	6.12 / 6.16	15.89 / 15.86	$C_{22}H_{27}N_5O_5$
4c	91	135—136	57.06 / 57.14	2.98 / 3.05	15.78 / 15.86	$C_{21}H_{23}N_5O_6$
3d	95	120—121	51.14 / 51.27	5.92 / 6.02	20.07 / 19.93	$C_{15}H_{21}N_5O_5$
3e	72	108—109	52.54 / 52.59	6.37 / 6.34	19.24 / 19.16	$C_{16}H_{23}N_5O_5$

Table 3. IR spectra of CH acids **2**

Compound	IR spectra, ν/cm^{-1} C≡N	C=O	Aromatic ring	NO_2	NH
2a	2244	1683	1612	1536, 1351	—
2b	2248	1677	1614	1551, 1353	—
2c	2252	1673	1612	1538, 1354	3396
2d	2251	1676	1597	1537, 1349	3393
2e	2250	1675	1601	1534, 1350	3289
2f	2250	1660	1597	1534, 1350	3274

Table 4. IR spectra of ammonium salts **3** and **4**

Compound	IR spectra, ν/cm^{-1}					
	C≡N	C=O	NO_2	NH	NH^+	Aromatic ring
3a[a]	2149	1594	1288, 1269	—	2652	—
4a	2160	1586	1277, 1247	—	2673	—
3b[b]	2155	1598	1299, 1270	—	2699	—
3c	2164	1586	1298, 1254	3390	2682	1634 [c]
4c	2170	1575	1287 ш	3378	2681	1616 [c]
3d	2154	1587	1288 ш	3340	2682	—
3e	2148	1595	1287 ш	3304	2674	—

[a] UV—Vis spectra: λ_{max} = 494 nm, ε = 32000.
[b] UV—Vis spectra (acetone): λ_{max} = 497 nm, ε = 28000.
[c] Concerns the *m*-tolyl ring.

changes the electron configuration of the benzene ring, that the IR spectra of salts **3** and **4** do not contain characteristic bands of aromatic compounds.

Interesting changes are observed in the ^{1}H and ^{13}C NMR spectra (see Tables 5, 6) on passage from CH acids **2** to their salts **3** and **4**. In the ^{1}H NMR spectra, the chemical shifts of protons of the C_6-ring with nitro groups experience the expected up-field shift by 0.5—0.8 ppm on passage from CH acids **2** to the corresponding salts **3** and **4**. This is a usual effect observed when a neutral compound passes to the corresponding anion.[7,12] More complicated dependence is observed in the ^{13}C NMR spectra of CH acids **2** and salts **3**, **4**. The low-field shifts of signals for the C(7) atom by 26—30 ppm suggest that, first, the resonance form **Ia** for anionic part of the salts **3** does not have considerable contribution. Second, taking into account data from IR and UV—Vis spectroscopy and X-ray diffractional analysis (see below), a conclusion can be made, that the negative charge is substantially delocalized with involvement all of the functional groups including the substituted benzene ring. Presently, it is quite difficult to say to what extent the electronic structure of the anionic part of salts **3** corresponds to the resonance forms **Ib**,**c**. The considerable low-field shift of ^{13}C NMR signals of C atoms of the CN and C=O groups almost by 10 ppm was quite unexpected. Additional study is needed for explanation of these facts.

The discussion of X-ray structural data for the salt **4a** is of considerable interest. The spatial configuration of the formula unit of salt **4a** is shown in Fig. 1, the most typical bond lengths and angle characteristics are presented in Table 7. It is reasonable to discuss the structure of **4a** in comparison with the literature data[13] for the neutral compound **5** closely similar in structure to CH acid **2a**. The character of distribution of bond lengths in anion **4a** (see Fig. 1, Table 6) compared to the neutral compound **5** (Fig. 2) shows that the delocalization of the negative charge occures actually with involvement of all functional groups. The ring with the nitro groups (C_6-ring) in **4a** is characterized by flattened boat conformation with atoms C(1) and C(4) deviated from the plane by 0.124(2) and 0.057(2) Å, whereas in **5** it is planar (the deviation of

Table 5. ^{1}H NMR spectra of compounds **2**—**4** (δ, *J*/Hz)*

Compound	H(3) (d, 1 H)	H(5) (dd, 1 H)	H(6) (d, 1 H)	H(7) (s, 1 H)
2a	9.01 (*J* = 2.3)	8.60 (*J* = 2.3, *J* = 8.6)	8.13 (*J* = 8.6)	5.98
3a	8.56 (*J* = 2.0)	7.88 (*J* = 2.0, *J* = 9.4)	7.33 (*J* = 9.4)	—
4a	8.32 (*J* = 2.5)	7.79 (*J* = 2.5, *J* = 9.5)	7.11 (*J* = 9.5)	—
2b	9.01 (*J* = 2.3)	8.57 (*J* = 2.3, *J* = 8.6)	8.11 (*J* = 8.6)	5.99
3b	8.55 (*J* = 2.3)	7.83 (*J* = 2.3, *J* = 9.4)	7.29 (*J* = 9.4)	—
2c	8.85 (*J* = 2.4)	8.71 (*J* = 2.4, *J* = 8.5)	8.10 (*J* = 8.5)	5.99
3c	8.30 (*J* = 2.4)	7.91 (*J* = 2.4, *J* = 9.3)	7.39 (br.s, 1 H)	—
4c	8.30 (*J* = 2.4)	7.91 (*J* = 2.4, *J* = 9.4)	7.39 (br.s, 1 H)	—
2d	8.82 (*J* = 2.3)	8.67 (*J* = 2.3, *J* = 8.6)	8.03 (*J* = 8.6)	5.85
3d	8.24 (*J* = 2.5)	7.83 (*J* = 2.5, *J* = 9.2)	7.42 (*J* = 9.2)	—
2e	8.82 (br.s, 1 H)	8.66 (*J* = 8.4)	8.03 (*J* = 8.4)	5.85
3e	8.24 (*J* = 2.4)	7.79 (*J* = 2.4, *J* = 9.5)	7.33 (br.s, 1 H)	—
2f	8.82 (*J* = 2.2)	8.68 (*J* = 2.2, *J* = 8.6)	8.04 (*J* = 8.6)	5.89

* Proton signals of the morpholine ring: **2a** — 3.66 (m, 2 H); 3.77 (m, 4 H); 3.89 (m, 2 H); **3a** — 3.67 (m, 4 H); 3.72 (m, 4 H); **4a** — 3.60 (m, 4 H); 3.73 (m, 8 H); 3.80 (m, 4 H); **4c** — 3.16 (bs, 4 H); 3.77 (bs, 4 H). Proton signals of the piperidine ring: **2b** — 1.63 (m, 2 H); 1.75 (m, 2 H); 1.83 (m, 2 H); 3.50 (m, 1 H); 3.62 (m, 1 H); **3b** — 1.63 (bs, 6 H); 3.53 (bs, 4 H). Proton signals of the Me group in *N*-methylmorpholine: **4a** — 2.58 (s, 3 H); **4c** — 2.78 (s, 3 H). Proton signals of the *m*-tolyl ring: **2c** — 6.96 (d, 1 H, *J* = 7.4); 7.25 (m, 1 H); 7.32 (m, 1 H); 7.37 (bs, 1 H); 2.29 (s, 3 H; Me); **3c**, **4c** — 6.75 (d, 1 H, *J* = 7.4); 7.09 (m, 1 H); 7.34 (m, 2 H); 2.29 (s, 3 H; Me). Proton signals of the Et group in Et_3N^+H: **3a**, **3b** — 1.16 (t, 9 H, Me, *J* = 7.3); 2.83 (q, 6 H, CH_2, *J* = 7.3); **3c**, **3e** — 1.17 (t, 9 H, Me, *J* = 7.2); 3.09 (q, 6 H, CH_2, *J* = 7.2). Proton signals in the amide group: **2c** — 10.84 (bs, 1 H); **3c**, **4c** — 8.87 (bs, 1 H); **2d** — 7.85 (s, 1 H); 8.13 (s, 1 H); **3d** — 6.20 (bs, 2 H); **2e** — 8.59 (q, 1 H, *J* = 4.24); 2.67 (d, 3 H, *J* = 4.2); **3e** — 6.86 (q, 1 H, *J* = 4.3); 2.59 (d, 3 H, *J* = 4.3); **2f** — 8.91 (bs, 1 H). Proton signals in the allyl group **2f**: 3.76 (bs, 2 H, CH_2); 5.10 (d, 1 H, *cis*-H, *J* = 10.2); 5.20 (d, 1 H, *trans*-H, *J* = 17.5); 5.79 (m, 1 H, =CH).

Table 6. ^{13}C NMR spectra (δ) of compounds **2—4**

Compound	C atoms in C_6-rings	C_H atoms in C_6-rings	C(7) *exo*-cyclic	C(9)=O	C(8)≡N	C atoms in heterocycles; the other C atoms
2a	132.7 (C(1)); 148.16 (C(2)); 147.1 (C(4))	121.0 (C(3)); 133.1 (C(5)); 128.1 (C(6))	39.0	159.7	113.8	43.6; 46.9; 65.9; 66.4 (morpholine ring)
3a	133.7; 136.5; 142.3	122.6; 123.6; 124.2	65.2	169.1	121.9	44.9; 65.7 (morpholine ring); 7.3 (Me)*; 44.1 (CH_2)*
4a	132.5; 136.8; 143.8	122.7 (br.s, 2 C); 124.6	69.9	167.7	122.7	45.2; 52.7; 63.5; 66.4 (morpholine ring); 42.7 (Me)**
2b	133.5 (C(1)); 147.8 (C(2)); 147.1 (C(4))	120.7 (C(3)); 133.0 (C(5)); 127.9 (C(6))	39.1	159.0	114.1	23.9; 25.1; 25.6; 44.5; 47.6 (piperidine ring)
3b	133.5; 137.4; 144.3	123.9; 124.1; 124.7	69.9	169.2	122.4	24.8; 26.2; 46.3 (piperidine ring); 8.60 (Me)*; 47.6 (CH_2)*
2c	132.8 (C(1)); 147.8 (C(2)); 147.8 (C(4)); 137.9; 138.5	120.8 (C(3)); 133.2 (C(5)); 128.6 (C(6)); 116.9; 120.2; 125.3; 128.9	42.4	160.5	116.3	21.1 (Me in the aromatic ring)
3c	134.2; 137.3; 139.5; 140.3; 142.8	116.5; 119.9; 122.6; 122.6; 124.7; 124.8; 128.1	69.1	164.8	123.6	8.6 (Me)*; 47.6 (CH_2)*; 21.2 (Me in C_6-ring)
4c	134.3; 137.4; 139.5; 140.3; 142.8	116.6; 119.9; 122.6; 122.7; 124.7; 124.8; 128.1	69.4	164.8	123.6	52.8; 63.6 (morpholine ring); 21.3 (Me in C_6-ring); 42.81**
2d	133.1 (C(1)); 147.8 (C(2)); 147.9 (C(4))	120.7 (C(3)); 133.5 (C(5)); 128.5 (C(6))	41.3	163.5	116.5	—
3d	134.0; 139.7; 143.4	123.0; 124.9; 124.8	68.6	168.3	124.4	9.0 (Me)*; 46.2 (CH_2)*
2e	132.8 (C(1)); 147.8 (C(2)); 147.9 (C(4))	120.8 (C(3)); 133.6 (C(5)); 128.5 (C(6))	41.1	162.3	116.4	26.6 (NMe)
3e	133.3; 138.9; 143.1	123.2; 124.3; 124.6	69.9	166.9	124.0	26.5 (NMe); 8.9 (Me)*; 46.2 (CH_2)*

* In Et_3N^+H.
** In *N*-methylmorpholine.

the other C atoms of the ring are less than 0.02 Å). The bond lengths in the C_6-ring of **4a** vary in quite a broad interval 1.367(1)—1.437(1) Å, whereas in **5** the interval of bond lengths is considerably narrower: 1.374—1.397 Å. Such a change in bond lengths is quite typical on radical anion of benzene,[14] which suggests high concentration of the negative charge in the ring. In addition to the changes in bond length distribution in the C_6-ring, a decrease in bond lengths C(1)—C(7) from 1.550 to 1.414(2) Å and increase in C(13)—N(3) bond lengths from 1.133 Å in **5** to 1.1564 Å in **4a** are observed. The cyano group is virtually coplanar with the C_6-ring, the torsion angle C(6)—C(1)—C(7)—C(13) is 14.5°. It should be noted that the amide group slightly deviates from the plane of the cyano group and the C_6-ring (torsion angles C(13)—C(7)—C(8)—N(4) and C(1)—C(7)—C(8)—O(5) are 41.2 and 27.9°, respectively). It seems that the observed conformation of amide group is caused by both cross-conjugation and steric reasons (see below). The nitro group at the C(2) atom is turned by 9.8°, whereas the nitro group at the C(4) atom is coplanar to the ring. The substituents at C(1) and C(2) atoms are bent in opposite directions by 10.3 and 10.1°, which in general is similar to the pattern observed in *peri*-substituted naph-

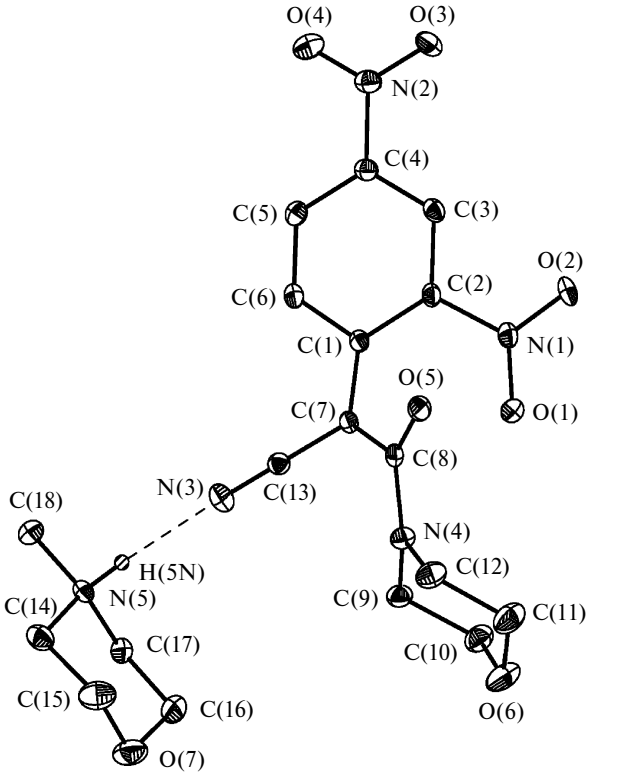


Fig. 1. General view of salt **4a** with atoms presented as thermal ellipsoids of vibrations (p = 50%).

Table 7. The main bond lengths and bond angles in crystal of **4a**

Parameter	Value	Parameter	Value	Parameter	Value
Bond length	*d*/Å	Bond length	*d*/Å	Bond angle	φ/deg
O(1)—N(1)	1.2318(13)	N(4)—C(12)	1.4621(15)	C(3)—C(2)—N(1)	115.19(9)
N(1)—O(2)	1.2430(12)	C(4)—C(5)	1.4102(15)	C(1)—C(2)—N(1)	121.94(9)
N(1)—C(2)	1.4544(14)	N(5)—C(18)	1.4929(15)	C(4)—C(3)—C(2)	119.01(10)
C(1)—C(7)	1.4143(16)	N(5)—C(14)	1.4990(15)	C(3)—C(4)—C(5)	121.04(10)
C(1)—C(2)	1.4350(14)	N(5)—C(17)	1.4994(15)	C(3)—C(4)—N(2)	119.08(10)
C(1)—C(6)	1.4366(15)	C(5)—C(6)	1.3673(16)	C(5)—C(4)—N(2)	119.86(10)
N(2)—O(4)	1.2377(13)	C(7)—C(13)	1.4136(15)	C(6)—C(5)—C(4)	118.85(10)
N(2)—O(3)	1.2418(13)	C(7)—C(8)	1.4821(15)	C(5)—C(6)—C(1)	123.30(10)
N(2)—C(4)	1.4457(15)	Bond angle	φ/deg	C(13)—C(7)—C(1)	117.91(9)
C(2)—C(3)	1.3941(16)	C(7)—C(1)—C(2)	125.51(10)	C(13)—C(7)—C(8)	117.30(9)
N(3)—C(13)	1.1564(14)	C(7)—C(1)—C(6)	120.36(9)	C(1)—C(7)—C(8)	122.27(9)
C(3)—C(4)	1.3808(15)	C(2)—C(1)—C(6)	114.09(9)	O(5)—C(8)—N(4)	121.17(10)
N(4)—C(8)	1.3583(15)	C(3)—C(2)—C(1)	122.45(10)	O(5)—C(8)—C(7)	120.09(10)
N(4)—C(9)	1.4603(15)			N(4)—C(8)—C(7)	118.54(9)

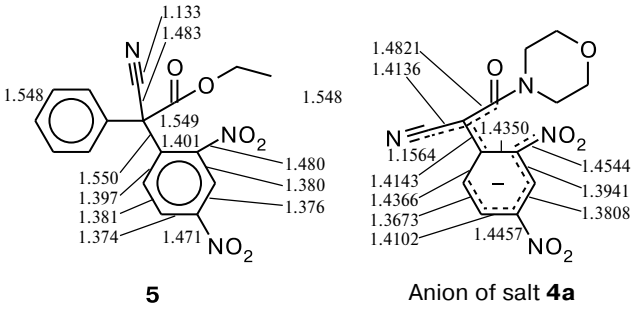


Fig. 2. A comparison of the structure of ethyl 2,4-dinitrophenyl(phenyl)cyanoacetate[12] **5** and anion of salt **4a**.

thalenes, and, probably, is caused by steric repultion.[15] Indeed, the length of the shortest intramolecular contact O(1)...C(8) in the structure **4a** is 2.619(2) Å.

Anions are joined into centrosymmetric dimers in the crystal due to stacking-interaction (the shortest contact C(6)...C(6) 3.335(2) Å) and interaction of the CN with the NO_2 groups (N(2)...—N(3) 3.111(2) Å). The anionic dimers are surrounded by four cations, which are bond due to a strong hydrogen bond with the cyano group (N(3)...N(5) 2.823(3) Å) and shortened contacts C—H...O (H...O 2.28 and 2.32 Å) with carbonyl group (Fig. 2, 3). It should be noted that the considered cation—

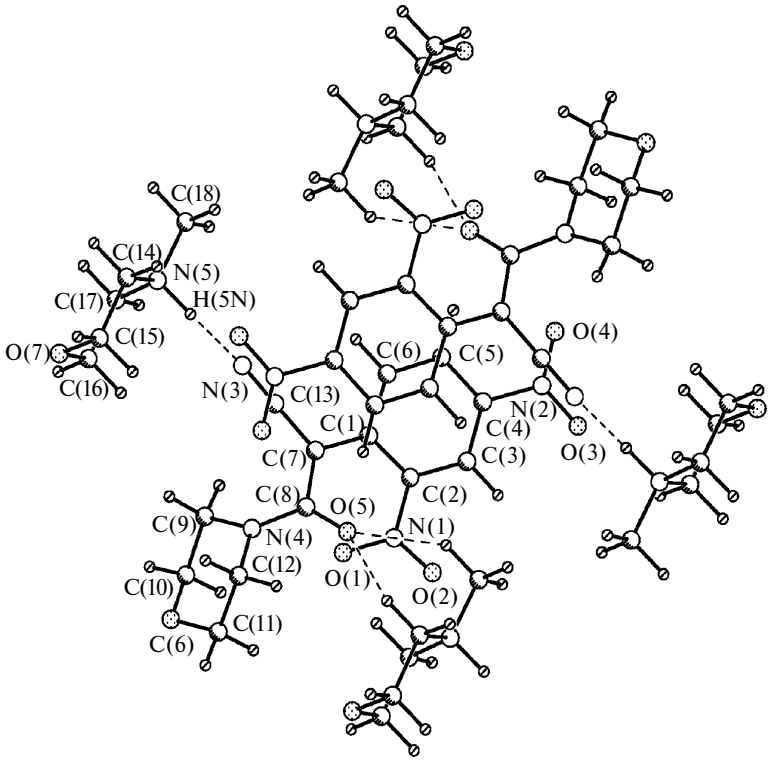


Fig. 3. A fragment of crystal packing illustrating cation—anion hydrogen bonds and anion—anion stacking interaction in the structure **4a**.

anionic interactions can also lead to redistribution of the charge in the anion due to withdrawal of the negative charge from the carbonyl and cyano groups.[16]

Experimental

NMR spectra were recorded on a Bruker AV-400 instrument (^{1}H, 400.26 MHz; ^{13}C, 100.68 MHz) in $CDCl_3$. IR spectra were registered on a FTIR spectrometer Magna-IR-750 "Nicolet" (pellets with KBr). The reactions were performed under dry nitrogen. The solvents were purified and dried prior to use.

2,4-Dinitrophenylcyanoacetic acid morpholide (2a), piperidide (2b), *m*-toluidide (2c), amide (2d), methylamide (2e), and allylamide (2f) were synthesized according to a general procedure. Finely ground freshly calcined potassium carbonate (9.0 g) was added to a solution of a cyanocetamide (0.02 mmol) and chloro-2,4-dinitrobenzene in absolute acetonitrile (30 mL). The mixture was stirred for 48 h at 20 °C, the solvent was removed, water (50 mL) and $CHCl_3$ (50 mL) were added to the residue. Then pH of aqueos layer was adjusted to 2—3 with dulute hydrochloric acid (1 : 5). The organic layer was separated, the aqueous layer was extracted with $CHCl_3$ (2S50 mL), the combined extracts were dried with sodium sulfate and potassium carbonate and filtered. The filtrate was concentrated, the residue was crystallized from chloroform—petroleum ether (2 : 1). The yields, melting points, and elemental analysis data of compounds **2a—f** are shown in Table 1, ^{1}H and ^{13}C NMR spectra in Tables 5 and 6, IR spectra in Table 3.

Triethylammonium carbamoyl(cyano)(2-nitro-4-acinitrohexa-2,5-dienyl)methanide (3d) and its *N*-derivatives — morpholinocarbonyl- (3a), piperidinocarbonyl- (3b), *m*-tolyl- (3c), methyl- (3e), and allyl- (3f), and *N*-methylmorpholinium (morpholinocarbonyl- (4a), *N*-*m*-tolyl- (4c), and *N*-methylcarbamoyl)-(cyano)(2-nitro-4-acinitrohexa-2,5-dienyl)methanide (4e) were synthesized according to a general procedure. A solution of triethylamine (0.2 g, 2 mmol) or *N*-methylmorpholine in ether (4 mL) was added dropwise to a solution of amide **2b** (1 mmol) in a mixture ether—MeCN (1 : 1, 7 mL). The mixture was stirred for 5 h at 20 °C. The carmine-red residue was separated, washed with ether, and dried *in vacuo*. Yields, melting points, and elemental analysis data of compounds **3a—e** and **4a**,**c** are shown in Table 2, ^{1}H and ^{13}C NMR spectra in Tables 5 and 6, IR spectra in Table 4.

X-ray diffraction experiment for 4a ($C_{18}H_{23}N_5O_7$). At 100 K crystals of **4a** are triclinic, space group *P*-1, a = 6.869(2) Å, b = 10.512(2) Å, c = 14.015(5) Å, α = 84.68(1)°, β = 87.301(12)°, γ = 77.949(8)°, V = 985.0(5) Å^3, Z = 2 (Z' = 1), M = 421.41, d_{calc} = 1.421 g cm^{-3}, μ(MoKα) = 1.11 cm^{-1} F(000) = 444. Intensities of 17789 reflections were measured with a Smart APEX II CCD diffractometer at 100 K (λ(MoKα) = 0.71072 Å, ω-scans, graphite monochromator, $2\theta_{max} < 60°$), and 4685 independent reflections (R_{int} = 0.0287) were used in the further refinement. The absorption correction and the merging of reflections were applied using the SADABS program. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.1111 and GOF = 1.015 for all reflections (R_1 = 0.0408 was calculated against F for 6037 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0 program package.

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