Dinitramide and its salts

7.* Spectra and structure of dinitramide salts

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The vibrational and electronic spectra of dinitramide salts $MN(NO_2)_2$ (M = K, Na, Li, NH_4, Fe, Ag, Mn, Mg, Rb, $C(NH_2)_3$) have been studied. The IR and Raman spectra of solutions and melts of the salts have been satisfactorily interpreted on the basis of the anion model with C_{2v} symmetry. The complication of the spectra in the crystalline phase has been explained by restructurization of the anion that reduces its symmetry and makes the nitro groups nonequivalent.

Key words: dinitramide salts, structure; IR spectra; Raman spectra; UV spectra.

In this paper we present the results of IR, Raman, and UV spectroscopic study of salts of dinitramide, $HN(NO_2)_2$ (DNA), carried out in order to elucidate structural peculiarities of the DNA anion in solutions, melts, and the crystalline state.

Experimental

We studied the spectra of DNA salts $MN(NO_2)_2$, where M = K, Na, Rb, Fe, Mn, NH_4, Ag, Mg, or $C(NH_2)_3$,[1] as crystalline films or pellets with KBr at ambient temperature or at liquid-nitrogen temperature, and also as solutions or melts. IR spectra were recorded on UR-20 and Perkin-Elmer 577 spectrophotometers. In order to eliminate the possibility of cation exchange with KBr, the IR spectra of the majority of the salts were obtained from crystalline samples deposited from a solvent onto a Ge or BaF_2 "glass" as films. Raman spectra were recorded on a DFS-12 spectrophotometer with a He—Ne laser. UV spectra were measured on Unicam Sp 800A and Specord UV spectrophotometers. $KN(^{15}NO_2)(^{14}NO_2)$ salt was prepared by decyanoethylation of $NCCH_2CH_2N(^{15}NO_2)(^{14}NO_2)$** (enrichment with ^{15}N was ~90 %).

Results and Discussion

Three types of structures that differ in the location of the negative charge may be ascribed *a priori* to the DNA anion, namely, (1) the charge is localized mostly at the amine N atom, (2) it is uniformly distributed among the two nitro groups, and (3) it is nonuniformly distributed among the nitro groups. It may be assumed that the IR and Raman spectra of these structures would be dissimilar.

It is known that the most pronounced distinctions between the vibrational spectra of nitro compounds of various types occur in the region of symmetrical stretching vibrations (~1200—1300 cm^{-1}) and asymmetrical vibrations (~1500—1600 cm^{-1}).[2] The spectra of a type **1** structure, at least in the high-frequency region, 1500—1600 cm^{-1} ($\nu_{as}NO_2$), should be similar to those of $HN(NO_2)_2$ and $MeN(NO_2)_2$. However, a comparison of the IR and Raman spectra of DNA salts (Tables 1—4) with the spectra of dinitramines[3] indicates that they are substantially different. For example, the IR spectrum of $MeN(NO_2)_2$ exhibits very strong bands at 1634 and 1645 cm^{-1} and also at 1243 cm^{-1}, whereas these are not typical of DNA salts. Therefore, one may believe that a type **1** structure is unlikely.

For the model with equivalent nitro groups (type **2**), the most probable structure of the anion has the C_{2v} symmetry. In the case of this symmetry, the vibrations are divided as follows: $\Gamma = 6A_1 + 2A_2 + 2B_1 + 5B_2$. According to the selection rules, the A_2 type vibrations are forbidden in the IR spectra, *i.e.*, 13 frequencies of 15 should be observed. In the Raman spectra, all of these types of vibrations are allowed; however, only six of them (of the A_1 type) are intense and polarized.

For the model in which the nitro groups are nonequivalent (structure **3**), an anion structure with no symmetry elements or a structure with the C_s symmetry (the planar anion) are possible. In the latter case, the 15 vibrations of the DNA anion are divided into two types: $\Gamma = 11A_1 + 4A_2$ (A_1 are vibrations that are symmetrical

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Table 1. Frequencies (ν/cm^{-1}) of the vibrational spectra of the K salt of DNA in solutions

^{14}N								^{15}N (in NO_2)	
IR		Raman						IR	Raman
H_2O or D_2O	MeCN	H_2O			DMSO			$H_2O(D_2O)$	H_2O
ν	ν	ν	*I*	ρ	ν	*I*	ρ	ν	ν
1535 s	1530 m	1520	2	—	1514	2	0.9	1515 s	
1445 w	1436 m	1436	7	0.56				1420 m	
1340 v.w		1330	80	0.20	1330	90	0.20	1330 v.w	1317 s
1195 s	1185 v.s	1220	7		1190	7	0.9	1190	
								1172 v.s	
1030 w	1020 m	1030	40	0.32				1025 m	1030 w
965 m		960	30	0.36	950	40	0.32		946 m
832 v.w	825 w	830	100	0.28	830	100	0.25	825 w	820 v.s
767 m	762 w	763	5					762 w	748 w
734 w	735 w	735	5					732 w	
		583	4						
		478	40	0.42	470	20	0.36		477 m
		287	50	0.21	287	30	0.21		302 m

Note. IR spectra (in H_2O or D_2O) were obtained for a moistened salt between BaF_2 or Ge "glasses." The intensities (*I*) for the Raman spectra (^{14}N) are given on a relative scale (I_{830} = 100); ρ is the depolarization ratio.

Table 2. Frequencies (ν/cm^{-1}) of the vibrational spectra of the K salt of DNA in the crystalline state

^{14}N			^{15}N (in NO_2)		Assignment
IR	Raman		IR	Raman	
ν	ν	*I*	ν	ν	
1535 c	1538	0	1532 s		$\nu_{as}(NO_2)_b$
	1510	21	1510 m		
			1495 sh		
1435 c	1432	7	1435 sh		$\nu_s(NO_2)_a$
			1432 m		
			1405 s		
1345 m	1332	85	1345 w		$\nu_s(NO_2)_b$
			1335 w		
			1320 w	1322 s	
1227 m			1225 sh		
1202 v.s	1195	10	1200 v.s	1188 w	$\nu_{as}(NO_2)_a$
1180 v.s	1160	15	1172 v.s	1160 w	
1038 s			1032 s		
1027 s	1020	37	1025 s	1010 m	$\nu(NN)_b$
970 w	970	5			
952 w	950	35	950 m	950 m	$\nu(NN)_a$
928 v.w					
830 w	830	100	830 w		δ(ONO)
			825 w		
			820 w	820 s	
762 m			762 m		
			758 m		δ(ONO)
752 v.w	750	25	754 v.w		
			751 v.w		
735 m	730	7	736 w		
	640	2	731 w		
480 w	495	5	721 m		
467 w	480	35		484 m	
	307	20		302 m	
	204	w		204 w	
	82	w		76 m	

Note. IR spectra were obtained for KBr pellets. See the note concerning the Raman spectra at Table 1.

Table 3. Frequencies (ν/cm^{-1}) of the vibrational spectra of the NH_4 salt of DNA

Crystal		Solution	
IR (films on Ge and BaF_2)	Raman	IR (MeCN)	Raman (H_2O)
1530 s	1505 v.w	1530 m	1524 w (dp)
1410 s	1402 v.w	1410 m	1436 w (dp)
1340 v.w	1335 v.s		1334 s (p)
1240 m			
1180 w	1174 m	1185 s	1182 w (dp)
1150 v.w			
1038 m	1025 v.w	1020 m	1039 m (p)
	955 m		955 m (p)
825 w	830 v.s	825 w	830 v.s (p)
755 w	755 v.w	755 w	751 w (dp)
735 w	738 w	735 w	
712 m	493 m		482 m (p)
	300 m		301 m (p)
	229 w		
	80 w		

with respect to the symmetry plane and A_2 are vibrations that are asymmetrical with respect to this plane).

Both types of vibrations are allowed by selection rules both in the IR and in the Raman spectra. In the Raman spectra, frequencies associated with the A_1 type vibrations should be more intense and polarized than those of the A_2 type vibrations. Thus, if structure **3** is realized, all 15 of the anion vibrations would be observed in both the IR and Raman spectra of DNA salts. Besides, 11 frequencies of 15 should be polarized in the Raman spectra. Thus, the spectra of the anions having structures **2** and **3** should be appreciably different, especially in the number of polarized Raman lines, which is 6 or 11.

Table 4. Frequencies (ν/cm^{-1}) of the vibrational spectra of DNA salts

$AgN(NO_2)_2$			$Mn[N(NO_2)_2]_2 \cdot H_2O$			$Fe[N(NO_2)_2] \cdot H_2O$			$Li[N(NO_2)_2] \cdot \cdot H_2O$		$NaN(NO_2)_2$	$Mg[N(NO_2)] \cdot \cdot H_2O$
IR[a]	IR[b]	Raman[c]	IR[c]	IR[d]	Raman[c]	IR[a]	IR[d]	Raman[c]	IR[e]	IR[f]	IR[d]	IR[a]
1555 s	1535 s		1530 s	1525 m		1525 m	1525 s		1550 m	1540 s	1520 m	1535 s
1470 sh		1500 w			1510 w							
1450 m	1425 m	1418 w	1435 m		1438 m		1440 m	1465 m	1450 m		1435 s	
1320 w	1325 s	1312 v.s			1332 s		1330 w	1340 v.s	1330 w	1358 w		1345 m
1240 w												
1225 w	1220 sh											1205 s
1080 v	1198 s	1186 w	1190 s	1190 s		1190 s	1180 s		1200 s		1190 s	1190
										1150 s		
1027 m	1040 m	1035 m	1035 s	1015 w	1024 w	1015 w	1030 s		1035 m	1030 w	1010 m	1030 s
	1025											
995 w	970 w	968 m	950 w		970 m		950 sh	970 m	970 sh	940 sh		970 sh
		926 v.w			910 v.w							955 w
830 m	830 m	830 s	830 w	830 v.w	827 s	830 s	830 m	827 s	830 s	845 w	830 w	830 w
	800 v.w									800 v.w		
762 m	770 w		755 m				750 m		785 s			765 m
									755 w			750 w
728	730 m		700 w				720 w					735 m
					640 w			638 w				
								507 m	565 s			
		490 m			498 m				525 m			
		318 m			318 m				445 m			
		153 m			202 w			318 m				
		82 w										

[a] The IR spectrum of salt deposited from MeCN onto Ge. [b] The IR spectrum of salt deposited from MeOH onto Ge. [c] The Raman spectrum of solid salt. [d] The IR spectrum of a MeCN solution. [e] The IR spectrum of salt deposited from ether onto Ge. [f] The IR spectrum of an ethereal solution.

The Raman spectra of solutions of the K salt of DNA, KN_3O_4 (KDNA), exhibit 12 frequencies (see Table 1), 6 of which are polarized (1330, 1030, 960, 830, 478, and 287 cm^{-1}), *i.e.*, the structure of the anion in a solution and apparently in the melt (according to the IR spectra) belongs to the C_{2v} symmetry group (type **2**). For this structure, two mutual arrangements of the nitro groups, *viz.*, a planar arrangement and that in which they are rotated about the N—N bonds by 90°, are theoretically possible. Relying on the general views of the electronic structure of anions and, in particular, of the conjugation of the nitro groups of the DNA anion, one may accept the planar structure as being the more energetically favorable.

Thus, in conformity with the vibrational spectra, the nitro groups in the "free" DNA anion are equivalent, and the negative charge is localized at these groups.

On going from solutions to the crystalline phase, the IR and Raman spectra of the DNA K salt become substantially more complicated (Figs. 1 and 2, see

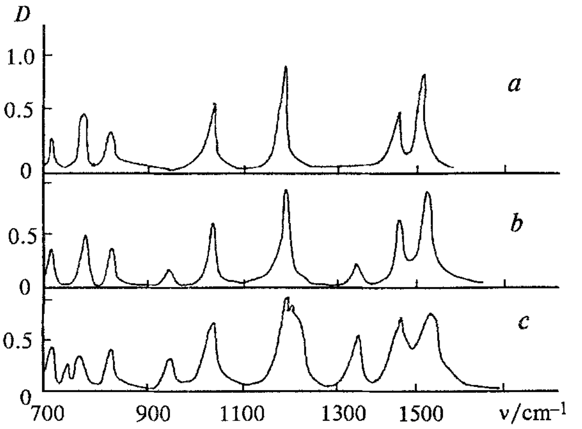

Fig. 1. IR spectra of the K salt of DNA: dilute solution in MeCN (*a*); concentrated aqueous solution (*b*); crystals in KBr (*c*).

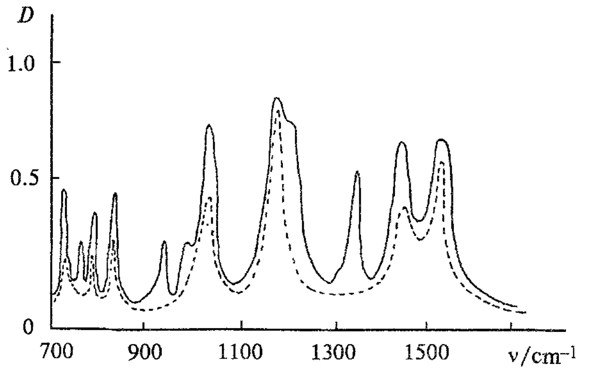

Fig. 2. IR spectra of the K salt of DNA (on KBr "glass"): the solid line corresponds to the crystalline film; the dashed line corresponds to the melt.

Table 5. Electronic spectra of DNA salts (λ/nm, ε/L mol^{-1} cm^{-1})

Compound	Crystal (film)	Solutions				
		H_2O		0.1 *N* KOH		98 % H_2SO_4
	λ_{max}	λ_{max}	ε	λ_{max}	ε	λ_{max}
KN_3O_4	220	221		222		210
	285	285	5645	285	5638	
	335	335				
$NH_4N_3O_4$		218		223		210
		285	5627	285	5640	
		335		335		
$LiN_3O_4 \cdot H_2O$		223		223		215
		284		285		
		335		335		
$C(NH_2)_3N_3O_4$		218		222		210
		285		285		
		335		335		

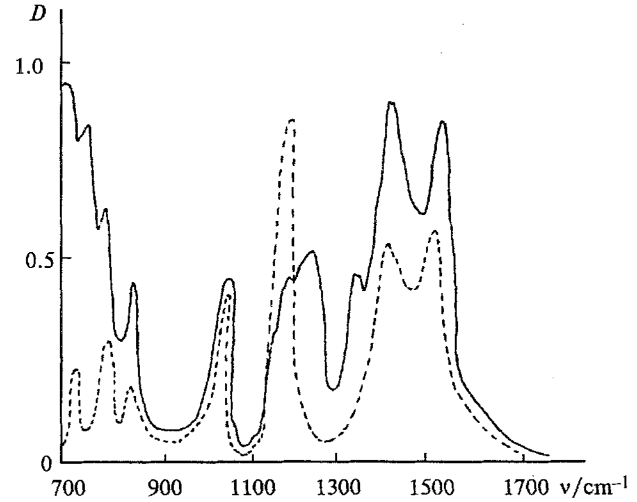

Fig. 3. IR spectra of $NH_4N_3O_4$: the solid line corresponds to the crystalline film on a BaF_2 plate; the dashed line corresponds to a solution in MeCN.

Table 2). The number of lines in the Raman spectra and the number of absorption bands in the IR spectra increase; some frequencies are displaced, intensities change, and some bands are substantially broadened. For example, the bands at 965 and 1345 cm^{-1} have considerable intensities in the IR spectrum of the crystalline salt and are virtually missing from the spectra of a dilute solution or melt.

One may assume that these changes, first of all the appearance of new bands, in the crystalline state are caused by dissimilar ways of coordination of the cation to the nitro groups of the anion. As a result of restructurization, the NO_2 groups are involved in the system of the cation-anion interaction to different degrees, and the distribution of the negative charge at them is different.

Based on the foregoing, we carried out preliminary interpretation of frequencies of the vibrational spectra of crystalline films (see Table 2). The assignment was based on a comparison of the IR and Raman spectra of KN_3O_4 with those of its isotope-substituted analog, $KN(^{15}NO_2)(^{14}NO_2)$, with allowance for the regularities of the variation of vibrational spectra of primary nitramines on their ionization.[2,4]

For convenience in the subsequent discussion, let us denote the different nitro groups $(NO_2)_a$ and $(NO_2)_b$. The interpretation suggested partially accounts for the variations occurring in the spectra on going from crystal to solution. In fact the band at 1345 cm^{-1} (crystal) was assigned to $\nu_s(NO_2)_b$, *i.e.*, it is associated with the nitro group that is weakly coordinated to the cation, and its spectral manifestations are similar to those of a nonionized NO_2 group. In solutions or melts both nitro groups of the anion are equivalent ($(NO_2)_a$), and the $\nu_s(NO_2)_b$ band in the 1300—1350 cm^{-1} region disappears.

A comparison of the IR and Raman spectra of the DNA ammonium salt, $NH_4N_3O_4$ (ADNA), in solutions (see Table 3, Fig. 3) with the spectra of KN_3O_4 indicates that they are similar (except for the band at 1410 cm^{-1} corresponding to the NH_4^+ cation). The IR spectra of the KN_3O_4 and $NH_4N_3O_4$ melts are also identical, which indicates that the structures of the anions of these salts in solutions and melts are similar.

As regards the crystalline phase, the IR and Raman spectra of $NH_4N_3O_4$ and KN_3O_4 differ substantially from one another (see Tables 1—3) both in frequencies and in intensities. The principle distinction between the spectra of $NH_4N_3O_4$ and KN_3O_4 in various phase states can be formulated as follows: variations in the spectra of $NH_4N_3O_4$ on going from crystal to solution (see Fig. 3) are much smaller than those in the case of KN_3O_4, and the structural nonequivalence of the nitro groups of the anion of KN_3O_4 in the crystalline state is larger than that in $NH_4N_3O_4$.

We studied the spectra of Na, Hg, and Fe salts of DNA, *etc.* Some of these data are presented in Table 4. One can see that the IR and Raman spectra of most other DNA salts in the crystalline state are similar to the spectra of crystalline KN_3O_4.* As a rule, the existing distinctions are small and, in our opinion, not fundamental. Therefore, one may conclude that all of the salts studied are ionic compounds in which the cations are coordinated to oxygen atoms of the nitro groups and the anions have structures of the C_s symmetry with nonequivalent nitro groups (in the crystalline state).

In addition to the IR and Raman spectra of the DNA salts, we also studied their UV spectra (Table 5), which practically did not differ from one another for all of the salts studied both in solutions and in solid films (the Hg salt of DNA is an exception).

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* We found basic spectral distinctions in the case of the Hg salt of DNA. The results of the study of this salt will be published elsewhere.

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