Dinitramide and its salts
4.* Molecular structure of dinitramide

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IR and UV spectroscopic studies of dinitramide have shown that in the covalent state it exists as two forms. In one of these forms, the proton is bound to the central nitrogen atom ($HN(NO_2)_2$). In the other form, the proton is equally bound to the two oxygen atoms of both nitro groups.

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

In the previous papers of this series we suggested a general "organic" method for generating the anion of dinitramide (DNA)[1,2] and described the preparation of DNA and its salts.[3,4] In the present work we have studied the IR and UV spectra of DNA and its salts and, for comparison, the spectral behavior of some primary nitramines and nitramides, the closest analogs of DNA.

Experimental

The DNA samples were prepared by two methods. According to the first method (method ***A***), a suspension of KN_3O_4 in an anhydrous solvent (ether, benzene, dichloromethane) was saturated with HCl with vigorous stirring at 0 °C; the resulting precipitate of KCl was filtered off, the filtrate was concentrated *in vacuo* at 0 °C, a fresh portion of the solvent was added, and the solution was concentrated again. This procedure was repeated 2—3 times until the HCl was entirely removed (according to an assay with an acetonitrile solution of $AgNO_3$). It was shown by UV spectroscopy that solutions of DNA at concentrations up to ~20 % do not decompose noticeably during the recording of the spectra. According to method ***B***, KN_3O_4 was dissolved in 65 % H_2SO_4 (or D_2SO_4), and DNA was extracted with dichloroethane (DCE) to give a solution of DNA in DCE. When treated with KOH, DNA is converted into the starting salt, KN_3O_4, irrespective of the method of its preparation.

IR spectra were recorded on UR-20 and Perkin-Elmer 577 instruments. Since DNA is an aggressive substance, cells with KBr, NaCl, KRS, and Ge glass turned out to be unsuitable for recording the spectra of DNA at room temperature, however, they can be used at low temperatures (~−160 °C). The spectra of DNA in organic solvents at ~20 °C were recorded in cells with BaF_2, CaF_2, and LiF glass as well as with KBr glass protected with thin Teflon or polyethylene films. Protected glass was also used to study solutions of DNA in H_2SO_4 (D_2SO_4). The spectra of dilute solutions of DNA in alkyl halides (the region between 2500 and 3800 cm^{-1}) were recorded in 4- and 100-mm cells with LiF glass. The spectra of solid DNA samples prepared by method ***A*** sprayed onto KBr glass (together with CH_2Cl_2) under a vacuum were also recorded at low temperatures; the thickness of the sprayed layer was monitored by the intensity of the spectral bands.

The results of the studies are presented in Table 1 and in Figs. 1—3; for comparison, characteristics of the IR spectra of methyldinitramine are given in Table 2. The UV spectra of solutions of DNA (and some nitramines and nitramides) were recorded on a Unicam SP-800A spectrophotometer. It was shown that the band with λ_{max} = 285 nm, which corresponds to the DNA anion, obeys Beer's law and, therefore, the concentration of DNA existing in the ionic form may be determined from its intensity.

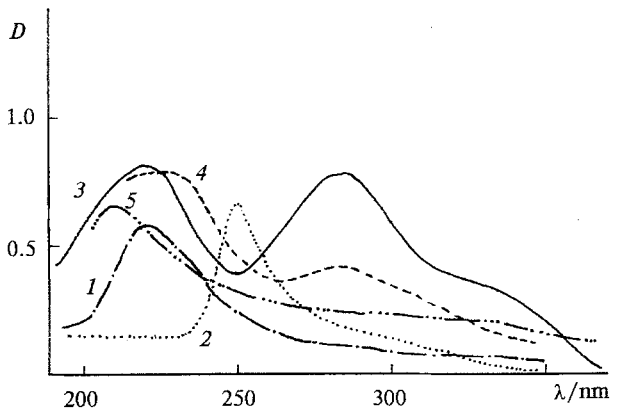

Fig. 1. UV spectra of DNA: in ether (*1*); K-DNA extracted with dichloroethane from 65 % H_2SO_4 (*2*); K-DNA in H_2O (*3*); K-DNA in 65 % H_2SO_4 (*4*); K-DNA in 98 % H_2SO_4 (*5*).

* For part 3, see *Russ. Chem. Bull.*, 1994, **43**, 1457.

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Table 1. Characteristics of the IR spectra of DNA (ν/cm^{-1})

Solution						Sprayed at −160 °C together with CH_2Cl_2
in CH_2Cl_2—CCl_4 mixture		in abs. ether (C < 20 %)		in CH_2Cl_2 (C < 20 %)		
C = 10 %	C = 0.01 %	Teflon	Polyethylene	Teflon	Polyethylene	
2885 s	2868 s					
2940 s	2935 s					
3243 s	3295 s					
		1645 s	1645 s	1645 s	1645 s	1660 s
		1625 s	1625 s	1625 s	1625 s	1630 sh
		1455 m		1455 m		1395 v.w
						1380 v.w
						1355 v.w
			1255 m		1255 m	1250 m
						1110 m
						1045 w
		910 m	910 m	910 m	910 m	945 m
		835 m	835 m	835 m		335 w

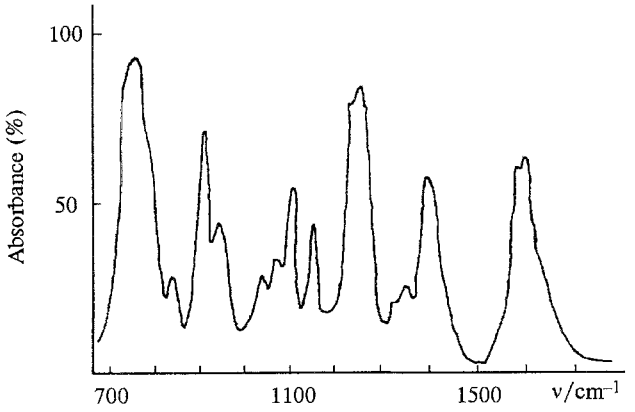


Fig. 2. The IR spectrum of DNA sprayed together with CH_2Cl_2 onto a KBr glass under a vacuum at ~−160 °C.

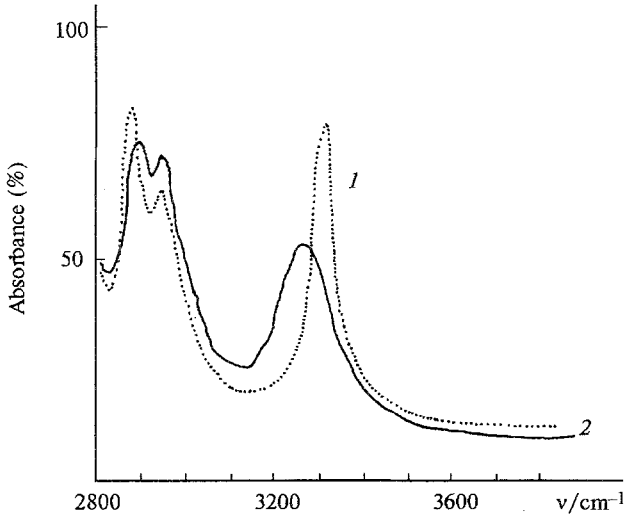


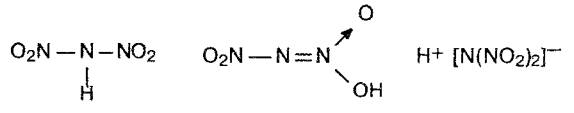
Fig. 3. The IR spectrum of a solution of DNA in a CH_2Cl_2—CCl_4 mixture: C = 0.01 % (*1*); C = 10 % (*2*).

Table 2. Characteristics of the IR spectra of $MeN(NO_2)_2$ (ν/cm^{-1})

Gas	Liquid film	Solution in CCl_4 (0.5 mol L^{-1})
3020 w	3040 w	3040 w
		3015 w
2960 w	2950 w	2929 m
2880 w	2875 w	2878 w
	2840 w	2845 w
1670 v.s	1640 s	1640 s
	1600 s	1610 s
1455 m	1447 m	1450 m
1425 m	1427 m	1418 m
1370 w		
1325 m	1326 m	1325 m
1270 v.s	1250 s	1250 s
1165 w	1164 w	1165 m
1080 w	1075 w	1075 w
1050 w	1020 w	
835 s	827 s	840 s
		700 s
580 w	590 w	590 w
535 w		500 w
480 w	480 w	480 w

Results and Discussion

On the basis of general considerations and taking into account possible analogies with some *C*- and *N*-nitro derivatives, it would be reasonable to expect that DNA in the individual state exists as the nitramine form (NH form) and/or the *aci*-form (OH form) and in solution it also forms the anion:



The spectral characteristics of these forms should be noticeably different. Therefore, by examining the spectra of DNA one should be able to establish which particular form of DNA occurs.

It was found that in fact DNA exists in three forms, depending on the method of its preparation and the medium, but the structure of one of these, in our opinion, does not correspond to the expected structure. The ionic form of DNA can be most easily and reliably identified by comparing the UV spectra of the samples studied with those of the alkaline salts of DNA (see Fig. 1). Aqueous solutions of the latter exhibit intense bands at 225 and 285 nm and a band of low intensity (a shoulder) at 335 nm. These bands can also be observed when DNA salts are dissolved in dilute acids. The intensities of these bands decrease as the concentration of the acid increases owing to suppression of the dissociation, and in the case of 98 % H_2SO_4, the spectrum exhibits only one maximum at 210 nm associated with the covalent form. Thus, the bands at 285 and 335 nm can be considered to be characteristic of the DNA anion, and its concentration can be determined from the intensity of the absorption at 285 nm (ε = 5640 L mol^{-1} cm^{-1}).

It was found that the ionic form of DNA exists in polar solvents including aqueous solutions of strong acids. In weakly polar organic solvents (benzene, chloroform, dichloromethane, dichloroethane, dioxane, *etc.*), no substantial amounts of the DNA anion are detected. Depending on the method of preparation, the covalent forms of DNA exhibit absorption maxima at 223 nm (in ether; prepared by method ***A***) or at 243—250 nm (dichloromethane, dichloroethane, dioxane; prepared by method ***B***). A certain analogy can be noted in the spectral behavior of nitrourethane, *N*-nitro-*p*-toluenesulfonamide, and *N*-nitro-*m*-toluenesulfonamide studied by us for comparison. The UV spectra of hexane solutions of these nitramides (the covalent state) display bands in the 225—232 nm range, and in the case of aqueous or alkaline solutions, additional bands at 252—260 nm, corresponding to the anions, appear.

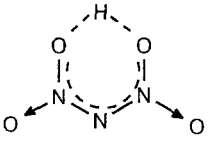
Examination of the IR spectra of covalent forms of DNA and comparison of these spectra with those of primary nitramines and nitramides,[5,6] which exist in the NH form, proved to be useful for structural investigations. The IR spectra of DNA prepared by method ***A*** in solutions in organic solvents and in the solid state at low temperatures contain intense absorption bands at 1645, 1625, and 1255 cm^{-1} (see Fig. 2). The fact that the nitro groups of methyl-*N*,*N*-dinitramine absorb practically in the same region of the IR spectrum (1645, 1605, 1250 cm^{-1}) supports the NH form of DNA prepared by this method. An examination of the 3000—3600 cm^{-1} spectral region leads to the same conclusion (see Fig. 3).

In the region under consideration concentrated solutions of DNA prepared by the same method exhibit a broad band with a maximum at ~3243 cm^{-1},* which becomes narrower and shifts to the high-frequency region, to 3295 cm^{-1}, as the solution is diluted (from 10 to 0.01 %). Under similar conditions, *N*-nitro-*p*-toluenesulfonamide is responsible for the maxima at 3310 and 3353 cm^{-1}.

One may assume that the low-frequency bands correspond to the NH vibrations in the associated forms of nitramides, and the high-frequency bands are due to these vibrations in the free forms. The assignment to NH vibrations seems to us all the more valid, because the stretching vibrations of free OH groups occur at higher frequencies.[7]

Thus, DNA prepared by method ***A*** has the structure of *N*,*N*-dinitramide (the NH form) in organic solvents. According to the IR spectra (and UV spectra), DNA prepared by method ***B*** is essentially different from that synthesized by method ***A***. The IR spectrum of its solution in dichloroethane exhibits two strong bands at 1515 and 1190 cm^{-1}, but exhibits no absorption bands in the 1200—1300 cm^{-1} and 1600—1650 cm^{-1} regions. This indicates that this sample contains no noticeable amounts of the NH form of DNA, but does not correspond to the above-mentioned *aci*-form of DNA, since the IR spectrum does not confirm the presence of a nitro group bound to an electronegative nitrogen atom in this compound.

We believe that DNA prepared by method ***B*** has the following structure:



This structure may formally be considered to be an *aci*-form with a strong intramolecular hydrogen bond (the H atom is equally bound to the two O atoms). This structure contains no nitro group as such, and the IR band whose frequency is the closest to that of the vibrations of the nitro group in the NH form is displaced to the low-frequency region by ~100 cm^{-1}. It should be noted in this connection that, according to calculations,[8] the enol form of acetylacetone is a six-membered ring in which the H atom is equally bound to two oxygen atoms. Its IR spectrum exhibits a band that is shifted ~100 cm^{-1} to the low-frequency region with respect to the signal corresponding to the carbonyl group of the 1,3-diketone form.

* We assigned the two other bands of DNA in this region (2940 and 2885 cm^{-1}) to compound frequencies based on their positions and the character of their changes on dilution.

Thus, depending on the method of preparation and the medium, DNA can exist in three forms: an ionic form and two covalent forms. One of the latter has the structure of *N,N*-dinitramide and the other is an *aci*-structure in which the proton is equally bound to two oxygen atoms.

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