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Electron Donor-Acceptor Phenomena between Mannitol and Some Pyrimidine and Purine Bases*)

by

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Summary. Charge transfer complexes are formed between D-mannitol hexanitrate as acceptors and some pyrimidine and purine bases and aprotic solvents such as hexamethylphosphotriamide or dimethylsulphoxide as donors.

Continuing our experiments on charge-transfer phenomena [1—3] we tried to establish the action of D-mannitol hexanitrate (MNH) as a strong electron acceptor on pyrimidine and purine bases as electron donors. Cytosine, urycyl, thymine, adenine and guanine were chosen for their important role played as a part of nucleosides and in the genetic code.

It is known that esters of nitric acid possess a strong biological activity and the authors of the present paper thought that the activity of the esters upon the living cell may be (partly at least) produced by their electron accepting property.

The role which can be played by CT-complexes in biochemical processes was suggested by Mulliken as early as in 1952 [4]. This problem has been discussed by Szent-Györgyi [5] and reviewed in a number of monographs [6—8].

So far pyrimidine and purine bases as electron donors have been examined with chloranil, *sym*-trinitrobenzene and iodine as electron acceptors [9—12].

The main experimental difficulty which we encountered consisted in finding a solvent of the bases in question: they are insoluble in both polar and non-polar solvent and it was necessary to use aprotic solvents. Hexamethylphosphotriamide (HMPT) and dimethylsulphoxide (DMSO) were found to be suitable dissolving both the bases and MHN.

However we found two characteristic features of the examined systems:

(1) MHN reacts with both solvents to give CT-bands, the solvents being electron donors. The property of aprotic solvents being electron donors with known acceptors has been pointed out by a few authors [11, 13—15].

*) Paper IV in the series [1—3]: Electron Donor-Acceptor Phenomena.

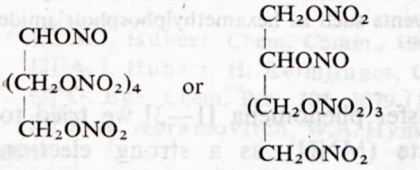
(2) Solutions of MHN in any of the two mentioned solvents react with the pyrimidine and purine bases to give a new strong CT-absorption band.

Thus, it was now found that tri-component CT-complexes are formed between MHN as an electron acceptors and DMSO or HMPT with pyridine or purine base as donors.

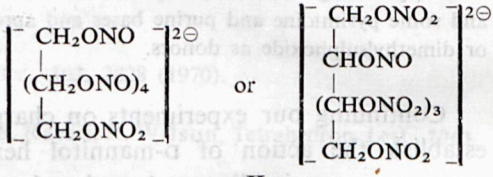
Here are the main results of our experiments.

1) *MHN and HMPT or DMSO.* When MNH was dissoved in HMPT or DMSO a new band appeared at 450 and 437 nm respectively. The formation of the band is a very fast process. By applying the Job method of continuous changes (as in our previous experiments [1—3]) we established the ratio MHN/solvent to be 1:2.

After a certain time the band disappeared and a new band was formed — identical with both solvents — with a multiplet structure of six maxima between 330 and 393 nm. We are suggesting to assign this to a nitrite group formed by a partial reduction of at least one O-nitro group of MHN. We are suggesting to represent it in the form of mixed nitric—nitrous esters [3] or (after accepting electrons from the donors) corresponding anions (**II**):

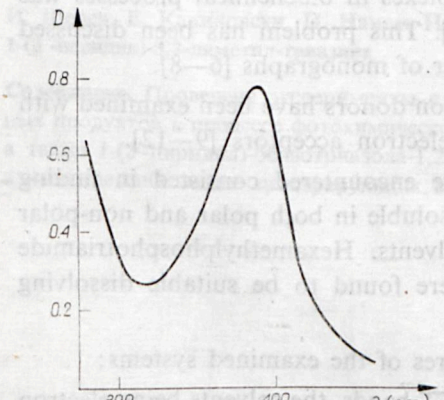


I



II

Unfortunately we could not confirm it in the experimental way by hydrolysing the esters: it is known that the hydrolysis of nitric esters yields a rather complicated mixture of a number of compounds including anions NO_3^- and NO_2^- [16]. Thus the presence of NO_2^- in the products of the hydrolysis cannot be taken as evidence of the presence of O-nitroso group or groups.



Electronic spectrum of 0.1 M solution of guanine in a saturated solution of D-mannitol hexanitrate in dimethylsulphoxide

2) *MHN and pyrimidine and purine bases in HMPT or DMSO.* In order to eliminate the spectrum of the products of the reaction of MHN with the solvents the spectrophotometric measurements were made with a compensation cell filled

with the solution of MHN in the appropriate solvent. The reaction occurred with the formation of a new strong band between 310 and 390 nm (Figure). Only adenine did not give the new band. The mehtod of Job established the ratio MHN/Base to be 1:1. The results with both solvents are given in the Table. It is noteworthy that the CT-band was shifted toward shorter waves with the increase of the ionization potential [6, 12].

TABLE

Base	λ_{max}		Ionization potential, I_D (eV) [11]
	HMPT	DMSO	
Guanidine	381	390	7.65
Cytosine	354	358	7.98
Tymine	314	312	8.25
Uracil	315	315	8.48

We suggest that the observed phenomena in the presence of MHN can be depicted diagrammatically as follows:

(1) $$MHN + 2HMPT \rightarrow \underset{\text{max. } ca \text{ 450 mm}}{[MHN^{2\ominus} - 2HMPT^{\oplus}]} \rightleftarrows \underset{\substack{\text{max. betwenn} \\ \text{330 and 393 mn}}}{MHN^{2\ominus} + 2HMPT^{\oplus}}$$

(2) $$\underset{\text{(the Bases)}}{MHN^{2\ominus}} + BH_2 \rightarrow [MHN^{2\ominus}2H^{\oplus}] + B^{2\ominus}$$

$$MHN^{2\ominus}2H^{\oplus} + B^{2\ominus} + 2HMPT^{\oplus} \rightleftarrows \underset{\text{max. between 310 and 390 nm}}{[MHN^{2\ominus}2H^{\oplus} - B^{2\ominus}2HMPT^{\oplus}]}$$

Experimental

Guanine, adenine, cytosine, thymine and uracile were obtained from Serva, Heidelberg. D-Mannitol hexanitrate was prepared as in paper [1].

Solvents: dimethylsulphoxideand hexamethylphosphotriamide of commercial grades were dried over molecular sieves Serva type 13x and distilled in the atmosphere of nitrogen.

The electronic absorption spectra were examined on a Unicam SP. 500 spectrophotometer with cells of 0.2—5 cm thickness of the liquid layer, and the concentration of components was 0.001—0.1 mol/l.

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Содержание. В настоящей работе описаны комплексы с переносом заряда, в которых выступают: D-маннитол гексанитрат (MHN) в качестве акцептора и некоторые пиримидиновые и пуриновые основания, а также апротонные растворители (гексаметилфосфотриамид и диметилсйльфоксид) в качестве доноров.