

SPECTRAL CHARACTERISTICS OF SOME NITRONAPHTHALENES: FORMATION OF ADDITION COMPLEXES WITH POLYNUCLEAR AROMATICS

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ABSTRACT

Assignment of ir-spectra of 1-nitro-, 1,5-dinitro-, 1, 4, 5, 8-tetranitro- and 1, 3, 6, 8-tetranitronaphthalene were investigated. The formation of CT — complexes of the last compound with some polynuclear aromatic compounds were studied, and the ir-spectra of the addition compounds were correlated with their structure.

INTRODUCTION

The addition compounds obtained from polynitrobenzenes with aromatic hydrocarbons, amines, or phenols were the subject of extensive study⁽¹⁻⁴⁾. Picric acid, picryl chloride, TNT, picramide as well as sym. trinitrobenzoic acid⁵ were used as acceptors, while the aromatic compounds are the donors. These studies, however, have little attention to polynitronaphthalenes, where the 1, 3, 6, 8-tetranitronaphthalene (IV) could act as a good acceptor capable of CT formation.

In the present work, (IV) is used to prepare a series of CT compounds with some aromatic hydrocarbons, naphthols, naphthylamines or nerolines. The ir spectra of some nitro-naphthalenes were investigated also the changes occurring in the spectra due to complexation are discussed, in order to, through light on the different possible modes of interaction.

EXPERIMENTAL

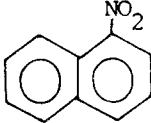
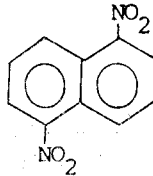
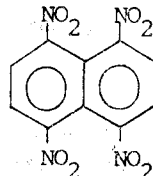
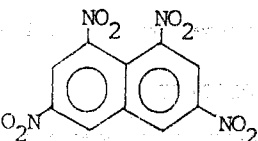
The nitronaphthalenes were prepared as usual⁶ and the resulting products were crystallised several times from the appropriate solvents till the reported m.p.

The CT complexes were obtained as usual², by mixing equimolar amounts of the donor and the acceptor in boiling chloroform, and the m.p. of the resulting complexes were determined after recrystallisation.

The ir-spectra were recorded for solid thin films between two NaCl plates or as KBr discs on a Pye-Unicam-SP 3-100 infrared spectrophotometer.

RESULTS AND DISCUSSION

The characteristic bands in the ir-spectra of the four nitronaphthalenes were assigned:

				
I	II	III	IV	
$\nu_{\text{C-H}}$	3070	3100	3000	3090
asym.	1510	1510	1540	1555, 1535
ν_{NO_2}				
sym.	1340	1350	1340	1344, 1320
m. p. °	61°	218°	340°	207°

The NO_2 group in 1-nitronaphthalene attains a planar configuration with the aromatic nucleus, exerting its full conjugative influence with the naphthalene moiety and thus the stretching vibration of the NO_2 group appears as sharp absorption band at 1510 cm^{-1} for the asym. and 1340 cm^{-1} for the sym. mode of vibration. This could be useful in explaining the ir spectrum of the compound II. The nitro groups are twisted by 49° from the plane of the nucleus by rotation about the C-N bond. There is also a considerable displacement of the C-N bonds within the molecular plane, leading to a reduction of the exocyclic valency angles to 114° . These slight in-plane displacement are very effective in reducing the magnitude of interplanar twisting of the nitro group to only 49° ⁷, where, the NO_2 absorption frequencies appeared at 1510 and 1350 cm^{-1} for the asym. and sym. vibrations respectively.

In 1, 8-dinitronaphthalene the serious interaction that would result from such an arrangement is avoided as follows i) the nitro groups

are rotated about the C-N axis by 45° in one direction, ii) the C-N bond undergo a splaying apart to increase the N...N distance to 2.93 Å from 2.42 Å in a hypothetically planar model, iii) the C-N bonds deviate from the aromatic plane by 0.37 Å in opposite directions, and iv) the carbon atoms bearing the nitro groups are also forced out of the plane of the molecule in the direction of the substituents resulting in slight nuclear distortion⁸. Thus the presence of the four nitro-groups in the 1,4-position results in the absence of conjugation with aromatic nucleus due to the non-planarity of all the NO₂ groups. In the same time the mutual interaction between the NO₂ groups present in the peri-position will lead to lower energy of vibration than expected. Thus, the absorption will occur as a single band at 1540 cm⁻¹ for the asym. vibration and 1340 cm⁻¹ for the symmetric one.

The 1, 3, 6, 8-tetranitronaphthalene represent a different situation, since it contains two different types of nitro groups whose stretching frequencies are not expected to be equivalent, namely the 1,8- and the 3,6-nitro groups. The first pair is expected to absorb at lower energy due to decreased resonance interaction with the naphthalene ring; while the other pair will absorb at higher wavenumber due to the strong attracting influence 1,8-nitro groups.

From the above it is clear that the attractive influence of the nitro groups in compound (IV) is maximum and more better than compound (III), i.e., the former is a good acceptor for electron clouds from the donor molecule. The CT compounds could be obtained only from 1, 3, 6, 8-tetranitro naphthalene, and not from any other nitronaphthalene under investigation. Many attempts to obtain CT complexes using (III), 1, 3, 4, 5, 8-tetranitronaphthalene with any type of donors were unsuccessful:

The Addition Complexes

At first glance the nitro-asymmetric stretching and C-H out of plane bending frequencies of the ten complexes appear to vary in a complex manner. However, on the basis of certain consistencies among these frequencies, there is a possibility of classifying the complexes into two main groups. This classification is reinforced by the significant similarities among donor molecules in each group⁹.

Group A: This group is composed of complexes formed with compounds containing no functional group capable of interaction with

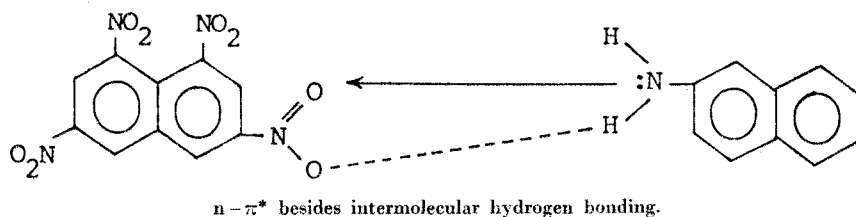
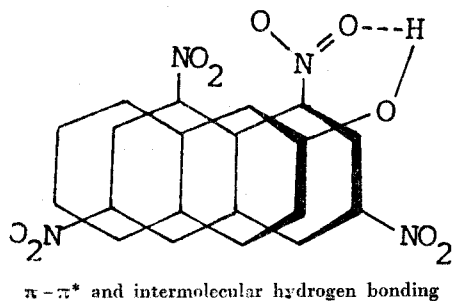
Table 1. Important bands in the IR-spectra of charge transfer complexes of 1, 3, 6, 8-tetratironaphthalene with some polynuclear aromatics.

Donor Acceptor	Naphthalene	Anthracene	Phenanthrene	α -Neroline	β -Neroline	α -Naphthol	β -Naphthol	α -Naphthylamine	β -Naphthylamine	Benzidine	Assignment
						3500 ν OH	3510 ν OH	3475 3340 ν NH ₂	3475 3385 ν NH ₂	3385	ν OH ν NH ₂
3090	3080	3078	3078	3080	3075	3090	3088	3080	3085	3082	ν C-H
1555						1554	1552	1555	1555	1555	
1535	1555	1554	1556	1557	1558	1538	1534	1533	1535	1535	ν NO ₂
1344						1344	1344			1342	ν NO ₂ syn.
1320	1344	1344	1342	1344	1346			1343	1344		
1120	1121	1118	1118	1126	1122	1120	1122	1120	1119	1120	ν CN
734	740	740	744	738	740	740	742	742	738	738	ν C-H
207°	191°	198°	200°	180°	189°	212°	205°	204°	211°	220°	m.p.
White	Yellow	Yellow	Orange	Yellow	Yellow	Red	Orange	Purple	Brown	Red	Colour

the acceptor nitro-groups, namely, naphthalene, anthracene phenanthrene, α - and β -neroline. All of the complexes obtained show a single broad nitro band with higher frequency than that of the free acceptor (IV). In the same time the corresponding C-H out of plane frequencies are all higher than in the acceptor. The increase in frequency of the asym. vibration of NO_2 group could be attributed to the donation of charges from the donor molecular to the acceptor naphthalene nucleus leading to a lower polarisation of the nitro into the complex. These compounds are classified as $\pi - \pi^*$ complexes where a charge transfer from the highest filled π -molecular orbital of the donor molecule to the lowest vacant antibonding π^* of the acceptor.

Group B: Comprises the CT complexes obtained with the acceptor and some substituted naphthalenes containing an α -or β -amino- or hydroxyl group capable of interaction with the nitro-group, through the conventional $n - \pi^*$ interaction resulting from intermolecular hydrogen bonding. Thus, the formation of the additon complexes occurs through the usual $\pi - \pi^*$ besides the $n - \pi^*$ interaction⁽¹⁻³⁾.

If one of the NO_2 -groups of the acceptor molecule faces the hydroxyl or the amino-group present in the donor molecule, a charge transfer from the latter could occur to a vacant antibonding levels of the NO_2 . This type of interaction leads to lowering of the ν_{OH} or the ν_{NH_2} frequencies, while bands of the NO_2 are shifted to higher energies.



The case of β -naphthol addition complex is a typical example illustrating the following points:

i) Bands due to ν_{OH} are still apparent, though shifted to lower frequency⁽¹⁰⁾.

ii) Bands due to asym. ν_{NO_2} vibration are shifted to higher or lower frequencies, the band of sym. NO_2 is still splitted as in the acceptor.

iii) The $\nu_{\text{C-N}}$ is affected, indicating an interaction between the components of the addition product.

Low-polarity solvents and high temperature favour the formation of the CT complexes since, the β -naphthol addition complex is decomposed completely in boiling methanol.

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