

INFRARED ABSORPTION STUDIES OF SOME NEW 1,8-NAPHTHALIMIDES

I. Grabchev¹, V. Bojinov², and Ch. Petkov³

Some new 4-nitro- and 4-allylamino-N-phenyl-1,8-naphthalimides comprising different substituents in the phenyl ring have been studied by infrared absorption spectroscopy. The effect of the nature of the substituents upon the vibration frequencies of the carbonyl groups has been discussed.

Keywords: 1,8-naphthalimides, IR studies.

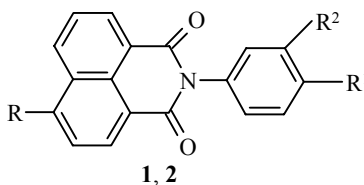
1,8-Naphthalimides and their 4-substituted derivatives have been of special interest due to the applications they find as laser active media [1, 2], potential photosensitive biologically active units [3], fluorescent markers in biology [4] and medicine [5, 6], and in sun energy collectors [7]. Recently they have been subjected to investigation in liquid crystal systems for utilization in electro-optical devices [8-10]. They possess intensive fluorescence and very good photostability [11-15].

The presence of a polymerizable group in the 4-aminosubstituted 1,8-naphthalimide dyes enables them to polymerize with some commercial monomers, hence to form copolymers with intensive fluorescence [16-21]. In recent years these dyes have been the scope of our research in view of their potential use as polymerizable fluorophores for synthetic polymers.

This paper reports on the infrared absorption frequencies of some new 4-nitro-N-phenyl-1,8-naphthalimides **1** and 4-allylamino-N-phenyl-1,8-naphthalimides **2**. The effect of substituents in the phenyl ring on the infrared spectral characteristics has been investigated.

EXPERIMENTAL

Materials and Methods. 4-Nitro- and 4-allylamino-1,8-naphthalimide derivatives were synthesized and purified by a method described previously [22]. The scheme below shows their general formulas:



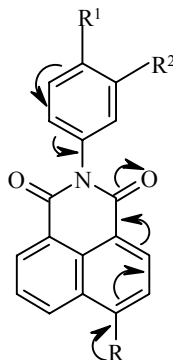
1 R = NO₂; **2** R = CH₂=CHCH₂NH; **1, 2 a**, e R¹ = H, **b** R¹ = Me,
c R¹ = OMe, **d** R¹ = Cl; **a-d** R² = H, **e** R² = OH

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The IR spectra of all 1,8-naphthalimide derivatives were measured on a Bruker IFS-113 v spectrometer at 2 cm^{-1} resolution using KBr pellets.

RESULTS AND DISCUSSION

The absorption characteristics of the 1,8-naphthalimides depend basically on the polarization of the naphthalimide molecule. Upon irradiation, polarization occurs as a result of the electron donor-acceptor interaction between the substituents at C(4) and the carbonyl groups of the imide structure of the chromophore system. The polarization effect on the absorption properties also depends on the interaction between the phenyl ring and the carbonyl groups. The donor-acceptor interaction and the path of the charge transfer are given by the scheme.



Stretching and deformation vibrations of the main functional groups in the infrared region of all compounds **1** and **2** are collected in Tables 1 and 2.

Compounds **1** comprising a nitro group give absorption bands in the $1344\text{-}1360\text{ cm}^{-1}$ region which is characteristic of the symmetrical vibrations. The bands in the $1531\text{-}1535\text{ cm}^{-1}$ region are assigned to the asymmetrical vibrations of the nitro group.

TABLE 1. Infrared Absorption Frequencies of 4-Nitro-1,8-naphthalimides **1**

Dyes	ν, cm^{-1}							σ, cm^{-1} , C-H (arom)
	C-H (arom)	NO ₂	NO ₂	<i>s</i> C=O	<i>as</i> C=O	C=C	CNC (imide)	
1a	3075	1530	1360	1709	1670	1589	1360	770, 746
1b	3079	1535	1358	1708	1668	1585	1364	785, 760
1c	3080	1533	1354	1712	1670	1587	1365	765, 743
1d	3070	1531	1348	1705	1672	1580	1368	762, 732
1e	3078	1532	1344	1708	1669	1590	1370	765, 725

TABLE 2. Infrared Absorption Frequencies of 4-Allylamino-1,8-naphthalimides **2**

Dyes	ν, cm^{-1}						σ, cm^{-1} , C-H (arom)
	NH	C-H (arom)	<i>s</i> C=O	<i>as</i> C=O	C-C	CNC (imide)	
2a	3350	3072	1686	1645	1586	1370	779, 760
2b	3390	3075	1689	1636	1582	1366	778, 762
2c	3408	3070	1689	1639	1585	1367	776, 758
2d	3352	3080	1685	1648	1580	1368	779, 759
2e	3404	3076	1690	1640	1585	1367	775, 758

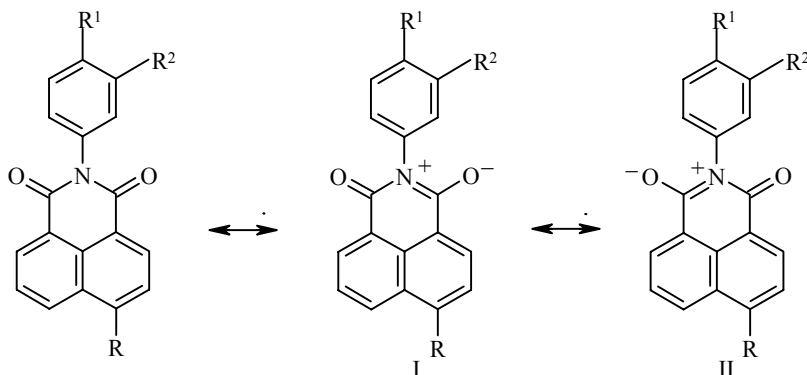
TABLE 3. Infrared Absorption Frequencies of Allylamino Group in 4-Allylamino-N-phenyl-1,8-naphthalimides **2**

Dyes	σ, cm^{-1}	
	CH ₂ =	CH=
2a	930	1002
2b	927	996
2c	933	998
2d	924	1000
2e	922	1004

After substitution of the nitro groups by allylamino groups, intense peaks appear in the stretching vibrations (ν_{NH}) region of 3350-3408 and in the 1540-1550 cm^{-1} deformation vibrations range. The allylic group ($\text{CH}_2\text{CH}=\text{CH}_2$) at the C(4) position of the naphthalene rings in dyes **2** has characteristic bands at 922-933 and 996-1004 cm^{-1} for the $=\text{CH}_2$ and $=\text{CH}$ groups, respectively (Table 3).

A weak band related to the stretching vibrations of the C–H group in naphthalene ring is distinguished in the 3070-3076 cm^{-1} spectral region. The bands at 1582-1586 cm^{-1} , assigned to the stretching C–C vibrations, are observed in the spectra of all compounds. They are characteristic of the aromatic system in the naphthalene ring of the naphthalimide structure. The bands at 758-779 cm^{-1} are characteristic of the aromatic ring deformation vibrations. It is well known that imides give rise to both frequency bands of the C=O absorption [23, 24]. The IR spectra of compounds **1** possess intense absorption bands at 1705-1712 and 1668-1672 cm^{-1} , respectively. The absorption bands for dyes **2** are in the 1686-1690 and 1636-1648 cm^{-1} regions. A comparison of the spectra reveals the strong influence of the polarization of the dye molecules upon the absorption properties. The IR spectra of dyes **1a** and **2a** in the 1500-1750 cm^{-1} region are presented for illustration in Fig. 1.

The bands for dyes **2** are hypsochromically shifted. These bands are characteristic of the symmetrical and asymmetrical carbonyl group vibrations, the latter being separated from each other in the compounds by 33-42 cm^{-1} for dyes **1** and 37-53 cm^{-1} for dyes **2** (structures I and II) in the scheme:



The structure **1a** gives rise to the peak at 1528 cm^{-1} characteristic of the vibration modes of the nitro group. After substitution of the latter by an allylamino group, the peak shifts to 1545 cm^{-1} , which is characteristic of the deformation vibrations of the secondary amino group.

Figure 2 shows the dependence of the two C=O frequency bands of dyes **1** and **2** on the Hammett constants σ . The data indicate that the position of the frequencies corresponding to the C=O groups depends negligibly on the nature of the substituent R in the phenyl ring. This is an indication of the insignificant effect of the substituents R upon the polarization of the molecules. But we have recently described a strong linear correlation between the carbonyl stretching frequencies of some carbonyl fluorophores (bis-1,8-naphthalimides and

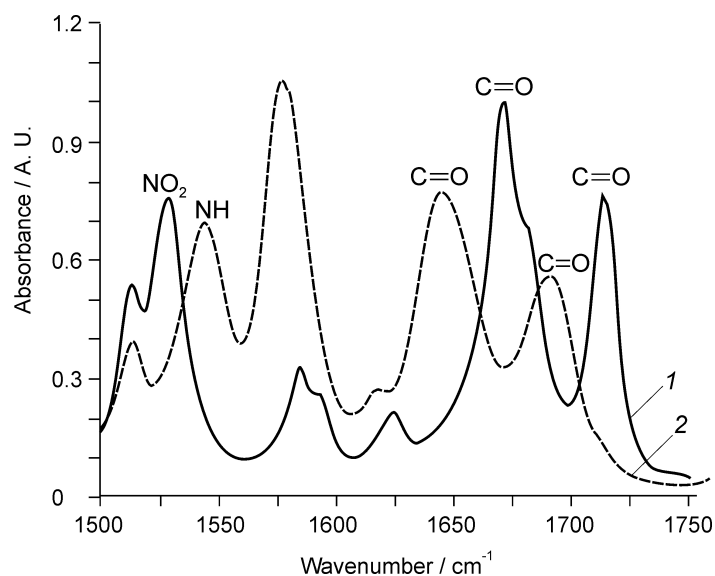


Fig. 1. Infrared spectra of 1,8-naphthalimides **1a** (1) and **2a** (2) in KBr pellets.

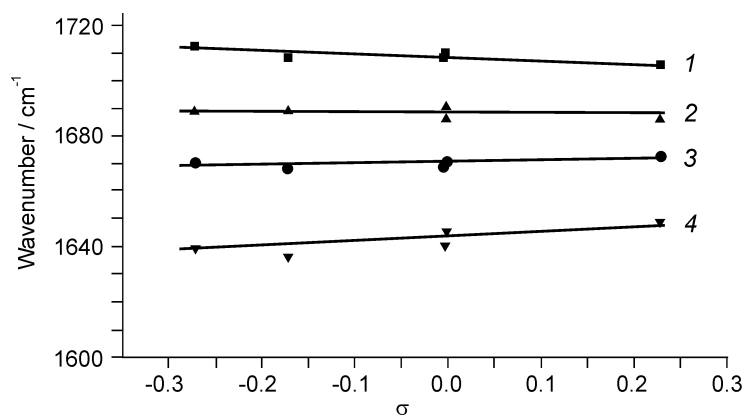


Fig. 2. Relationship between ν_s , (1, 2) and ν_{as} (3, 4) C=O stretching vibrations and Hammett substituent constants in the phenyl ring σ for 4-nitro-1,8-naphthalimides **1** (1, 3) and 4-allylamino-1,8-naphthalimides **2** (2, 4).

benz[*d,e*]anthracen-7-one) and Hammett substituent constants of the groups in positions C(4) or C(3) respectively, in their chromophoric systems [25, 26].

The absorption bands in the 1366-1370 cm^{-1} region are characteristic of the imide C–N–C bonds for all **1** and **2** dyes.

The spectra of dyes **1c** and **2c** comprising a methoxy group have absorption bands at 1240 cm^{-1} for the C–O–C group and at 1462 cm^{-1} for the asymmetrical δ_{as} deformation vibrations of the methyl group.

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