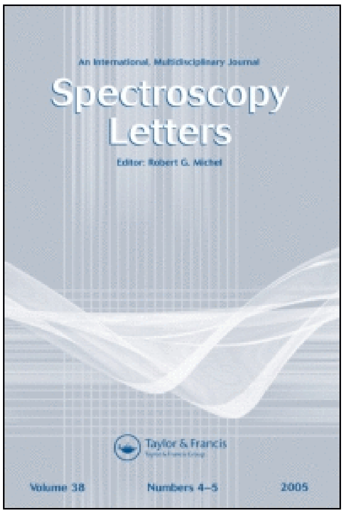

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Vibrational Assignment of N-Phenylphthalimide and ^{15}N-Phenylphthalimide

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VIBRATIONAL ASSIGNMENT OF N-PHENYLPHTHALIMIDE AND ^{15}N-PHENYLPHTHALIMIDE

KEY WORDS: IR spectra; Raman Spectra; vibrational assignment;
isotope labelling ;^{15}N–phenylphthalimide

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ABSTRACT

The i.r. spectra of N-phenylphthalimide and ^{15}N-phenylphthalimide have been measured in 4000-100 cm^{-1} frequency range as KBr and polyethylene pellets and as chloroform solutions. The Raman spectra (4000-50) cm^{-1} of microcrystalline powder of the of the same compounds have also been investigated.

A detailed assignment of most of the observed frequencies has been proposed on the basis of the group vibrational concept, isotopic shift data and analogies with the spectra of related molecules. Some literature data have been discussed and some frequencies are reassigned.

INTRODUCTION

This work is part of current investigations of the vibrational dynamics of N-phenylphthalimide and some of its isotopic isomers and meta- and para- phenyl substituted derivatives. Interest in the investigation of this group of molecules also arises from the fact that N-substituted phthalimide derivatives are model compounds for aromatic polyimides - one of the most important classes of thermostable polymers. A wealth of experimental IR vibrational data is available for N-phenylpthalimide, namely, in solid phase [1,2,4], and in various solvents (but only C=O region 1600-1900 cm^{-1}) [3]. The IR spectra of N-phenylphthalimide and some deuterated derivatives have been investigated in DMSO-d_6 in 1800-1200 cm^{-1} frequency region [5]. The UV/VIS spectrum of the same compound was studied by Magomedova [7] . The X-ray diffraction studies [6,7] show space group Pbca, 8 molecules per unit cell with dimensions 23.76 , 11.66 and 7.65 A for a, b and c respectively. It is noteworthy that certain phthalimides exhibit an apreciable photoelectric sensitivity and have been suggested for use in electrophotography [8]. In this paper we present the results of Raman and IR spectroscopic investigations and propose a prelimi-

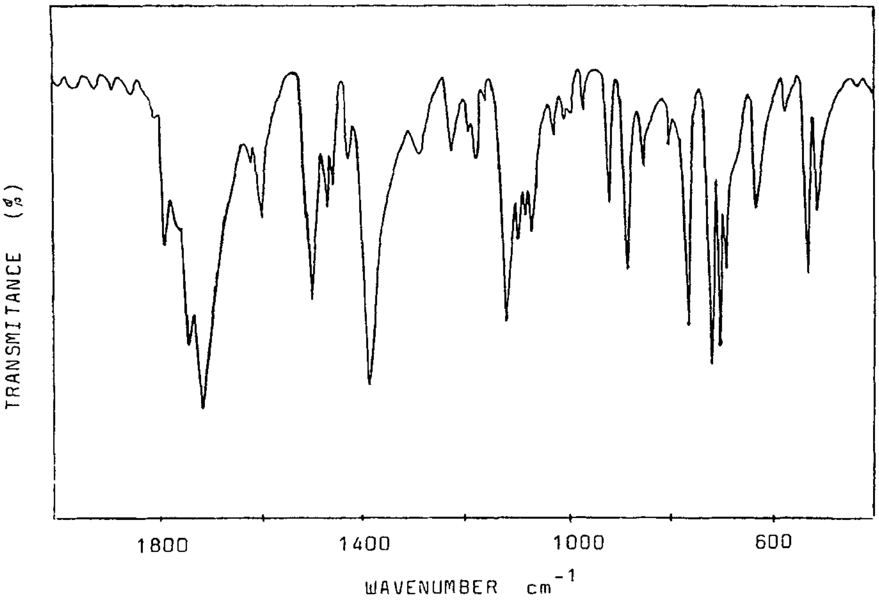

Fig. 1. Infrared spectrum of N-phenylphthalimide in the frequency range 2000–400 cm^{-1} , contained in KBr pellet.

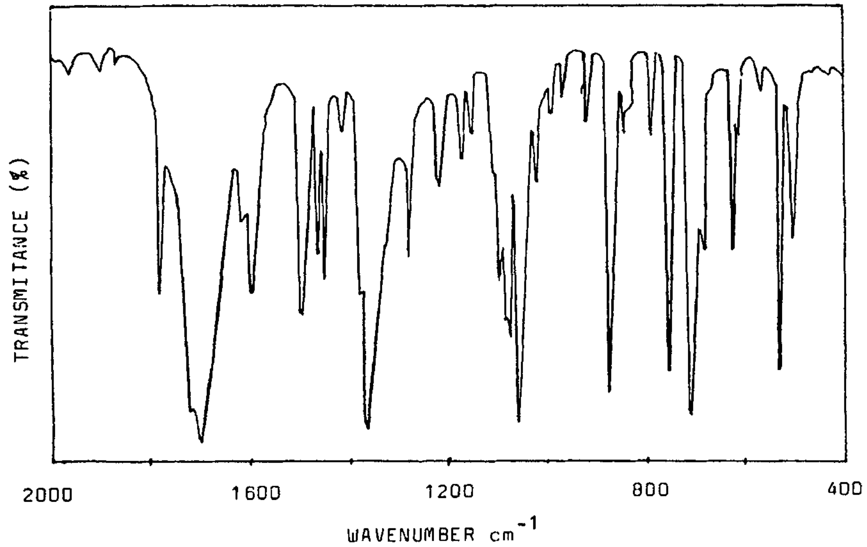

Fig. 2. Infrared spectrum of ^{15}N–phenylphthalimide in the frequency range 2000–400 cm^{-1} , contained in KBr pellet.

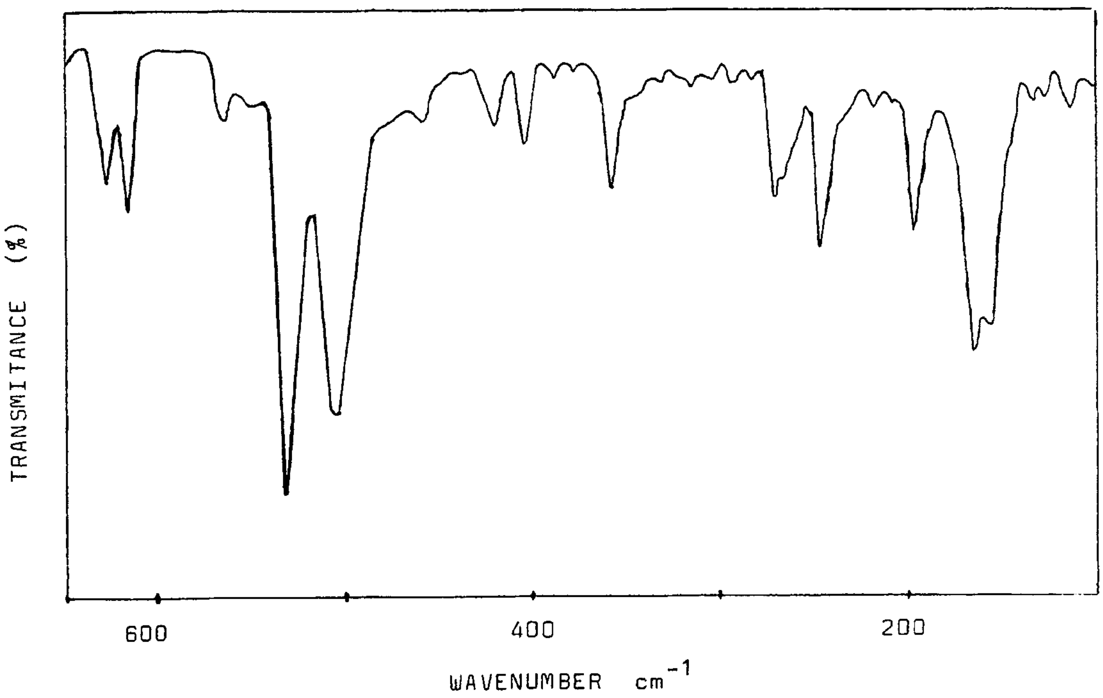

Fig. 3. Far infrared spectrum of N–phenylphthalimide in the frequency region 650–100 cm^{-1} . Polyethylene pellet.

nary assignment used as the basis of a normal coordinate analysis which is in progress.

EXPERIMENTAL

N-Phenylphthalimide was obtained by standard method [9] from phthalic anhydride and aniline in a glacial acetic acid. The product was purified by multifold recrystallization from acetic acid and finally from anhydrous ethanol (mp: 217-217.5°C). The preparation of ^{15}N-phenylphthalimide was carried out according to ref. 5. from phthalic anhydride and aniline-^{15}N (97.2 at. % enrichment ^{15}N). The compound was purified by the same procedure as N-phenylphthalimide.

The mid-infrared spectra of the powder in KBr pellets were recorded on a Bruker IFS-113v FTIR spectrometer equipped with a high-intensity Globar source, Ge/KBr beam splitter and DTGS detector in the 2000-400 cm^{-1} region (Figs. 1,2). The far-infrared spectra were recorded as a polyethylene pellets on the same spectrometer equipped with a high-pressure Hg arc lamp, a Mylar beam splitter and DTGS detector in the 650-100 cm^{-1} region (Figs. 3,4). All spectra were recorded at room temperature at a resolution 1 cm^{-1} with 100 scans.

The Raman spectra of the polycrystalline powder were recorded on a Coderg Model T800 spectrometer at room temperature in the 4000-50 cm^{-1} frequency range (Figs.5,6) using 514.5-nm argon ion laser exitation.

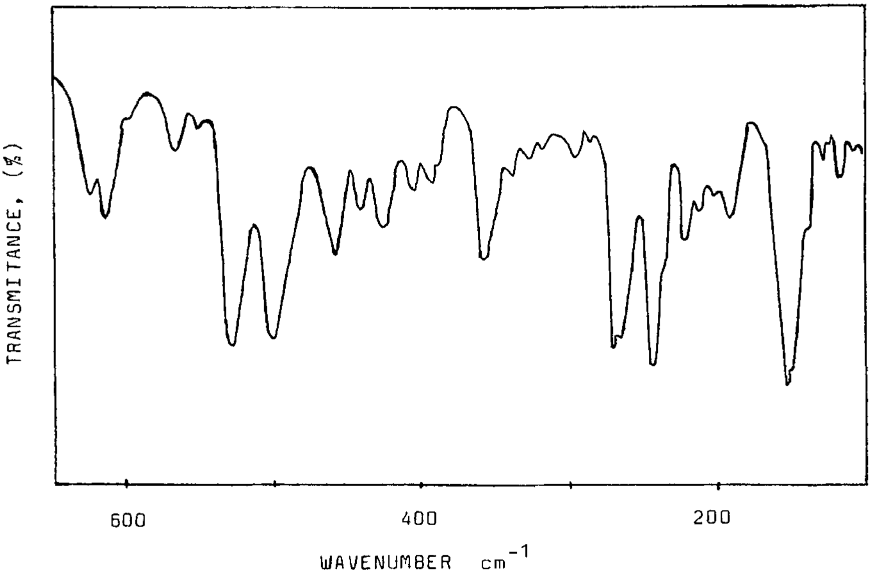

Fig. 4. Far infrared spectrum of ^{15}N-phenylphthalimide in the frequency rergion 650-100 cm^{-1} . Polyethylene pellet.

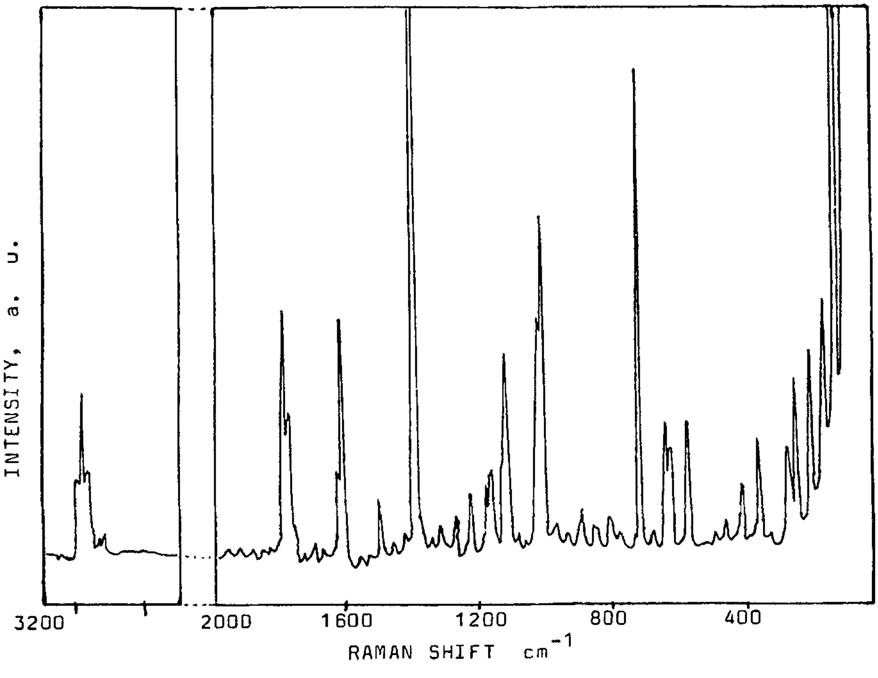

Fig. 5. Raman spectrum of polycrystalline N-phenylphthalimide in the 2000-50 cm^{-1} frequency range.

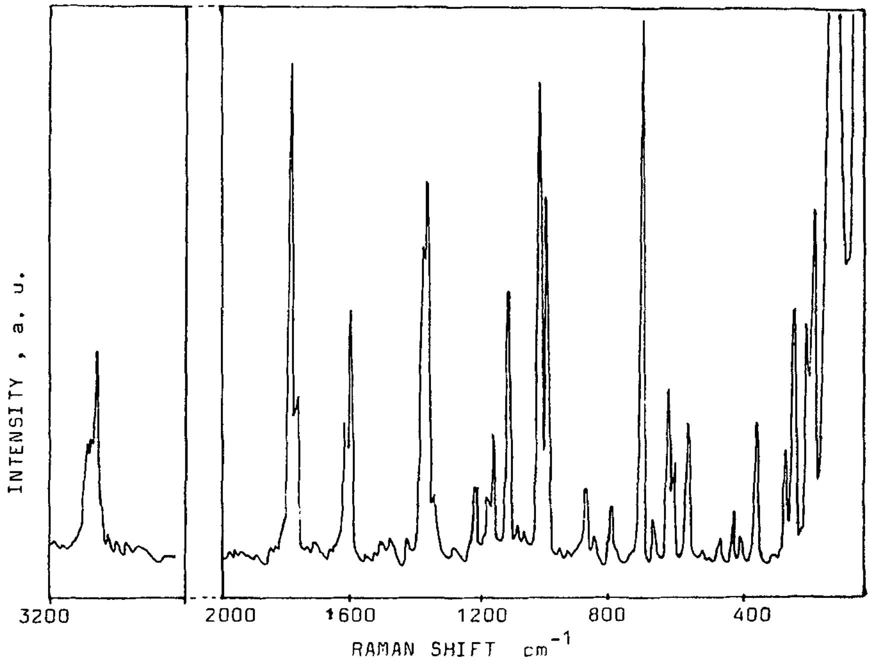

Fig. 6. Raman spectrum of polycrystalline ^{15}N–phenylphthalimide in the 2000–50 cm^{-1} frequency range.

RESULTS AND DISCUSSION

The observed bands and their assignments are given in Table 1. The assignment of the vibrational spectra of the N-phenylphthalimide (NPPI) was done on the assumption of a C_1 molecular symmetry. For nomenclature of the normal mode of vibration, a substituted benzene in ortho position was considered, while the Wilson nomenclature was maintained for the benzene ring vibrations. On the other hand, for substituent vibrations (imidic cycle) the symbols ν(cycle),δ(cycle) and γ(cycle) were used, exept for those vibrations

Table 1. Vibrational assignment of N-phenylphthalimide and ^{15}N-phenylphthalimide

ν_i cm^{-1}	N–phenylphthalimide		^{15}N–phenylphthalimide		Assignment
	Infrared	Raman	Infrared	Raman	
1	3096	3097	3096	3096	2 (pt)
2	3091		3092		20a (ph)
3	3084	3081	3087	3083	7b (pt)
4	3074	3074	3074	3075	20a (ph)
5	3071	3070	3071	3069	7b (pt)
6	3056	3052	3056	3052	2 (ph)
7	3050	3052	3050	3052	20b (pt)
8	3032	3038	3033	3037	7a (ph)
9	3012	3009	3011	3008	13 (ph)
10	1779	1783	1780	1781	$\nu^{sym}_{C=O}$
11	1735	1766		1762	Ferm. res.
12	1707		1702		$\nu^{as}_{C=O}$
13	1614	1616	1615	1615	8a (pt)
14	1608	1605	1605	1603	8a (ph)
15	1594		1594		8b (pt)

Table 1. (continued)

	N-phenylphthalimide		^{15}N-phenylphthalimide		
ν_i cm^{-1}	Infrared	Raman	Infrared	Raman	Assignment
16	1590		1589		8b (ph)
17	1501	1500			19a (pt)
18	1495	1496	1501		19a (ph)
19	1465	1469	1467	1470	19b (pt)
20	1453	1454	1453	1456	19b (ph)
21	1422	1425	1416	1421	14 (pt)
22	1385	1393	1361	1377	ν(cycle) - $\nu^{as}_{N-C(O)}$
23	1284	1279	1284		ν(cycle) - $\nu^{sym}_{C-C(O)}$
24	1219	1222	1217	1222	ν(cycle) - $\nu^{sym}_{N-C(O)}$
25	1209		1209		comb.
26	1185		1170	1181	ν(cycle)
27	1174	1176			9a (ph)
28	1170	1164		1165	9a (pt)
29	1157sh		1157		9b (ph)
30	1117	1119	1060		ν_{N-Ph}

(continued)

Table 1. (continued)

	N-phenylphthalimide		^{15}N-phenylphthalimide		
ν_i cm^{-1}	Infrared	Raman	Infrared	Raman	Assignment
31	1096	1097	1100		18a (pt)
32	1079		1079		15 (ph)
33	1067	1067	ovlp	ovlp	9b (pt)
34	1025	1020	1025	1023	18b (ph)
35	1002	1009		1005	1 (breathing)
36	993	995	994		5 (ph)
37	967		968		17a (ph)
38	916	915	921		d
39	881		876	882	10a (ph)
40	848		842	842	δ(cycle)
41	837	831	837	830	δ(C=O)
42	829		829sh	805	11 (ph)
43	795	796	790	790	10a (pt)
44	761		755		d_1
45	717	713	713	711	12 (pt)

Table 1. (continued)

	N-phenylphthalimide		^{15}N-phenylphthalimide		
ν_i cm^{-1}	Infrared	Raman	Infrared	Raman	Assignment
46	703	702	703	703	4 (ph)
47	690	690	688		δ(C=O)
48	667		677	672	6a (ph)
49	626	636	624	631	6a (pt)
50		623		619	comb.?
51	616		614		6b (ph)
52	567	576	565	571	γ(C=O)
53	531		528		16a
54	508		504		16a (pt)
55	463		456		comb.
56	423	423	424	423	16b
57	407	411			16b
58	391		392		17b
59	379		379		δ (cycle)
60	273	272	272	272	δ (cycle)

(continued)

Table 1. (continued)

ν_i cm^{-1}	N-phenylphthalimide Infrared	N-phenylphthalimide Raman	^{15}N-phenylphthalimide Infrared	^{15}N-phenylphthalimide Raman	Assignment
61	247	251	242	248	δ (cycle)
62	197	206	190	186	γ ph-ring
63	165	167	159		γ (cycle)
64	153		149		γ (cycle)
65	127		128	123	τ(Ph-N)
66	116	116	109	109	latt. vibr.
67		83		83	latt. vibr.
68		53		52	latt. vibr.

which correspond to the C=O and N-Ph groups, for which ν(X), δ(X) and γ(X), with X=CO, N-Ph were used. The nomenclature of Kohlrausch and Pongratz [10] further developed by Datin and Lebas [11], La Lau and Snyder [12], is also used here for description of the vibrational modes of monosubstituted benzene ring. The new spectral information includes the Raman and IR data for ^{15}NPPI, and Raman data for NPPI

Briefly, to simplify the interpretation of these complex vibrational spectra, the vibrations can be divided into three groups: phenyl ring vibrations(Ph), vibrations of the imidic cycle and ortho-phenylene ring vibrations(Pt).

C–H STRETCHING VIBRATIONS

In the 3200–3000 cm^{-1} region 9 frequencies were expected: 5 frequencies belonging to the ν(C–H)phenyl ring vibrations and 4 belonging to the ortho-substituted benzene ring. All 9 frequencies were assigned to the corresponding ν(C–H) vibrational modes. Arenas et al. [13] attributed the IR bands at 3095, 3085 and 3050 cm^{-1} and the Raman bands at 3096,3080 and 3052 cm^{-1} to the 2, 7b and 20b stretching vibrations of phthalimide. The same authors found that ^{15}N substitution influenced the band at 3061 cm^{-1} isotopic shift: 11.8 cm^{-1} They observed the band at 3071 cm^{-1} corresponding to the 20a normal mode only in IR of phthalimide. We observed this band at 3071 cm^{-1} in IR and 3070 cm^{-1} in Raman for the NPPI and at 3071 cm^{-1} and 3069 cm^{-1} for the ^{15}NPPI. Evans [15] atributed the bands at 3094, 3074, 3050, 3040 and 3013 cm^{-1} (IR) to the 5 stretching vibrations of the aniline molecule. We found these bands at nearly the same positions. The isotopic substitution with ^{15}N practically do not affect C–H stretching bands (see Table 1).

RING VIBRATIONS

Arenas et al [13] studied the spectra of three isotopomers of the phthalimide molecule, but their explanation given for the bands at 1800-1700 cm^{-1} both found in the infrared and Raman spectra is probably not sufficient. These authors consider a system of four oscillators C=O with a centrosymmetric structure in which two oscillators are not perturbated by the formation of hydrogen bonds. Nevertheless in the case of NPPI and ^{15}NPPI there is no possibility to form the hydrogen bond we observed nearly the same spectral picture: three bands at 1780, 1735 and 1707 cm^{-1} in IR and two bands at 1783 and 1766 cm^{-1} in Raman. Hence the hydrogen bonding could not cause this splitting. The asymmetric C=O stretching vibration in IR was seen with strong relative intensity in all phthalic derivatives as was also observed for phthalic anhydride [16] . However, the C=O frequency in the NPPI compounds was lower compared with phthalic anhydride, indicating a weaker conjugation between the C=O bands. The higher frequency band at 1780 cm^{-1} (IR) and 1783 cm^{-1} (Raman) was assigned to the symmetric C=O stretching vibration. The lower frequency at 1707 cm^{-1} only IR active, was atributted the antisymmetric vibration of the two C=O groups. The second IR band at 1735 cm^{-1} also only IR active was interpreted as Fermi resonance according to to the assignment of Fayat and Foucaud [5].

The ^{15}N substitution prominently influences only the characteristic vibrations connected with the imidic cycle. The strong IR band at 1385 cm^{-1} underwent 24 cm^{-1} isotopic shift. In the Raman spectrum we observed the corresponding band at 1393 cm^{-1} . In the spectrum of labelled molecule this band splits in two components at 1377 and 1368 cm^{-1} . The C–C(O) stretching band apears at 1284 cm^{-1} (IR) and 1279 cm^{-1} (Raman) and is practically out of isotopic substitution influence in the isotopic derivative. The other ^{15}N substitution sensitive vibration is found at 1185 cm^{-1} (IR) while the Raman one is not observable. The isotopic shift is 15 cm^{-1} . This frequency is assigned to ν(N–C=O) of the imidic cycle. The ν(N–Ph) is found at 1117 cm^{-1} (IR). The isotopic shift (57 cm^{-1}) confirms the band assignment. The frequency lowering of this vibration in comparison with the aniline molecule was explaned with a decrease of conjugation of the free electron pair of N atom and phenyl ring because the dihedral angle between the imidic cycle and phenyl ring is 58° [17]. Hence the assignment of the bands at 1388 and 1376 cm^{-1} reported in [13] is revised here. The band at about 1388 cm^{-1} previously assigned as 19a [13] is most probably imidic cycle vibration.

In the 1600-1300 cm^{-1} region lie the stretching vibratuin of benzene rings: mono- and disubstituted one. The vibtations 8a, 8b, 19a, 19b and 14 are not influenced by the isotopic substitution and were assigned on the basis of the apearence intervals given by Varsanyi [18] for substituted derivatives in ortho position and by other authors [11–13] for monosubstituted benzenes. The assignment reported in ref. 14 for C–C stretching vibration of perylene tetracarboxylic diphenyl-diimide is in accordance with our observations but only the assignment of the band at 1376 cm^{-1} is reassigned here.

The bands belonging to the the breathing vibrations were found at 1002 cm^{-1} (IR) and 1009 cm^{-1} (Raman) for phenyl ring and at 795 cm^{-1} (IR) and 796 cm^{-1} (Raman) for ortho disubstituted ring. The remaining ring deformation vibrations namely 6a, 6b, 4 and 16a are found in the frequency interval estabblished by Varsanyi [18] and other authors [11,12].

C-H IN-PLANE-DEFORMATION VIBRATIONS

The C-H in-plane bendings are found in 1180-1020 cm^{-1} frequency region. The frequencies corresponding to the normal vibration 3 was not found. Most probably it is overlapped by the strong and broad bands of the imidic cycle. The bands at 1174, 1096 and 1079 cm^{-1} were assigned to the 9b, 15 and 18b vibrational motion according to Wilson's nomenclature, which do not show any shifts with the isotopic substitution. The bands at 1170, 1157, 1067 and 1025 cm^{-1} were attributed to the 9a, 9b, 18a and 18b modes arising from the monosubstituted benzene ring.

C-H OUT-OF-PLANE-DEFORMATION VIBRATIONS

As it is known these vibration cover relative large region of 995-720 cm^{-1} . In this region some deformations of imidic cycle also appear as well as those involving the C=O bonds. Of the four out-of-plane vibrational modes γ(C-H) belonging to the phthaloyl ring only two could be assigned: the 11 vibration to the band at 717 cm^{-1} (IR) and 713 cm^{-1} (Raman) and 10a to the 975 cm^{-1}.

The bands are insensitive to the isotopic substitution. The two remaining modes are only active in the Raman spectra, and they have not been observed, probably because of the weak intensity with which they are recorded (ortho-benzene derivatives). The phenyl ring posesses 5 C-H out-of-plane-vibration. The bands at 993, 967, 916, 881 and 829 cm^{-1} were assigned to 5, 17a, 17b, 10a and 11 modes.

X-SENSITIVE VIBRATIONS

The X-sensitive vibration e [10,11] is associated with stretching motions of the C atom of phenyl ring towards the N atom of imidic cycle. We assign the strong IR band at 1117 cm^{-1} to the mass sensitive vibration e on the basis of the isotopic shift 57 cm^{-1} . The great lowering of the ν(N-Ph) could be explained with the conjugation lowering between the free electron pair of the N-atom with imidic cycle and the phenyl ring in comparison with the aniline molecule [15]. In this way the C-N bond order decreases and ν(C-N) decreses also. This suggestion was confirmed by the X-ray determination for the NPPI molecule [17]. It was not easy to find the position of the C-N in-plane-deformation band. One can suppose in advance that it should appear at a frequency lower than that of aniline [15] due to the lower bond order of this bond. Nevertheless the assignment of this vibration is arbitrary.

The bands below 390 cm^{-1} are connected with the in-plane- and out-of-plane vibrations of the two benzene rings an the imidic cycle. Some lattice vibrations could be also present e.g. below 150 cm^{-1} which make the assignment not enough reliable.

On the basis of measurements of the infrared and Raman spectra of NPPI and ^{15}NPPI in the solid state we propose the assignment of the observed bands to the internal fundamentals. The assignment shows that the frequency of the N-Ph bond decreases because of lowering of conjugation between N atom electron pair and phenyl ring. The vibration connected with the N atom were assigned and some literature data were corrected. We believe that this assignment may make it possible to provide a more complete interpretation of the molecular motion giving rise to the lattice modes which may help to a better understanding of the molecular and crystal dynamics of NPPI and the corresponding polymers.

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