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The study of the solubility of naphthalene diimides with various bulky flanking substituents in different solvents by UV–vis spectroscopy

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Abstract

A systematic quantitative study of the solubility of various naphthalene diimides in apolar and polar solvents with different lipophilicity has been done by means of UV–vis spectroscopy.

It has been found that the most soluble naphthalene diimide derivative is *N*,*N*′-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide.

The conclusion that the introduction of bulky aliphatic substituents is the most appropriate way to improve the solubility of naphthalene diimides has been made.

It has been estimated that, in contrast to the case of bulky alkyl substituents, the introduction of bulky aryl substituents does not increase the naphthalene diimide solubility considerably.

Keywords: Solubility; Naphthalene diimides; UV–vis spectra

1. Introduction

Naphthalene diimides are useful in different branches of science and technology [1]. They are used as optical brighteners, laser dyes, fluorescent labeling systems, conducting materials, metallomacrocycles, intercalators for DNA and models for the photosynthetic reaction center [2–5]. On the other hand, naphthalene diimides are found to form stable anion radicals on reduction during the photooxidation of α-terpinene etc. [6,7].

The challenging problem related to the usage of perylene diimides is their low solubility, because of aggregation.

One of the possible solutions to this solubility problem is chemical modification of the naphthalene diimides—i.e. introduction of flank (flanking) bulky aliphatic and aromatic substituents in order to prevent naphthalene diimide aggregation.

To the best of our knowledge of literature, there are no quantitative data concerning the solubility of various naphthalene diimide derivatives in different solvents.

This work is linked with the synthesis and study of solubility of various substituted naphthalene diimides (Scheme 1) by means of UV–vis spectroscopy. The aim of the present work is to elucidate the link between the

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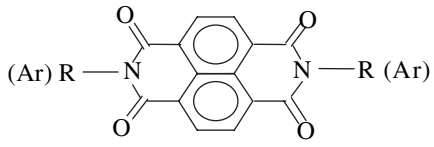

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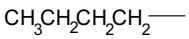
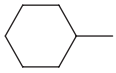
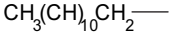
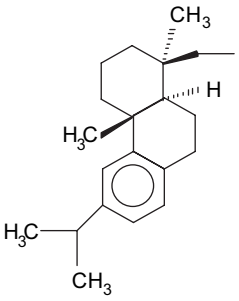
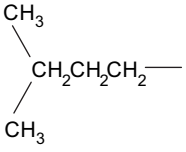
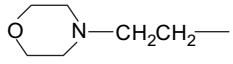
IMD-I n-butyl		IMD-V cyclohexyl	
IMD-II n-dodecyl		IMD-VI dehydroabietyl	
IMD-III isoamyl			
IMD-IV N-(2-ethyl morpholine)			

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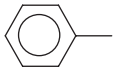
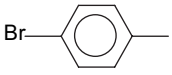
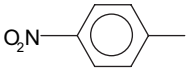
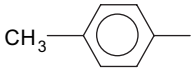
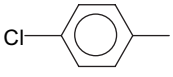
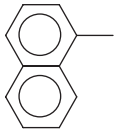
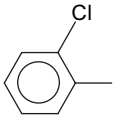
IMD-VII Phenyl		IMD-XI p-bromophenyl	
IMD-VIII p-nitrophenyl		IMD-XII p-toluidine	
IMD-IX p-chlorophenyl		IMD-XIII α- naphthyl	
IMD-X o-chlorophenyl			

Scheme 1.

chemical structure of naphthalene diimide derivatives with various introduced flanking substituents (see Scheme 1) and their solubility.

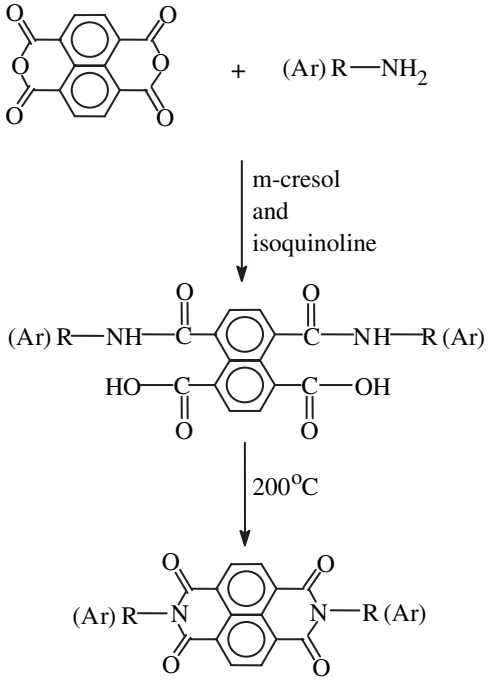
2. Experimental details

2.1. Materials

1,4,5,8-Naphthalene dianhydride, aniline, α-naphthyl amine, *n*-dodecyl amine, *p*-chloroaniline, cyclohexyl amine, *p*-nitroaniline, *p*-toluidine, *n*-butyl amine, *t*-butyl amine, *N*-(2-aminoethyl)-morpholine, dehydroabietyl amine, *o*-chloroaniline, isoamyl amine, and *p*-bromoaniline were obtained from Fluka and Merck, and were used as supplied. All the organic solvents that were used (xylene, toluene, ethylacetate, DMFA, acetonitrile, THF, dichloromethane, chloroform) were of spectrophotometric grade.

2.2. Organic synthesis

Naphthalene *N*,*N*′-disubstituted imides were prepared by the method that was employed for the synthesis of *N*-substituted perylene diimides [7]. Naphthalene diimides were synthesized by condensation of naphthalene 1,4,5,8-tetracarboxylic dianhydride and alkyl (aryl) primary amines (see Scheme 2) in the absence of solvent (*m*-cresol and isoquinoline). Refluxing periods were varied between 15 and 48 h. The temperature was increased gradually. Firstly, an amic acid formed in the reaction. The reaction temperature was nearly 203 °C. Reactants were heated in a 100 ml two-neck flask, fitted with a thermometer and a condenser. It was found that the temperature range and heating period critically affected the yields. The best results were obtained when the reaction temperature was increased to 200 °C gradually from 80 °C. Molecular structures were analyzed by means of IR and proton NMR spectroscopy.



Scheme 2.

2.2.1. *N*,*N*′-bis-alkyl derivatives of 1,4,5,8-naphthalene diimide (*I–VI*)

All of the *N*-alkyl derivatives of naphthalene diimides (I–VI) have been synthesized by a procedure analogous to that used for the synthesis of *N*,*N*′-bis-*n*-butyl-1,4,5,8-naphthalene diimide (**I**).

The procedure used for synthesis of *N*,*N*′-bis-*n*-butyl-1,4,5,8-naphthalene diimide (**I**): a mixture of 1,4,5,8-naphthalene dianhydride (1 g, 3.75 mmol) and *n*-butyl amine (0.7 g, 10 mmol) was dissolved in 20 ml *m*-cresol and a few drops of isoquinoline were added. The temperature was gradually increased to 160 °C. The mixture was kept at this temperature for 6 h under nitrogen. The viscous solution was diluted with 20 ml *m*-cresol and poured slowly into 50 ml of methanol while stirring. The precipitate was filtered and washed thoroughly with warm acetone. The crude product was purified by column chromatography, using dichloromethane as eluent. *N*,*N*′-bis-*n*-butyl-l,4,5,8-naphthalene diimide (**VIII**), $C_{22}H_{22}N_2O_4$, MW: 378.4 g/mol, was obtained in 0.46 g, 32% yield.

The following *N*-alkyl derivatives of naphthalene diimides (**I–VI**) have been synthesized.

N,N′-bis(n-butyl)-1,4,5,8-naphthalene diimide (**I**): as needle-orange crystals (32%); mp >300 °C; IR (KBR): 2950, 1700, 1650, 1580, 1452, 1381, 1250, 1180, 1080, 990, 880, 750; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.76 (4H, s), 4.20 (4H, t), 1.74 (4H, m), 1.46 (4H, m).

N,N′-bis(n-dodecyl)-1,4,5,8-naphthalene diimide (**II**): as white crystals (60%); mp >300 °C; IR (KBR): 2955, 2922, 2848, 1707, 1648, 1581, 1459, 1379, 1335, 1247, 1080, 967, 889, 725, 608, 566; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.72 (4H, s), 4.16 (4H, t), 1.71 (4H, m), 1.40 (4H, m), 1.33 (4H, m), 1.22 (4H, m), 2.46 (4H, dq), 1.87–1.91 (4H, d^{broad}).

N,N′-bis(isoamyl)-1,4,5,8-naphthalene diimide (**III**): as pink crystals (86%); mp >300 °C; IR (KBR): 2950, 2920, 1700, 1653, 1580, 1450, 1380, 1340, 1262, 1220, 1190, 1150, 1090, 990, 890, 760; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.69 (4H, s), 4.15 (4H, t), 1.68 (2H, m), 1.57 (4H, m), 0.97 (12H, d).

N,N′-bis(N-(2-ethylmorpholine))-1,4,5,8-naphthalene diimide (**IV**): as dark orange-yellow crystals (65%); mp >300 °C; IR (KBR): 2950, 2900, 1710, 1670,

Table 1
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in xylene

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Xylene	2.27	1.4958	*n*-butyl	340	5369	359	7079	380	6962	1.01×10^{-5}
			n-dodecyl	342	3911	360	5140	380	5138	7.4×10^{-6}
			isoamyl	342	7922	359	10,279	379	10,146	1.46×10^{-5}
			2-ethylmorpholine	342	8316	360	10,602	378	10,424	1.50×10^{-5}
			cyclohexyl	342	6578	362	8668	381	8697	1.26×10^{-5}
			dehydroabietyl	342	13,825	362	17,583	381	17,286	2.49×10^{-5}
			phenyl	340	6123	359	7864	377	7258	1.05×10^{-5}
			p-nitrophenyl	–	–	–	–	–	–	–
			p-chlorophenyl	342	1657	360	1982	376	1917	2.8×10^{-6}
			o-chlorophenyl	342	1834	359	2363	376	2262	3.3×10^{-6}
			p-bromophenyl	342	2339	358	2642	377	2679	3.9×10^{-6}
			p-tolyl	342	6968	360	8740	376	8141	1.18×10^{-5}
			α-naphthyl	340	13,480	361	17,530	381	17,290	2.49×10^{-5}

Table 2
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in toluene

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Toluene	2.38	1.4961	*n*-butyl	342	4918	362	7034	382	7507	1.08×10^{-5}
			n-dodecyl	342	4021	362	5665	381	6121	1.08×10^{-5}
			isoamyl	342	8139	361	11,525	380	12,318	1.78×10^{-5}
			2-ethylmorpholine	342	6475	362	9223	381	9677	1.39×10^{-5}
			cyclohexyl	343	11,451	363	17,329	383	18,573	2.68×10^{-5}
			dehydroabietyl	342	13,955	361	22,997	382	26,063	3.76×10^{-5}
			phenyl	342	8089	361	10,966	381	10,958	1.58×10^{-5}
			p-nitrophenyl	–	–	–	–	–	–	–
			p-chlorophenyl	342	2458	362	3095	379	3109	4.5×10^{-6}
			o-chlorophenyl	342	2278	359	3101	379	3146	4.5×10^{-6}
			p-bromophenyl	342	2072	362	2593	379	2614	3.7×10^{-6}
			p-tolyl	342	8706	359	11,871	379	11,291	1.7×10^{-6}
			α-naphthyl	341	7512	359	10,943	379	11,382	1.64×10^{-5}

Table 3
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in chloroform

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Chloroform	4.81	1.4459	*n*-butyl	342	18,000	358	25,800	379	31,600	4.56×10^{-5}
			n-dodecyl	342	7352	359	12,151	380	13,373	1.93×10^{-5}
			isoamyl	342	7858	358	12,692	379	13,174	1.90×10^{-5}
			2-ethylmorpholine	342	8422	359	14,049	380	15,714	2.27×10^{-5}
			cyclohexyl	343	18,570	360	29,552	380	33,159	4.79×10^{-5}
			dehydroabietyl	343	30,210	359	45,667	380	49,229	7.10×10^{-5}
			phenyl	342	15,106	358	24,058	379	24,604	3.55×10^{-5}
			p-nitrophenyl	–	–	–	–	–	–	–
			p-chlorophenyl	342	9037	358	14,084	379	14,088	2.03×10^{-5}
			o-chlorophenyl	341	8234	358	13,114	378	13,720	1.98×10^{-5}
			p-bromophenyl	342	6169	359	9781	379	10,136	1.46×10^{-5}
			p-tolyl	342	14,784	359	24,719	379	26,483	3.82×10^{-5}
			α-naphthyl	341	19,397	358	32,712	379	36,923	5.33×10^{-5}

Table 4
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in ethylacetate

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Ethylacetate	6.02	1.3723	*n*-butyl	340	5510	356	9156	376	10,584	1.53×10^{-5}
			n-dodecyl	340	5342	356	8916	376	10,300	1.54×10^{-5}
			isoamyl	340	5304	356	8824	376	10,050	1.45×10^{-5}
			2-ethylmorpholine	340	5640	356	8776	376	10,117	1.46×10^{-5}
			cyclohexyl	340	5411	357	8726	377	10,095	1.46×10^{-5}
			dehydroabietyl	340	11,063	357	17,100	377	18,439	2.66×10^{-5}
			phenyl	338	7720	355	12,281	375	12,320	1.78×10^{-5}
			p-nitrophenyl	340	2392	356	2936	376	3244	4.7×10^{-6}
			p-chlorophenyl	340	2212	355	3647	375	4167	6.1×10^{-6}
			o-chlorophenyl	338	4214	354	6265	374	6882	9.9×10^{-6}
			p-bromophenyl	338	2994	355	4035	375	4394	6.3×10^{-6}
			p-tolyl	338	5190	355	8125	375	8290	1.19×10^{-5}
			α-naphthyl	337	7497	355	12,251	375	13,272	1.92×10^{-5}

Table 5
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in tetrahydrofuran

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
THF	7.6	1.4076	*n*-butyl	341	10,457	357	17,381	377	19,733	2.85×10^{-5}
			n-dodecyl	340	6506	357	10,738	378	12,189	1.76×10^{-5}
			isoamyl	340	8191	357	13,500	378	14,583	2.11×10^{-5}
			2-ethylmorpholine	340	7180	357	11,729	377	12,301	1.76×10^{-5}
			cyclohexyl	342	9952	358	15,716	378	16,055	2.32×10^{-5}
			dehydroabietyl	342	19,887	358	30,027	378	31,261	4.51×10^{-5}
			phenyl	341	11,502	356	17,874	376	19,106	2.76×10^{-5}
			p-nitrophenyl	340	13,494	357	20,916	377	21,297	3.07×10^{-5}
			p-chlorophenyl	340	2177	357	3216	377	3717	5.4×10^{-6}
			o-chlorophenyl	340	4356	356	7202	376	7939	1.15×10^{-5}
			p-bromophenyl	340	4891	357	7652	377	7941	1.15×10^{-5}
			p-tolyl	340	9655	356	14,940	376	14,853	2.14×10^{-5}
			α-naphthyl	337	17,801	356	31,750	376	34,205	4.94×10^{-5}

Table 6
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in dichloromethane

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Dichloromethane	8.93	1.4242	*n*-butyl	342	14,256	359	25,837	379	32,416	4.68×10^{-5}
			n-dodecyl	341	5479	359	9323	379	11,284	1.63×10^{-5}
			isoamyl	342	6946	359	11,770	379	12,598	1.82×10^{-5}
			2-ethylmorpholine	341	7218	359	12,190	379	13,211	1.91×10^{-5}
			cyclohexyl	342	14,498	360	24,427	381	29,306	4.23×10^{-5}
			dehydroabietyl	342	28,880	359	45,320	381	51,960	7.50×10^{-5}
			phenyl	341	16,764	358	28,656	379	32,776	4.73×10^{-5}
			p-nitrophenyl	341	8285	359	13,503	379	16,651	2.40×10^{-5}
			p-chlorophenyl	341	6743	359	11,075	379	12,124	1.75×10^{-5}
			o-chlorophenyl	341	7795	358	12,657	378	12,754	1.84×10^{-5}
			p-bromophenyl	341	6561	358	10,698	379	11,413	1.64×10^{-5}
			p-tolyl	341	18,019	359	30,988	379	35,265	5.09×10^{-5}
			α-naphthyl	341	23,560	358	42,276	379	49,384	7.12×10^{-5}

Table 7
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in dimethylformamide

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
DMFA	36.7	1.4303	*n*-butyl	342	5819	360	9687	381	11,276	1.63×10^{-5}
			n-dodecyl	342	5633	359	9014	380	10,253	1.48×10^{-5}
			isoamyl	342	7705	359	12,324	379	13,846	1.99×10^{-5}
			2-ethylmorpholine	342	8341	359	13,241	379	14,346	2.07×10^{-5}
			cyclohexyl	342	4814	360	7265	382	8095	1.17×10^{-5}
			dehydroabietyl	343	14,077	361	22,997	382	26,132	3.77×10^{-5}
			phenyl	342	13,156	360	20,890	381	22,780	3.29×10^{-5}
			p-nitrophenyl	342	15,171	359	23,341	379	24,637	3.56×10^{-5}
			p-chlorophenyl	342	8370	359	13,213	379	14,249	2.06×10^{-5}
			o-chlorophenyl	342	9389	358	14,363	378	14,178	2.05×10^{-5}
			p-bromophenyl	342	7040	359	10,948	379	11,248	1.62×10^{-5}
			p-tolyl	342	10,137	359	16,224	379	17,285	2.49×10^{-5}
			α-naphthyl	342	15,577	360	25,447	380	27,398	3.95×10^{-5}

1580, 1470, 1380, 1450, 1200, 1150, 980, 760; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.68 (4H, s), 4.02 (4H, t), 2.91 (4H, t), 2.43 (4H, t), 3.44 (4H, t).

N,N′-bis(cyclohexyl)-1,4,5,8-naphthalene diimide (**V**): as pale yellow crystals (70%); mp >300 °C; IR (KBR): 2950, 1710, 1650, 1570, 1460, 1350, 1240, 1100, 980, 870, 750; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.68 (4H, s), 4.99 (2H, m), 1.74–1.72 (6H, d^{broad}), 1.23–1.48 (6H, m).

N,N′-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide (**VI**): as yellow crystals (67%); mp >300 °C; IR (KBR): 2950, 2900, 2850, 1707, 1666, 1580, 1495, 1380, 1315, 1445, 1245, 1160, 1050, 980, 880, 810, 765; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.78 (4H, s), 7.33 (2H, s), 7.19 (2H, d), 7.03 (2H, d), 4.33 (4H, q), 2.9 (2H, m), 1.4–1.5 (2H, t), 1.4–1.5 (20H, t), 2.8 (12H, s), 1.6 (12H, d).

2.2.2. *N,N′-bis-aryl derivatives of 1,4,5,8-naphthalene diimide (**VII–XIII**)*

All the *N*-aryl derivatives of naphthalene diimide (**VII–XIII**) have been synthesized by a procedure analogous to that used for the synthesis of *N,N′*-bis-phenyl-1,4,5,8-naphthalene diimide (**VII**).

The procedure used for the synthesis of *N,N′*-bis-phenyl-1,4,5,8-naphthalene diimide (**VII**): a mixture of 1,4,5,8-naphthalene dianhydride (1 g, 3.75 mmol) and aniline (0.7 g, 7.5 mmol) was dissolved in 40 ml *m*-cresol and a few drops of isoquinoline were added. The temperature was gradually increased to 200 °C. The mixture was kept at this temperature for 24 h. The viscous solution was poured slowly into 50 ml of stirred acetone. The precipitate was filtered and washed thoroughly with warm acetone. The crude product was re-dissolved in chloroform and poured into acetone and filtered for purification. *N,N′*-bis-phenyl-l,4,5,8-naphthalene diimide (**VII**; PNDI), $C_{24}H_{14}N_2O_4$, MW: 396.4 g/mol, was obtained in 0.92 g, 62% yield.

The following *N*-aryl derivatives of naphthalene diimide (**VII–XIII**) have been synthesized.

N,N′-bis(phenyl)-1,4,5,8-naphthalene diimide (**VII**): as pale pink crystals (62%); mp >340 °C; IR (KBR): 3080, 1711, 1672, 1584, 1496, 1457, 1359, 1252, 1202,

Table 8
UV–vis spectroscopic data (λ/nm and ε/l mol^{-1} cm^{-1}) and solubility (C_x/mol l^{-1}) of NDI in acetonitrile

Solvent	ε	n	R (Ar)	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	C_x
Acetonitrile	37.5	1.3441	*n*-butyl	340	6989	356	11,639	376	12,021	1.74×10^{-5}
			n-dodecyl	338	1099	356	1407	378	1553	2.3×10^{-6}
			isoamyl	340	2275	357	3744	377	4397	6.3×10^{-6}
			2-ethylmorpholine	339	4412	356	7565	376	8773	2.09×10^{-5}
			cyclohexyl	340	8076	357	13,490	377	14,499	6.3×10^{-6}
			dehydroabietyl	340	17,585	357	28,110	378	31,497	4.55×10^{-5}
			phenyl	339	9810	356	16,054	376	15,977	2.31×10^{-5}
			p-nitrophenyl	339	8952	356	14,395	376	16,970	2.45×10^{-5}
			p-chlorophenyl	340	4078	356	6617	376	7391	1.07×10^{-5}
			o-chlorophenyl	338	5280	355	9219	375	10,732	1.55×10^{-5}
			p-bromophenyl	339	3734	356	5123	376	5670	8.2×10^{-6}
			p-tolyl	338	6292	356	10,523	376	11,618	1.68×10^{-5}
			α-naphthyl	340	9058	356	14,707	376	15,179	2.19×10^{-5}

1124, 987, 899, 860, 771, 723, 605, 517; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (4H, s), 7.35 (4H, d), 7.60 (6H, m).

N,N′-bis(p-nitro)-1,4,5,8-naphthalene diimide (**VIII**): as dark yellow crystals (30%); mp >300 °C; IR (KBR): 3090, 1710, 1677, 1570, 1482, 1340, 1250, 1100, 980, 830, 760; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.95 (4H, s), 8.29 (4H, dd), 7.81 (4H, dd).

N,N′-bis(p-chloro)-1,4,5,8-naphthalene diimide (**IX**): as yellow crystals (42%); mp >300 °C; IR (KBR): 1716, 1677, 1602, 1582, 1509, 1453, 1354, 1256, 1224, 1201, 1155, 982, 867, 840, 769, 749, 557, 529, 417; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.95 (4H, s), 7.67 (4H, dd), 7.53 (4H, dd).

N,N′-bis(o-chlorophenyl)-1,4,5,8-naphthalene diimide (**X**): as yellow crystals (64%); mp >320 °C; IR (KBR): 3072, 1718, 1677, 1582, 1478, 1351, 1250, 1151, 1057, 984, 861, 768, 745, 695, 623; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.94 (4H, s), 7.38–7.42 (2H, dd), 7.47–7.57 (4H, m), 7.63–7.67 (2H, dd).

N,N′-bis(p-bromo)-1,4,5,8-naphthalene diimide (**XI**): as dark yellow crystals (40%); mp >300 °C; IR (KBR): 1712, 1680, 1577, 1489, 1447, 1343, 1254, 1195, 1119, 1072, 1012, 850, 826, 767, 742, 512; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.95 (4H, s), 7.41 (4H, dd), 7.43 (4H, dd).

N,N′-bis(p-tolyl)-1,4,5,8-naphthalene diimide (**XII**): as pale orange crystals (70%); mp >300 °C; IR (KBR): 3080, 2950, 1710, 1670, 1581, 1456, 1332, 1252, 1120, 769, 564; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.93 (4H, s), 7.57–7.18 (4H, dd), 2.46 (6H, s).

N,N′-bis(α-naphthyl)-1,4,5,8-naphthalene diimide (**XIII**): as bright-yellow crystals (72%); mp >300 °C; IR (KBR): 3059, 1714, 1675, 1582, 1510, 1446, 1392, 1342, 1249, 1196, 1120, 983, 881, 802, 772, 626, 554, 418; ^{1}H NMR ($CDCl_3$): δ (ppm) 8.91 (4H, s), 7.45–7.77 (10H, m), 8.00–8.08 (4H, d).

2.3. Spectroscopic measurements

Synthesized compounds were analyzed with a Schimadzu IR4570 spectrophotometer for IR spectroscopy, a JASCO V-530 UV–vis spectrophotometer for UV–vis spectroscopy, and a JEOL JNM-GX 400FT 400 MHz NMR for NMR spectroscopy analysis.

3. Results and discussion

UV absorption spectra of naphthalene diimides have shown three characteristic bands at 377, 357 and 340 nm in all the solvents used (Tables 1–8, Fig. 1). The positions of the bands are constant and do not depend on changes in solvent polarity.

Because *N*-aryl (alkyl) substitution does not alter the π-system of the molecules, the molecular extinction coefficients ε for all the compounds have to be the same [8].

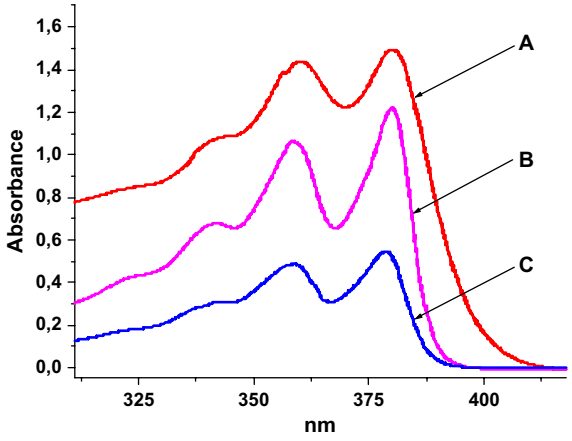


Fig. 1. Absorption spectra of *N,N′*-bis-phenyl-1,4,5,8-naphthalenediimide (**VII**) in: (A) toluene, (B) dichloromethane, (C) acetonitrile.

Moreover, because the positions of absorption bands of all the compounds (the energy gap S_0–S_1) remain constant and do not depend on solvent, the molecular extinction coefficients of all compounds remain the same for all the solvents used.

Knowing that the molecular extinction coefficients are the same for all the studied compounds in all the used solvents, one can evaluate the solubilities quantitatively.

The case where the molecular extinction coefficient was the highest was considered as the case where solute was dissolved entirely (*N,N′*-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide derivative in dichloromethane, ε = 51,960).

All the saturated solution concentrations of the rest of the studied compounds have been calculated on the basis of the above molecular extinction value. The results (the saturated solution concentrations of studied compounds) are presented in Tables 1–8.

Because the studied naphthalene diimides consist of the lipophilic naphthyl group, lipophilic flank substituents and polar carbonyl groups, they could be dissolved in low-polar lipophilic solvents (toluene, xylene, chloroform) and in polar (dichloromethane, acetonitrile, dimethylformamide) solvents.

The polarity of naphthalene diimides remains constant for *N*-alkyl or *N*-aryl substitutions. But, the molecule's "bulkiness" (sterical hindrances for aggregate formation) and the molecule's lipophilicity varies [9]. The experimental results obtained on the solubility of different naphthalene diimide derivatives should be interpreted in terms of the change of the molecular "bulkiness" and the change of the molecular lipophilicity on the substitution.

It is convenient to consider the solubility of the naphthalene diimides on going from less polar solvents to most polar ones. Tables 1 and 2 present data on solubilities of various naphthalene diimides in xylene

(Table 1) and in toluene (Table 2). In these solvents the solubility of the studied compounds is found to be the lowest.

As one could see from Tables 1 and 2, the solubility of *N*-alkyl derivatives decreases on going from *n*-butyl to *n*-dodecyl. This result could be explained by increase of aggregation in case of *n*-dodecyl because of its greater lipophilicity (log P = 23.6) in comparison with *n*-butyl (log P = 9.62).

On going from *n*-dodecyl to dehydroabietyl, the solubility increases monotonically. This is in good accordance with the increase of "bulkiness" of the flanking substituent on going from *n*-dodecyl up to dehydroabietyl, which prevents naphthalene diimide aggregation due to sterical hindrances.

The solubility of *N*-aryl derivatives decreases on going from *N*-phenyl to *N*-*p*-bromophenyl. This could be explained by the increase of lipophilicity on introduction of a lipophilic substituent in flanking phenyl groups. Such increases of lipophilicity cause enhancements in aggregation of the *p*-chlorophenyl, *o*-chlorophenyl, and *p*-bromophenyl derivatives.

On the contrary, the solubility of *p*-tolyl and α-naphthyl derivatives is found to be higher in all of the *N*-alkyl derivatives of naphthalene diimides. This result is in line with the branching nature of *p*-methyl substituent in flanking phenyl groups of the *p*-tolyl derivative and, also, in accordance with the more bulky nature of α-naphthyl in comparison with phenyl ring.

It should be noted that *p*-nitrophenyl derivative containing the rather polar nitro group is insoluble in low-polar solvents xylene and toluene.

The same tendencies in solubility could be noticed on consideration of the rest of the solvents (see Tables 3–8): (i) the solubility increases with the increase of "bulkiness" of the flanking substituent on going from *n*-dodecyl to dehydroabietyl, and (ii) the introduction of bulky aryl substituents does not increase the naphthalene diimide solubility considerably. The difference between low-polar and strongly polar solvents is that in polar solvents, the *p*-nitro derivative becomes more soluble and, in general, the solubility increases with the growth of polarity. The highest solubilities of *N*-alkyl (*N*-aryl) derivatives of naphthalene diimides are observed in dichloromethane (Table 6) and chloroform (Table 3). Such great solubilities of the studied naphthalene diimide derivatives in dichloromethane and chloroform could be explained as resulting from the appropriate combination of high solvent polarity and high solvent lipophilicity in both solvents.

As a result, the solubilities of *N*-alkyl or *N*-aryl derivatives of naphthalene diimides are found to increase in the following order:

$$\text{Xylene} < \text{Toluene} < \text{Ethylacetate} < \text{DMFA} < \text{Acetonitrile} < \text{THF} < CHCl_3 < CH_2Cl_2$$

From the above order, one can see that solvent polarity is a more important factor than lipophilicity to dissolve the studied naphthalene diimides.

In general, the solubility of alkyl-substituted naphthalene diimides exceeds the corresponding solubility of aryl-substituted naphthalene diimides.

4. Conclusions

- A systematic quantitative study of the solubility of various naphthalene diimides in different solvents has been done by means of UV–vis spectroscopy.
- It has been found that the most soluble naphthalene diimide derivative is *N*,*N*′-bis(dehydroabietyl)-1,4,5,8-naphthalene diimide. The conclusion that the introduction of bulky aliphatic substituents is the most appropriate way to improve the solubility of naphthalene diimides in all the solvents studied has been made.
- In contrast to the case of bulky alkyl substituents, the introduction of bulky aryl substituents does not increase the naphthalene diimide solubility considerably. This is because of the fact that despite the effect of bulkiness, which suppresses aggregation and, hence, increases solubility, the increase of solute lipophilicity on aryl substitution favors aggregation, and, thus, tends to decrease solubility.

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