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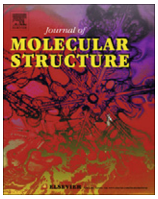

Polyamines. IV. Spectroscopic properties of *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine and supramolecular interactions in its crystals

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ABSTRACT

A new derivative of polyamine, *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine has been synthesized and its structure studied by X-ray diffraction, FTIR, ^{1}H and ^{13}C NMR spectroscopy. The B3LYP and DFT calculations have been carried out. The molecular conformation is folded and stabilized by intramolecular C—H···O interaction. A close similarity to the conformation of *N*,*N*-bis-(phthalimidopropyl)-*N*-propylamine and *N*,*N*-bis-(phthalimidopropyl)-*N*-octylamine has been found. The supramolecular structure is driven by π···π interactions and by weak C—H···O hydrogen bonds. The optimized bond length as well as bond angles for *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine calculated by B3LYP/3-21G approach are compared with the X-ray data. The screening constants for ^{13}C and ^{1}H atoms have been calculated by GIAO/B3LYP/3-21G approach and analyzed. Linear correlation between the experimental ^{1}H and ^{13}C chemical shifts and the computed screening constants have been obtained. Similarly, a linear relationship between the experimental ($\nu_{\mathrm{exp.}}$) and calculated wavenumbers ($\nu_{\mathrm{calc.}}$) for *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine has been obtained.

1. Introduction

Derivatives of 1,8-naphthalenedicarboximide (NDCI, Scheme 1) have been extensively studied in recent decades primarily owing to their interesting photophysical properties. Many NDCI chromophores, characterized by both strong absorption and good fluorescence yields were prepared and used as fluorescent agents [1], azo dyes [2], antitumor [3,4] and antiviral drugs [5]. The NDCI derivatives are also reagents and intermediates in the synthesis of rigid-chain heterocyclic polymers used for preparing various super strength materials possessing special properties (for example – nonlinear optical, photoconducting, electroconducting, etc.) [6–8].

It has been shown that the photophysical properties of 1,8-naphthalimides are governed both, by substituent effects [9–15] as well as by the environment around fluorophore [16–22]. In another words, the solid state photophysical properties of organized NDCI assemblies depend highly on their supramolecular structures.

The NDCI unit is known as a π-electron-deficient ring system and it has been established that intermolecular interactions between π-deficient and π-deficient functionalities are the most favorable [23], thus forming π···π stacking in the supramolecular structures and the NDCI unit has been recognized as a supramolecular synthon [24–29]. Admittedly, hydrogen bonding is a wider used tool in crystal engineering because its directionality and robustness enable facile and reliable transfer from one system to the other. In contrast, π···π stacking is less predictable due to the fact that in the solid state variable orientations of the moieties involved often occur in order to maximize the electrostatic attraction between the σ framework and the π electron density of the stacked groups [23,25,29].

A search of the CSD database (Version 5.31, November, 2009) identified a moderate number of crystal structures incorporating the 1,8-naphthalimide group, altogether 66, a part of them meeting the requirements for a π···π stacking interaction with the dipole vectors which run from the center of the fused aromatic groups through the nitrogen atom of the 1,8-naphthalimide groups (Scheme 1) oriented at 180°. Supramolecular structures of *N*-(3-picolyl)-, *N*-(4-picolyl)- or *N*,*N*-(benzyl)-derivatives of 1,8-naphthalimide are good examples [29]. The π···π stacking of 1,8-naphthalimide units with a head-to-tail disposition of the dipole vectors is maintained in the structures of rhenium complexes with bidentate *bis*-(pyrazolyl)-methane ligands [24].

In conclusion, 1,8-naphthalimide is a reliable, robust supramolecular synthon that can be transferred from one system to another and we have been aiming to report here the synthesis and struc-

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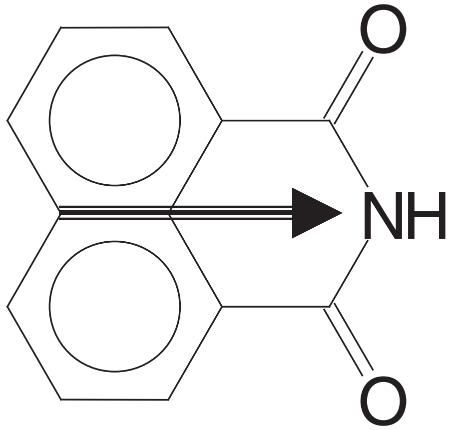

Scheme 1. 1,8-Naphthalimide group, the arrow shows the dipole moment of the naphthalimide moiety.

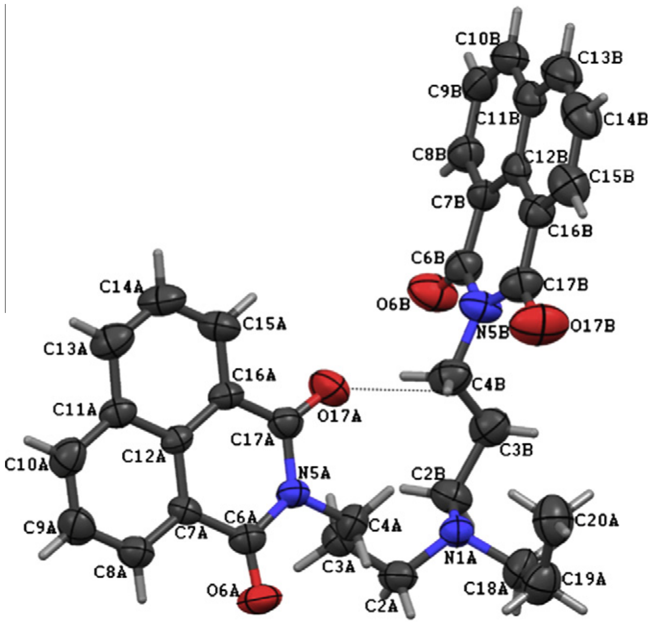

Fig. 1. A perspective view of the molecule of *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine (**1**) together with the atom numbering scheme.

ture, both in solid and liquid states of *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine, hereafter (**1**). In this molecule two naphthalimide units are joined through a flexible tertiary amine linker (Fig. 1). One can anticipate that the supramolecular structure should be directed by concerted π· · ·π interactions and the C—H· · ·O weak hydrogen bonds between molecules of (**1**).

2. Experimental

2.1. Synthesis

N,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine (**1**) was prepared by reaction of 1,8-naphthalic anhydride with *N*,*N*-bis-(3-aminopropyl)-*N*-propylamine. The mixture of 0.510 g (2.94 mmol) *N*,*N*-bis-(3-aminopropyl)-*N*-propylamine in 10 ml of absolute ethanol was added dropwise during 10 min. to continuously stirred suspension of 1.166 g (5.88 mmol) 1,8-naphthalic anhydride in 20 ml absolute ethanol. The mixture was stirred at room temperature for 24 h. The precipitated solid was filtered off, washed with diethyl ether, dried and crystallized from acetonitrile. The product was obtained as bright, amber crystals. Yield 78%. M.p. 141–142 °C. Elemental analysis: calc. C, 74.28%; H, 5.86%; N, 7.87%. Found: (C, 74.04%; H, 5.88%; N, 8.09%).

Table 1
Crystal data, data collection and structure refinement for (**1**).

Compound	(**1**)
Empirical formula	$C_{33}H_{31}N_3O_4$
Formula weight	533.61
T (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	
a (Å)	8.6780(6)
b (Å)	21.434(2)
c (Å)	14.6194(9)
β (°)	98.114(6)
Volume (Å^3)	2692.0(3)
Z, D_x (Mg/m^3)	4, 1.317
μ (mm^{-1})	0.087
F(0 0 0)	1128
θ Range for data collection (°)	4.08–26.37
hkl range	$-10 \leqslant h \leqslant 9$ $-26 \leqslant k \leqslant 26$ $-18 \leqslant l \leqslant 18$
Reflections	
Collected	31,725
Unique (R_{int})	5487 (0.139)
Observed ($I > 2\sigma(I)$)	1539
Data/restraints/parameters	5487/0/362
Absorption correction	Multi-scan
Goodness-of-fit on F^2	0.832
$R(F)$ ($I > 2\sigma(I)$)	0.0429
$wR(F^2)$ (all data)	0.1022
Max/min Δρ (e/Å^3)	0.165/−0.164

Table 2
Hydrogen bonding geometry (Å and °) for (**1**).

D—H· · ·A	*d* (D—H)	*d* (H· · ·A)	*d* (D· · ·A)	<(DHA)
C(4B)—H(4C)· · ·O(17A)	0.97	3.11	3.825(4)	132
C(8A)—H(8A)· · ·O(17A)^a	0.93	2.65	3.267(4)	124
C(9A)—H(9A)· · ·O(17A)^a	0.93	2.65	3.259(4)	124
C(3A)—H(3A)· · ·O(6B)^a	0.97	2.67	3.577(4)	156
C(14A)—H(14A)· · ·O(6A)^b	0.93	2.52	3.282(4)	139
C(9B)—H(9B)· · ·O(6A)^c	0.93	2.59	3.464(4)	156

Symmetry codes:
[a] *x* – ½, –*y* + ½, *z* – ½.
[b] *x* – ½, –*y* + ½, *z* + ½.
[c] *x* + 1, *y*, *z* + 1.

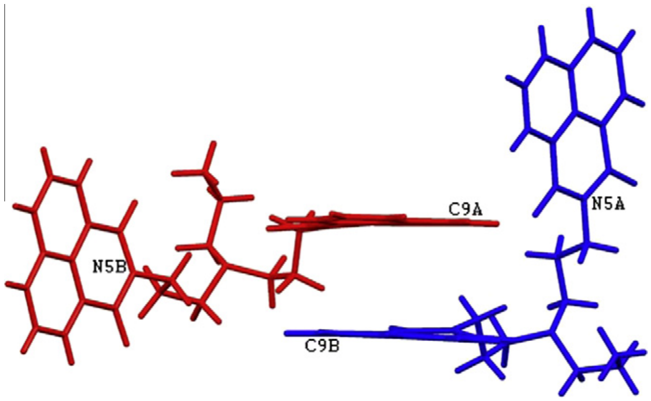

Fig. 2. The dimeric self-association of the molecules of *N*,*N*-bis-(1,8-naphthalenedicarboximidopropyl)-*N*-propylamine (**1**).