Zeitschrift für Kristallographie

International journal for
structural, physical, and chemical
aspects of crystalline materials

R. Oldenbourg Verlag
München

Zeitschrift für Kristallographie 210, 760–765

Crystal and molecular structure of *N*-phenyl substituted 1,2-, 2,3- and 1,8-naphthalimides

Y. Dromzée*

Université Pierre et Marie Curie, URA 419, Laboratoire de Chimie des Métaux de Transition, Boite 42, 4 place Jussieu, F-75252-Paris Cedex 05, France

J. Kossanyi, V. Wintgens, P. Valat

CNRS, Laboratoire des Matériaux Moléculaires, 2–8, rue H. Dunant, F-94320-Thiais, France

L. Biczók, A. Demeter and T. Bérces

Hungarian Academy of Science, Central Research Institute for Chemistry, Pusztaszeri út 59/67, 1025-Budapest, Hungary

Received October 18, 1994; accepted March 27, 1995

Crystal structure / N-phenyl naphthalimides / Conformation / Spectroscopic properties in the solid state

Abstract. The three structures were solved by direct methods and refined by full-matrix least-squares procedure. 2-phenyl-1 *H*-benz[*f*]isoindole-1,3(2 *H*)-dione, (compound **1**): orthorhombic, space group *Pcab*, $a = 7.618(1)$ Å, $b = 11.717(2)$ Å, $c = 28.540(4)$ Å, $V = 2547.4(7)$ Å^3, $Z = 8$ and $d = 1.425$ Mg m^{-3}, $R = 0.038$ ($Rw = 0.038$) for 190 parameters and 820 observations with $I > 2.5\sigma(I)$. 2-phenyl-1 *H*-benz[*e*]isoindole-1,3(2 *H*)-dione (compound **2**): orthorhombic, space group $Pc2_1b$, $a = 6.7042(9)$ Å, $b = 7.4589(9)$ Å, $c = 26.441(7)$ Å, $V = 1322.4(4)$ Å^3, $Z = 4$ and $d = 1.373$ Mg m^{-3}, $R = 0.037$ ($Rw = 0.032$) for 190 parameters and 1186 observations with $I > 3\sigma(I)$. 2-phenyl-1 *H*-benz[*de*]isoquinoline-1,3(2 *H*)-dione (compound **3**): monoclinic, space group $C2/c$, $a = 13.501(3)$ Å, $b = 13.212(4)$ Å, $c = 8.305(2)$ Å, $\beta = 116.24(2)°$, $V = 1329(9)$ Å^3, $Z = 4$, and $d = 1.366$ Mg m^{-3}, $R = 0.038$ ($Rw = 0.033$) for 71 parameters and 754 observations with $I > 3\sigma(I)$.

The plane of the *N*-phenyl substituent has an axis which lies in the plane of the naphthalimide part and passes by the carbon atom bound to the nitrogen atom and by the carbon in para position. It makes a dihedral angle with the plane of the naphthalimide moiety of 59.2°, 46.5° and 69.4° for the compounds **1**, **2** and **3** respectively. This difference in geometry between the three molecules brings new insights into their spectroscopic properties.

* Correspondence author

Introduction

The spectral behavior of the *N*-alkyl naphthalimides is strongly dependent on where the dicarboximide function is attached to the naphthalene nucleus. When bound to positions 1 and 2, the molecule shows (Wintgens, Valat, Kossanyi, Biczók, Demeter, Bérces, 1994) a long-lived excited singlet state (τ of the order of 60 nanoseconds) while in positions 2,3 the singlet lifetime drops to ca. 8 nanoseconds, and to the order of 100 picoseconds when the dicarboximide group is fixed at the 1,8-positions on the naphthalene ring.

Substitution of the *N*-alkyl group by a phenyl nucleus modifies strongly these data and all three types of naphthalimides show now singlet lifetimes shorter than 30 picoseconds. In addition, 2-phenyl-1 *H*-benz[*f*]isoindole-1,3(2 *H*)-dione **1** presents a dual fluorescence, one around 380 nm exactly at the same spectral position than its *N*-methyl homologue, and the other shifted to the red by ca. 100 nanometers (Valat, Wintgens, Kossanyi, Biczók, Demeter, Bérces, 1992). Decreasing the temperature of the medium shows that the fluorescence found below the solvent glass transition temperature is only the one at short wavelengths.

Such dual fluorescence could have two origins, both being related to the rotation of the phenyl group bound to the dicarboximide nitrogen atom. The short-wavelength emission could be attributed to a structure in which the *N*-phenyl substituent is either in the same plane as, or in a plane orthogonal to the naphthalimide moiety, while the long-wavelength emission would then originate from the orthogonal or the coplanar structure, respectively:

– in the former case, the phenomena would be attributed to a TICT (twisted intramolecular charge transfer)-type phenomena which has received quite an important attention from several groups (Grabowski,

Rotkiewicz, Siemarczuk, Cowley, Baumann, 1979; Herbich, Dobkowski, Rullière, Nowacki, 1989; Lipinski, Chojnacki, Grabowski, Rotkiewicz, 1980; Lippert, Rettig, Bonacic-Koutecky, Heisel, Miehé, 1987; Meech Phillips, 1985; Rettig, 1982; Rettig, 1986), and which has been proposed as a potential electronic device for molecular electronics (Launay, 1989; Warman, Shuddeboom, Jonker, de Haas, Paddon-Row, Zachariasse, Launay, 1993) using an external perturbation to be switched "on" and "off";

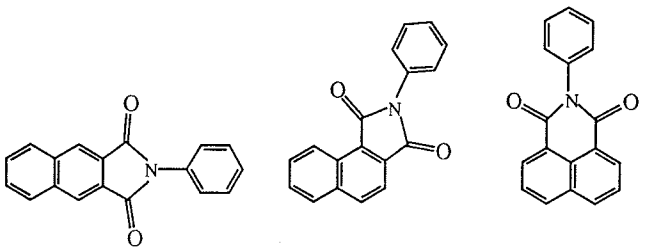
– in the latter case, the short-wavelength emitting species would have an orthogonal structure while the long-wavelength emission would correspond to a planar structure in which a complete electron delocalization could occur. In both cases, slowing down the rotation of the phenyl group by decreasing the temperature limits the emission to originate from the conformation which has the same geometry as the ground state. But this still leaves open the question of the structure of the latter.

An additional information is obtained by introducing an *ortho*-tertiobutyl substituent on the *N*-phenyl group. Such a bulky substitution blocks the rotation of the phenyl group and favors a conformation in which this phenyl is orthogonal to the naphthalene ring. In such a case, the ground state of the molecule would have a geometry in which the plane of the two moieties, the naphthalimide on one hand, and the phenyl substituent on the other hand, are orthogonal to each other. Then, the geometry of the excited molecule would be similar to that of the ground state and, therefore, the two emissions of molecule **1** could be attributed to specific structures. That only the short-wavelength emission is found for **1** with the *o*-tertiobutyl-substituted *N*-phenyl group (Valat, Wintgens, Kossanyi, Biczók, Demeter, Bérces, 1992), is a good indication of the orthogonal position of the two moieties of the molecule. Compound **2** emits only weakly in the long-wavelength region, while **3**, which shows also only a weak fluorescence band emits now in the short-wavelengths region. Consequently, the X-ray analysis should confirm the ground state geometry of molecule **1**. At the same time, analysis of the three substituted naphthalimides would bring information which could help understanding the high discrepancy found in the spectroscopic properties among molecules **1**, **2** and **3**.

Experimental part

Preparation of the products

2-phenyl-1 *H*-benz[*f*]isoindole-1,3(2 *H*)-dione, **1** (further named *N*-phenyl-2,3-naphthalimide), 2-phenyl-1 *H*-benz-[*e*]isoindole-1,3(2 *H*)-dione **2** (further designated as *N*-phenyl-1,2-naphthalimide) and 2-phenyl-1 *H*-benz[*de*]isoquinoline-1,3(2 *H*)-dione, **3** (further named *N*-phenyl-1,8-naphthalimide) were prepared by refluxing a mixture of



1 **2** **3**

Table 1. Crystal data (293 K).

	Compound **1**	Compound **2**	Compound **3**
formula	$C_{18}H_{11}NO_2$	$C_{18}H_{11}NO_2$	$C_{18}H_{11}NO_2$
colloquial name	2,3-NI	1,2-NI	1,8-NI
fw (a.m.u.)	273.3	273.3	273.3
system	orthorhombic	orthorhombic	monoclinic
space group; *Z*	*Pcab* (N° 61); 8	$Pc2_1b$ (N° 29); 4	*C2/c* (N° 15); 4
a, (Å)	7.618(1)	6.7042(9)	13.501(3)
b, (Å)	11.717(2)	7.4589(9)	13.212(4)
c, (Å)	28.540(4)	26.441(7)	8.305(2)
β, (°)			116.24(2)
V, (Å^3)	2547.4(7)	1322.4(4)	1329(9)
μ(MoK_α), cm^{-1}	0.88	0.84	0.84
$d_{calc.}$, g cm^{-3}	1.425	1.373	1.366
2θ range, °	$3 < 2\theta < 50$	$3 < 2\theta < 56$	$3 < 2\theta < 50$
scan width, °	$0.8 + 0.34 \operatorname{tg} \theta$	$1.0 + 0.34 \operatorname{tg} \theta$	$1.0 + 0.34 \operatorname{tg} \theta$
scan speed, ° min^{-1}	$1.7 \ll 10.1$	$2.2 \ll 10.1$	$1.8 \ll 20.1$
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
no. of reflctns collected	2236	1716	1316
no. of unique reflctns	2236	1716	1173
no. of reflctns with $I > 3\sigma(I)$	820 $I > 2.5\sigma(I)$	1186	754
R^a	0.038	0.037	0.038
R_w (unit weight)^b	0.038	0.032	0.033
no. of variables	190	190	71
Max. peak final ΔF map e Å^{-3}	0.14	0.12	0.15
secondary-extinction values	$192 * 10^{-6}$	$220 * 10^{-6}$	$92 * 10^{-6}$

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$

[b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_c)^2]^{1/2}$

the corresponding naphthalene dicarboxylic acid or anhydride with an excess of aniline following the procedure already described (Cava, Deana, Muth, 1959) for the synthesis of **1**. Flash chromatography over silicagel (elution by dichloromethane or chloroform) was followed by sublimation before slow recrystallization from ethyl acetate or from a benzene/hexane mixture.

Table 2-1. Fractional atomic coordinates (e.s.d.'s) for compound **1**: 2,3-naphthalimide.

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$[a]
N	0.3883(5)	0.6144(3)	0.8622(1)	0.0345
O(1)	0.2223(5)	0.4500(3)	0.8678(1)	0.0497
O(2)	0.5356(5)	0.7807(3)	0.8817(1)	0.0495
C(1)	0.2948(7)	0.5297(4)	0.8866(2)	0.0370
C(2)	0.3084(7)	0.5582(4)	0.9365(2)	0.0348
C(3)	0.2452(6)	0.5041(4)	0.9747(2)	0.0373
C(4)	0.2752(6)	0.5511(4)	1.0198(2)	0.0343
C(5)	0.2092(7)	0.5008(4)	1.0611(2)	0.0418
C(6)	0.2393(8)	0.5490(5)	1.1037(2)	0.0439
C(7)	0.3365(8)	0.6491(5)	1.1080(2)	0.0463
C(8)	0.4048(7)	0.6996(4)	1.0687(2)	0.0384
C(9)	0.3751(6)	0.6536(4)	1.0235(2)	0.0328
C(10)	0.4427(6)	0.7069(4)	0.9829(2)	0.0328
C(11)	0.4063(6)	0.6593(4)	0.9408(2)	0.0328
C(12)	0.4533(7)	0.6962(5)	0.8931(2)	0.0385
C(13)	0.4058(7)	0.6210(4)	0.8126(2)	0.0341
C(14)	0.4859(7)	0.5336(5)	0.7887(2)	0.0445
C(15)	0.5078(7)	0.5422(5)	0.7404(2)	0.0491
C(16)	0.4486(8)	0.6370(5)	0.7166(2)	0.0494
C(17)	0.3673(7)	0.7232(5)	0.7415(2)	0.0493
C(18)	0.3448(7)	0.7150(5)	0.7895(2)	0.0442

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix.

Table 2-2. Fractional atomic coordinates (e.s.d.'s) for compound **2**: 1,2-naphthalimide.

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$[a]
N	0.3881(4)	0.7000(4)	0.1311(1)	0.0410
O(1)	0.1059(3)	0.5964(4)	0.1728(8)	0.0441
O(2)	0.6983(4)	0.8283(4)	0.1169(1)	0.0568
C(1)	0.2689(5)	0.6604(4)	0.1741(1)	0.0368
C(2)	0.3931(4)	0.7121(4)	0.2185(1)	0.0329
C(3)	0.3497(4)	0.6987(4)	0.2707(1)	0.0341
C(4)	0.1687(5)	0.6314(4)	0.2901(1)	0.0399
C(5)	0.1399(5)	0.6214(5)	0.3415(1)	0.0499
C(6)	0.2918(6)	0.6776(5)	0.3748(1)	0.0543
C(7)	0.4660(6)	0.7415(5)	0.3571(1)	0.0506
C(8)	0.5033(5)	0.7564(4)	0.3041(1)	0.0395
C(9)	0.6840(5)	0.8241(5)	0.2847(1)	0.0476
C(10)	0.7198(5)	0.8351(5)	0.2340(1)	0.0468
C(11)	0.5704(5)	0.7784(4)	0.2014(1)	0.0382
C(12)	0.5707(5)	0.7756(5)	0.1451(1)	0.0440
C(13)	0.3264(6)	0.6697(4)	0.0797(1)	0.0440
C(14)	0.1418(6)	0.7218(6)	0.0640(1)	0.0556
C(15)	0.0850(7)	0.6902(7)	0.0139(2)	0.0736
C(16)	0.2162(9)	0.6103(7)	−0.0189(1)	0.0706
C(17)	0.3997(8)	0.5586(6)	−0.0032(2)	0.0611
C(18)	0.4594(6)	0.5873(6)	0.0468(1)	0.0547

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix.

Table 2-3. Fractional atomic coordinates (e.s.d.'s) for compound **3**: 1,8-naphthalimide.

Atom	*x/a*	*y/b*	*z/c*	$U_{eq.}$[a]
N	0.0000	0.2220(2)	0.25000	0.0469
O	−0.1532(2)	0.2220(1)	0.2961(3)	0.0704
C(1)	−0.0840(2)	0.1730(2)	0.2753(4)	0.0508
C(2)	−0.0832(2)	0.0620(2)	0.2744(3)	0.0485
C(3)	−0.1639(2)	0.0096(2)	0.2973(4)	0.0591
C(4)	−0.1654(2)	−0.0965(2)	0.2934(4)	0.0667
C(5)	−0.0858(3)	−0.1484(2)	0.2700(4)	0.0669
C(6)	0.0000	−0.0978(3)	0.25000	0.0555
C(7)	0.0000	0.0091(3)	0.25000	0.0469
C(13)	0.0000	0.3312(3)	0.25000	0.0468
C(14)	−0.0810(2)	0.3836(2)	0.1085(4)	0.0592
C(15)	−0.0804(2)	0.4873(2)	0.1096(4)	0.0700
C(16)	0.0000	0.5392(3)	0.25000	0.0693

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$ where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix.

X-ray crystallographic studies

X-ray data collection and reduction

Selected crystals were set up on an Enraf Nonius CAD4 diffractometer. Accurate unit cell dimensions and crystal orientation matrices together with their estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 reflections. Two standard reflections were monitored periodically; no intensity decay occured during any of the data collections. Corrections were made for Lorentz and polarization effects. Crystallographic data and other pertinent informations are summarized in Table 1.

Structure solution and refinement

Compound **3**: *N*-phenyl-1,8-naphthalimide.

The observed systematic absences are compatible with two space groups *Cc* (No. 9) or *C2/c* (No. 15). The centrosymmetric space group was chosen under the basis of statistical tests and confirmed by subsequent results. As we found four molecules of the title compound in the cell while the *C2/c* space group has eight equivalent positions, the molecule must lie on a symmetry element. Each molecule lies along a twofold axis (0, *y*, 1/4) which passes through the N, C(6), C(7), C(13), and C(16) atoms.

Computations were performed by using CRYSTALS (Watkin, Carruthers, Betteridge, 1988) adapted on a MicroVax II. Scattering factors for all atoms were as incorporated in CRYSTALS.

Structures were solved by direct method. All remaining non-hydrogen atoms were found by successive electron density map calculations. Their atomic coordinates were refined together with anisotropic temperature factors. At this stage, hydrogen atoms were located on a difference electron density map; their coordinates were refined with an overall isotropic temperature factor.

Atomic coordinates are given in Tables 2-1, 2-2 and 2-3. Selected bond distances and bond angles are given in Tables 3-1, 3-2 and 3-3.

Table 3-1. Interatomic distances (Å) and bond angles (deg) for compound **1**: 2,3-naphthalimide.

N	C(1)		1.406(6)	C(7)	C(8)		1.370(7)
N	C(12)		1.393(6)	C(8)	C(9)		1.416(6)
N	C(13)		1.425(6)	C(9)	C(10)		1.414(6)
C(1)	O(1)		1.211(6)	C(10)	C(11)		1.354(6)
C(1)	C(2)		1.466(7)	C(11)	C(12)		1.472(7)
C(2)	C(3)		1.349(7)	C(12)	O(2)		1.216(5)
C(2)	C(11)		1.405(6)	C(13)	C(14)		1.374(7)
C(3)	C(4)		1.419(6)	C(13)	C(18)		1.365(7)
C(4)	C(5)		1.413(7)	C(14)	C(15)		1.393(7)
C(4)	C(9)		1.426(6)	C(15)	C(16)		1.377(8)
C(5)	C(6)		1.358(7)	C(16)	C(17)		1.381(7)
C(6)	C(7)		1.392(7)	C(17)	C(18)		1.384(7)
C(1)	N	C(12)	110.6(4)	C(4)	C(9)	C(10)	120.3(4)
C(1)	N	C(13)	125.3(4)	C(8)	C(9)	C(10)	121.4(4)
C(12)	N	C(13)	123.9(4)	C(9)	C(10)	C(11)	118.2(4)
N	C(1)	O(1)	123.7(5)	C(2)	C(11)	C(10)	122.2(4)
N	C(1)	C(2)	106.5(4)	C(2)	C(11)	C(12)	107.2(4)
O(1)	C(1)	C(2)	129.7(5)	C(10)	C(11)	C(12)	130.6(5)
C(1)	C(2)	C(3)	130.7(5)	C(11)	C(12)	O(2)	127.7(5)
C(1)	C(2)	C(11)	108.3(4)	N	C(12)	C(11)	107.2(4)
C(3)	C(2)	C(11)	121.0(5)	N	C(12)	O(2)	125.0(5)
C(2)	C(3)	C(4)	119.5(4)	N	C(13)	C(14)	119.7(5)
C(3)	C(4)	C(5)	122.7(5)	N	C(13)	C(18)	119.5(5)
C(3)	C(4)	C(9)	118.8(4)	C(14)	C(13)	C(18)	120.8(5)
C(5)	C(4)	C(9)	118.6(5)	C(13)	C(14)	C(15)	119.4(5)
C(4)	C(5)	C(6)	120.9(5)	C(14)	C(15)	C(16)	120.4(6)
C(5)	C(6)	C(7)	121.3(5)	C(15)	C(16)	C(17)	119.0(5)
C(6)	C(7)	C(8)	119.6(5)	C(16)	C(17)	C(18)	120.9(5)
C(7)	C(8)	C(9)	121.4(5)	C(13)	C(18)	C(17)	119.5(5)
C(4)	C(9)	C(8)	118.3(4)				

Table 3-2. Interatomic distances (Å) and bond angles (deg) for compound **2**: 1,2-naphthalimide.

C(1)	O(1)		1.193(4)	C(9)	C(10)		1.364(5)
C(1)	C(2)		1.491(4)	C(10)	C(11)		1.387(5)
N	C(1)		1.421(4)	C(11)	C(12)		1.490(5)
C(2)	C(3)		1.414(4)	C(12)	O(2)		1.202(4)
C(2)	C(11)		1.364(4)	N	C(12)		1.398(4)
C(3)	C(4)		1.410(4)	N	C(13)		1.439(4)
C(3)	C(8)		1.424(4)	C(13)	C(14)		1.362(5)
C(4)	C(5)		1.376(4)	C(13)	C(18)		1.389(5)
C(5)	C(6)		1.410(5)	C(14)	C(15)		1.399(5)
C(6)	C(7)		1.346(5)	C(15)	C(16)		1.372(6)
C(7)	C(8)		1.425(5)	C(16)	C(17)		1.355(7)
C(8)	C(9)		1.410(5)	C(17)	C(18)		1.397(6)
O(1)	C(1)	C(2)	129.6(3)	C(2)	C(11)	C(10)	122.3(3)
O(1)	C(1)	N	125.2(3)	C(2)	C(11)	C(12)	109.1(3)
C(2)	C(1)	N	105.2(2)	C(10)	C(11)	C(12)	128.6(3)
C(1)	C(2)	C(3)	129.5(3)	C(11)	C(12)	O(2)	128.1(4)
C(1)	C(2)	C(11)	108.7(3)	C(11)	C(12)	N	105.6(3)
C(3)	C(2)	C(11)	121.9(3)	O(2)	C(12)	N	126.2(4)
C(2)	C(3)	C(4)	123.9(3)	C(1)	N	C(12)	111.4(3)
C(2)	C(3)	C(8)	115.8(3)	C(1)	N	C(13)	124.2(3)
C(4)	C(3)	C(8)	120.3(3)	C(12)	N	C(13)	124.4(3)
C(3)	C(4)	C(5)	120.0(3)	N	C(13)	C(14)	120.2(3)
C(4)	C(5)	C(6)	120.0(3)	N	C(13)	C(18)	118.5(3)
C(5)	C(6)	C(7)	120.9(3)	C(14)	C(13)	C(18)	121.3(4)
C(6)	C(7)	C(8)	121.5(3)	C(13)	C(14)	C(15)	119.2(4)
C(3)	C(8)	C(7)	117.3(3)	C(14)	C(15)	C(16)	119.9(4)
C(3)	C(8)	C(9)	120.2(3)	C(15)	C(16)	C(17)	120.7(4)
C(7)	C(8)	C(9)	122.5(3)	C(16)	C(17)	C(18)	120.5(4)
C(8)	C(9)	C(10)	122.1(3)	C(13)	C(18)	C(17)	118.4(4)
C(9)	C(10)	C(11)	117.7(3)				

Table 3-3. Interatomic[a] distances (Å) and bond angles (deg) for compound **3**: 1,8-naphthalimide.

N	C(1)		1.400(3)	C(4)	C(5)		1.360(4)
N	C(13)		1.442(4)	C(5)	C(6)		1.410(3)
C(1)	O		1.210(3)	C(6)	C(7)		1.412(5)
C(1)	C(2)		1.467(3)	C(13)	C(14)		1.386(3)
C(2)	C(3)		1.373(3)	C(14)	C(15)		1.371(4)
C(2)	C(7)		1.411(3)	C(15)	C(16)		1.374(4)
C(3)	C(4)		1.401(4)				
C(1)	N	C(1')	124.9(3)	C(4)	C(5)	C(6)	121.3(3)
C(1)	N	C(13)	117.5(1)	C(5)	C(6)	C(5')	123.3(4)
N	C(1)	C(2)	117.0(2)	C(5)	C(6)	C(7)	118.3(2)
N	C(1)	O	120.1(2)	C(2)	C(7)	C(2')	120.7(3)
O	C(1)	C(2)	122.9(2)	C(2)	C(7)	C(6)	119.7(2)
C(1)	C(2)	C(3)	119.7(2)	N	C(13)	C(14)	120.0(2)
C(1)	C(2)	C(7)	120.2(2)	C(14)	C(13)	C(14')	120.1(3)
C(3)	C(2)	C(7)	120.1(2)	C(13)	C(14)	C(15)	119.6(3)
C(2)	C(3)	C(4)	120.4(3)	C(14)	C(15)	C(16)	120.3(3)
C(3)	C(4)	C(5)	120.2(3)	C(15)	C(16)	C(15')	120.2(4)

[a] (') as superscript refers to the following equivalent position relative to the x, y, z set: $-x$, y, $1/2 - z$.

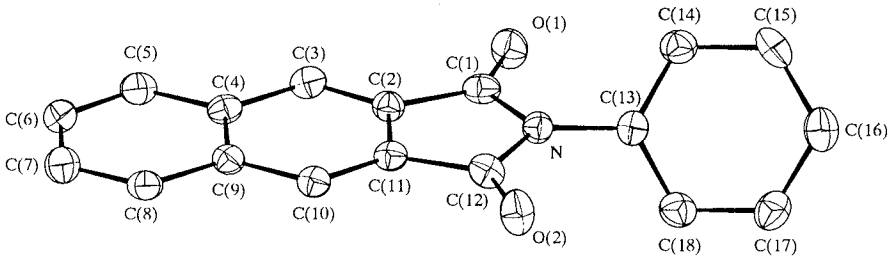


Fig. 1-1. View of the *N*-phenyl 2,3-naphthalimide showing the numbering scheme.

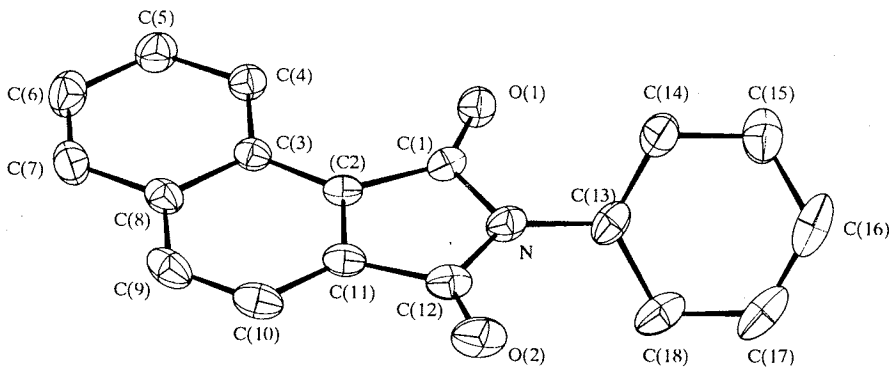


Fig. 1-2. View of the *N*-phenyl 1,2-naphthalimide showing the numbering scheme.

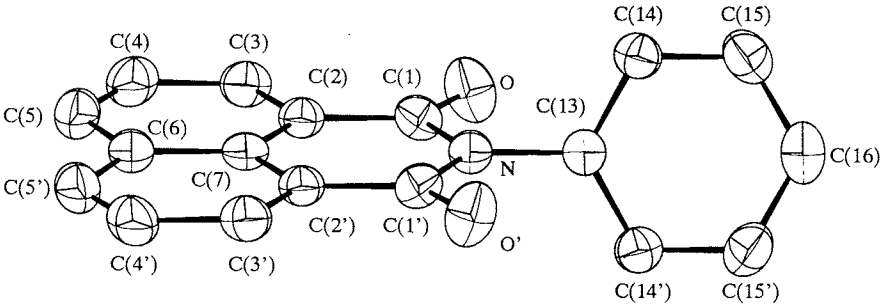


Fig. 1-3. View of the *N*-phenyl 1,8-naphthalimide showing the numbering scheme.

The molecular geometry and the atom numbering schemes are shown in Figs. 1-1, 1-2 and 1-3. Listings of thermal parameters, all bond distances and angles and Tables of F_{obs} have been deposited. [1]

Results and discussion

Dihedral angles between phenyl substituent and naphthalene group least-square planes are respectively 59.2° 46.5° and 69.4° for compound **1**, **2**, and **3**. From the crystal structure results, the angle between the two carbonyl groups is ca. 137° and 138° for **1** and **2**, respectively, and only ca. 115° for compound **3**. Therefore, the larger angle (69.4°) between the two planes of the molecule, the naphthalimide one and the *N*-phenyl substituent one, may result from a larger steric hindrance between the carbonyl groups and the *ortho*-hydrogens of the *N*-phenyl substituent of compound **3**, than in compounds **1** and **2**. On the other hand, we have no explanation for the difference of angle found between these two planes in **1** and **2**.

The four atoms, N, C(1), C(1'), and C(13) are strictly in the same plane for **3**. In **1**, and **2** atomic deviations for the corresponding least-square planes N C(1) C(12) C(13) are less than 0.02 Å for **1** and 0.007 Å for **2**. Bond lengths between the nitrogen atom and the carbon atoms of the carbonyl groups range between 1.393(6) Å to 1.421(4) Å. These values are comparable with those found in *N*-ethyl-1,8-naphthalimide (Easton, Gulbis, Hoskins, Scharfbillig, Tiekink, 1992). The *N*-phenyl bond length ranges from 1.426(6) Å to 1.442(4) Å. It is shorter than the 1.482(7) Å value of the *N*-ethyl bond found in *N*-ethyl-1,8-naphthalimide (Easton, Gulbis, Hoskins, Scharfbillig, Tiekink, 1992).

Slow recrystallization of compound **3**, in which the plane of the phenyl group makes a 69° angle with that of the naphthalimide moiety, yielded a large single crystal. Its fluorescence emission has a maximum at 432 nm, and it is red-shifted by 64 nm from the position of the emission of the same compound taken in solution, where the two planes of the molecule are known to be close to 90°. Insertion of the same molecule in a silico-aluminum oxide glass using the sol-gel technique (Bentivegna, Canva, Georges, Brun, Chaput, Malier, Boilot, 1993), induces an important strain to the molecule configuration during the formation of the Si–O–Si–O–Si bonds. Effectively, when the glass obtained is perfectly transparent, thus indicating that molecule **3** is uniformally distributed inside the silico-aluminum oxide glass, then the fluorescence emission is red-shifted by ca. 70 nm from its position found with the single crystal. The spectral range where this emission occurs is expected from a planar structure of the molecule; such long-range emission was not found in solution. On the other hand, when the glass is by far perfect, then it is only translucent, due to the formation of small aggregates of the inserted naphthalimide **3**. In such cases, the emission is localized in a spectral range similar to that found with the single crystal.

Our findings support the attribution of the long-wavelength emission of **1** to a planar structure of the molecule as a result of a large rotation of the *N*-phenyl ring, and not to a TICT-like conformation where the two moieties should be orthogonal (Valat, Wintgens, Kossanyi, Biczók, Demeter, Bérces, 1992).

Acknowledgements. We thank Dr. J. P. Boilot and Dr. F. Chaput at the Ecole Polytechnique in Palaiseau (France) for having kindly prepared these samples for us.

[1] Additional material to this paper can be ordered referring to the no. CSD 401548 for 1,8-NI, CSD 401549 for 1,2-NI, CSD 401550 for 2,3-NI, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.

References

Bentivegna, F.; Canva, M.; Georges, P.; Brun, A.; Chaput, F.; Malier, L.; Boilot, J. P.: Reverse saturable absorption in solid xerogel matrices. Appl. Phys. Lett. **62** (1993) 1721–1723.

Cava, M. P.; Deana, A. A.; Muth, K.: Condensed cyclobutane aromatic compounds. VIII. Mechanism of formation of 1,2-dibromobenzocyclobutene; a new Diels-Alder synthesis. J. Am. Chem. Soc. **81** (1959) 6458–6460.

Easton, C. J.; Gulbis, J. M.; Hoskins, B. F.; Scharfbillig, I. M.; Tiekink, E. R. T.: Crystal and molecular structure of N-ethyl-1,8-naphthalimide. Z. Kristallogr. **199** (1992) 249–254.

Grabowski, Z. R.; Rotkiewicz, K.; Siemarczuk, A.; Cowley, D. J.; Baumann, J.: Twisted intramolecular charge transfer states (TICT). A new class of excited states with a full charge separation. Nouv. J. Chim. **3** (1979) 443–454.

Herbich, J.; Dobkowski, J.; Rullière, C.; Nowacki, J.: Low temperature dual fluorescence in 9-morpholino-acridine. J. Lumin. **44** (1989) 87–95.

Launay, J.-P.: Toward molecular switches. In: *Molecular Electronics, Science and Technology* (Ed. A. Aviram), p. 237–245. Engineering Foundation, New-York 1989.

Lipinski, J.; Chojnacki, H.; Grabowski, Z. R.; Rotkiewicz, K.: Theoretical model for the double fluorescence of p-cyano-*N*,*N*-dimethylaniline in polar solvents. Chem. Phys. Lett. **70** (1980) 449–453.

Lippert, E.; Rettig, W.; Bonacic-Koutecky, V.; Heisel, F.; Miehé, J. A.: Photophysics of internal twisting. In: *Advances in Chemical Physics*, p. 1–173. J. Wiley, New-York **68** (1987).

Meech, S. R.; Phillips, D.: Complex kinetics of a* state formation in the DMABN-ethanol system. Chem. Phys. Lett. **116** (1985) 262–267.

Rettig, W.: Intramolecular rotational relaxation of compounds which form twisted intramolecular charge transfer (TICT) excited states. J. Phys. Chem. **86** (1982) 1970–1976.

Rettig, W.: Charge separation of excited states of decoupled systems. TICT compounds and implications regarding the development of new laser dyes and the primary processes of vision and photosynthesis. Angew. Chem. Int. Ed. Engl., **25** (1986) 971–988.

Valat, P.; Wintgens, V.; Kossanyi, J.; Biczók, L.; Demeter, A.; Bérces, T.: Influence of geometry on the emitting properties of 2,3-naphthalimides. J. Am. Chem. Soc. **114** (1992) 946–953.

Warman, J. M.; Shuddeboom, W.; Jonker, S. A.; de Haas, M. P.; Paddon-Row, M. N.; Zachariasse, K. A.; Launay, J.-P.: Intramolecular switching between dipolar resonance structures in singlet and triplet excited states detected by TRMC. Chem. Phys. Lett. **210** (1993) 397–404.

Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W.: Crystals, an advanced crystallographic program system; chemical crystallography laboratory. University of Oxford, Oxford, England 1988.

Wintgens, V.; Valat, P.; Kossanyi, J.; Biczók, L.; Demeter, A.; Bérces, T.: Spectroscopic properties of aromatic dicarboximides. Part 1. N–H and N-methyl substituted naphthalimides. J. Chem. Soc. Farad. T. **90** (1994) 411–421.