Influence of steric and electronic effects of substituents on the molecular structures and conformational flexibility of 1,8-naphthalenedicarboximides

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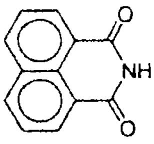
A series of 1,8-naphthalenedicarboximide derivatives containing substituents of different steric and electronic nature were studied by X-ray diffraction analysis. *Ab initio* quantum-chemical calculations in the HF/3-21G approximation demonstrated the high conformational flexibility of the imide tetrahydro ring in the molecules of these compounds. The electronic nature of the substituents has no effect on the geometry and conformational flexibility of naphthalenedicarboximides due to weak conjugation between the imide and naphthalene fragments in the molecules. However, the steric effects of the bulky substituents noticeably affect the equilibrium geometry of the imide ring by increasing its conformational flexibility.

Key words: 1,8-naphthalenedicarboximide, molecular structure, conjugation, conformational flexibility, quantum-chemical calculations.

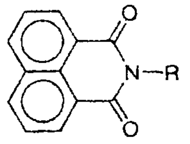
1,8-Naphthalenedicarboximide (NDCI) and its derivatives attract the attention of researchers primarily because of their luminescent characteristics and the ability to undergo further chemical transformations. These compounds are used as luster-imparting fluorescent agents,[1] azo dyes,[2] and antitumor[3,4] and antiviral[5] drugs as well as for structural dyeing of NDCI-based polymers.[6,7] The NDCI derivatives are also reagents and intermediates in the synthesis of rigid-chain heterocyclic polymers used for preparing various superstrength materials possessing special properties (for example, nonlinear optical, photoconducting, electroconducting, *etc.*).[8–10]

Therefore, data on the structural and conformational parameters of NDCI are necessary for an understanding of physicochemical characteristics of compounds synthesized based on NDCI. Thus, it was demonstrated[11] that it is the conformationally rigid structure of the NDCI derivative prepared by the reaction of 1,8-naphthalic anhydride with 3-aminoquinuclidine that is the major factor responsible for the properties of the product as an antagonist of 5-HT3 receptors.

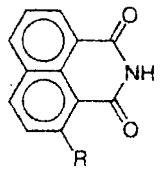
Previously,[12] we have demonstrated that the imide ring in NDCI exhibits the high conformational flexibility. The transition from the planar equilibrium conformation to a sofa conformation with a C(Ar)—C(=O)—NH—C(=O) torsion angle of ±20° leads to an increase in the energy of the molecule by only 0.5 kcal mol^{-1}. Consequently, the steric and electronic effects of the substituents would be expected to substantially affect the conformational characteristics of the imide tetrahydro ring.



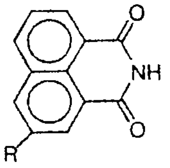
1



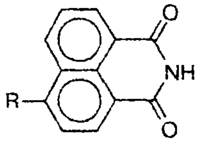
2a—c



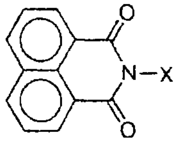
3a—c



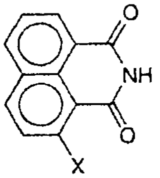
4a—c



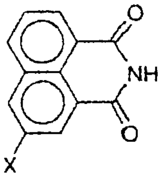
5a—c



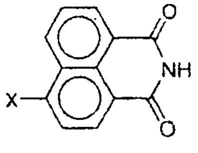
6a,b



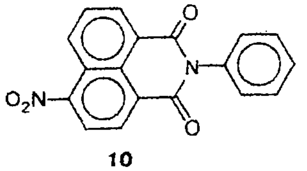
7a,b



8a,b



9a,b



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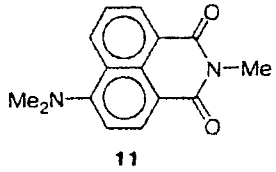

11

2—5: R = Me (**a**), Ph (**b**), Bu^t (**c**)
6—9: X = NH$_2$ (**a**), NO$_2$ (**b**)

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Table 1. Crystallographic data for compounds **1**, **6a**, **10**, and **11**

Parameter	**1**	**6a**	**10**	**11**
Molecular formula	$C_{12}H_7NO_2$	$C_{12}H_8N_2O_2$	$C_{15}H_{14}N_2O_2$	$C_{18}H_{10}N_2O_4$
Color, form	Colorless parallelepipeds	Yellow platelets	Yellow parallelepipeds	Yellow parallelepipeds
Molecular weight	197.19	212.20	254.28	318.28
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P1$	$P2_1$	Cc
Z	4	4	2	4
Temperature/K	293(2)	293(2)	170(2)	293(2)
a/Å	11.009(2)	7.320(1)	4.042(1)	14.085(3)
b/Å	5.4134(8)	9.351(2)	12.035(5)	14.770(3)
c/Å	15.675(3)	14.649(3)	12.421(5)	7.363(1)
α/deg		81.47(1)		
β/deg	108.92(2)	79.83(1)	95.74(3)	114.95(1)
γ/deg		69.65(1)		
V/Å^3	883.7(3)	921.2(3)	601.2(4)	1388.9(5)
d_{calc}/g cm^{-1}	1.482	1.530	1.405	1.522
μ/mm^{-1}	0.103	0.107	0.095	0.110
$F(000)$	408	440	268	656
Number of measured reflections	1654	4273	2077	1778
Number of independent reflections	1568	3949	1845	
R_{int}	0.058	0.013	0.038	
Diffractometer		Siemens P3/PC		
$2\theta_{max}$/deg	50	54	60	60
Reflections in the refinement, number of parameters	1448	3895	1810	1727
Reflections with $F > 4\sigma(F)$	951	2610	1177	1155
R_1 (all reflections)	0.048	0.049	0.066	0.056
wR_2 (all reflections)	0.114	0.123	0.149	0.136
S (all reflections)	1.033	1.052	1.048	1.038

With the aim of studying the structural characteristics and the effect of substituents of different nature on the geometry and conformational flexibility of 1,8-naphthalenedicarboximide (**1**) and its derivatives **2**—**11** containing various substituents, compounds **1**, **6a**, **10**, and **11** were studied by X-ray diffraction analysis, and *ab initio* quantum-chemical calculations of molecules **1**—**9** were carried out.

Experimental

Compounds **1**, **6a**, **10**, and **11** were synthesized according to a known procedure[13] by condensation of naphthalic anhydride with the corresponding primary amine at high temperature.

Crystals of compound **1** suitable for X-ray diffraction analysis were prepared by sublimation under reduced pressure. Crystals of compounds **6a**, **10**, and **11** were grown by slow evaporation of their solutions in DMF. The crystallographic data for compounds **1**, **6a**, **10**, and **11** are given in Table 1. We carried out the profile analysis of the X-ray intensity data sets according to Strel'tsov—Zavodnik's procedure[14] (compounds **6a** and **10**) or to Blessing's procedure[15] (compound **11**).

All structures were solved by direct methods using the SHELXTL PLUS 5 program package.[16] The positions of the hydrogen atoms were revealed from difference electron density syntheses (compounds **1**, **6a**, and **11**) or were calculated

Table 2. Principal bond lengths (d) in molecules **1**, **6a**, **10**, and **11**

Bond	d/Å
Compound **1**	
O(1)—C(9)	1.221(2)
O(2)—C(10)	1.228(2)
N(1)—C(10)	1.377(2)
N(1)—C(9)	1.389(2)
C(1)—C(8′)	1.422(2)
C(1)—C(9)	1.476(3)
C(8)—C(8′)	1.419(2)
C(8)—C(10)	1.469(3)
Compound **6a**	
O(1A)—C(9A)	1.220(2)
O(2A)—C(10A)	1.219(2)
N(1A)—C(10A)	1.385(2)
N(1A)—C(9A)	1.389(2)
N(1A)—N(2A)	1.427(2)
C(1A)—C(8′A)	1.413(2)
C(1A)—C(9A)	1.468(2)
C(8A)—C(8′A)	1.412(2)
C(8A)—C(10A)	1.477(2)
O(1B)—C(9B)	1.218(2)
O(2B)—C(10B)	1.219(2)
N(1B)—C(10B)	1.390(2)
N(1B)—C(9B)	1.397(2)
N(1B)—N(2B)	1.424(2)
C(1B)—C(8′B)	1.416(2)
C(1B)—C(9B)	1.477(2)
C(8B)—C(8′B)	1.411(2)
C(8B)—C(10B)	1.473(2)
Compound **10**	
O(1)—C(9)	1.201(5)
O(2)—C(10)	1.212(5)
N(1)—C(10)	1.380(5)
N(1)—C(9)	1.417(5)
N(1)—C(11)	1.446(5)
C(1)—C(8′)	1.403(6)
C(1)—C(9)	1.475(6)
C(8)—C(8′)	1.408(5)
C(8)—C(10)	1.486(6)
Compound **11**	
O(2)—C(10)	1.214(4)
N(1)—C(9)	1.385(5)
N(1)—C(10)	1.403(5)
N(1)—C(11)	1.481(5)
C(1)—C(8′)	1.416(5)
C(1)—C(9)	1.475(5)
C(8)—C(8′)	1.416(5)
C(8)—C(10)	1.469(5)

Table 3. Principal bond angles (ω) in molecules **1**, **6a**, **10**, and **11**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Compound **1**		N(1A)—C(10A)—C(8A)	116.0(1)	O(2)—C(10)—N(1)	120.8(4)
C(10)—N(1)—C(9)	126.9(2)	C(10B)—N(1B)—C(9B)	125.9(1)	O(2)—C(10)—C(8)	121.7(4)
O(1)—C(9)—N(1)	119.9(2)	C(10B)—N(1B)—N(2B)	118.2(1)	N(1)—C(10)—C(8)	117.4(3)
O(1)—C(9)—C(1)	123.8(2)	C(9B)—N(1B)—N(2B)	115.9(1)	Compound **11**	
N(1)—C(9)—C(1)	116.3(2)	O(1B)—C(9B)—N(1B)	120.4(2)	C(9)—N(1)—C(10)	125.3(3)
O(2)—C(10)—N(1)	119.7(2)	O(1B)—C(9B)—C(1B)	123.4(2)	C(9)—N(1)—C(11)	117.8(3)
O(2)—C(10)—C(8)	123.5(2)	N(1B)—C(9B)—C(1B)	116.2(1)	C(10)—N(1)—C(11)	116.9(3)
N(1)—C(10)—C(8)	116.9(2)	O(2B)—C(10B)—(1B)	119.7(1)	C(5)—N(2)—C(13)	116.0(3)
Compound **6a**		O(2B)—C(10B)—C(8B)	123.1(1)	C(5)—N(2)—C(12)	116.0(3)
C(10A)—N(1A)—C(9A)	126.8(1)	N(1B)—C(10B)—C(8B)	117.1(1)	C(13)—N(2)—C(12)	110.9(3)
C(10A)—N(1A)—N(2A)	116.1(1)	Compound **10**		O(1)—C(9)—N(1)	120.4(3)
C(9A)—N(1A)—N(2A)	117.1(1)	C(10)—N(1)—C(9)	124.5(3)	O(1)—C(9)—C(1)	122.0(3)
O(1A)—C(9A)—N(1A)	119.4(1)	C(10)—N(1)—C(11)	117.7(3)	N(1)—C(9)—C(1)	117.6(3)
O(1A)—C(9A)—C(1A)	124.3(1)	C(9)—N(1)—C(11)	117.7(3)	O(2)—C(10)—N(1)	120.0(3)
N(1A)—C(9A)—C(1A)	116.3(1)	O(1)—C(9)—N(1)	120.2(4)	O(2)—C(10)—C(8)	123.7(3)
O(2A)—C(10A)—N(1A)	119.9(1)	O(1)—C(9)—C(1)	123.6(4)	N(1)—C(10)—C(8)	116.3(3)
O(2A)—C(10A)—C(8A)	124.1(1)	N(1)—C(9)—C(1)	116.2(3)		

Table 4. Comparison of the selected experimental and calculated bond lengths (*d*/Å) in the structures of **1** and **12—14**

Bond	**1.**	**12**		**13.**	**14.**
	HF /3-21G	X-ray analysis[a]	HF /3-21G	HF /3-21G	X-ray analysis[b]
O(1)—C(9)	1.214	—	1	1.204	1.219
O(2)—C(10)	1.214	—	—	1.204	1.219
N(1)—C(10)	1.380	—	—	1.375	1.382
N(1)—C(9)	1.380	—	—	1.375	1.382
C(1)—C(2)	1.360	1.373	1.357	—	—
C(1)—C(8′)	1.411	1.425	1.415	—	—
C(1)—C(9)	1.476	—	—	—	1.490
C(2)—C(3)	1.408	1.407	1.414	—	—
C(3)—C(4)	1.360	1.368	1.357	—	—
C(4)—C(4′)	1.411	1.425	1.415	—	—
C(4′)—C(5)	1.411	1.419	1.415	—	—
C(4′)—C(8′)	1.405	1.420	1.409	—	—
C(5)—C(6)	1.360	1.373	1.357	—	—
C(6)—C(7)	1.408	1.407	1.414	—	—
C(7)—C(8)	1.360	1.368	1.357	—	—
C(8)—C(8′)	1.411	1.419	1.415	—	—
C(8)—C(10)	1.476	—	—	—	1.490

[a] Literature data.[25]

[b] Literature data.[26]

geometrically (compound **10**). All hydrogen atoms in the structures of **1**, **10**, and **11** were refined using the riding model with variable parameters U_{iso} (**1** and **11**) or with fixed parameters $U_{iso} = nU_{eq}$ (**10**) of the nonhydrogen atoms to which the H atoms are attached (n = 1.5 for the Me groups and 1.2 for the remaining H atoms). The hydrogen atoms in the structure of **6a** were refined isotropically. The selected bond lengths and bond angles in molecules **1**, **6a**, **10**, and **11** are given in Tables 2 and 3, respectively.

Ab initio quantum-chemical calculations of the equilibrium geometries of compounds **1—9** were carried out by the Hartree—Fock method (HF) with the 3-21G basis set and with full geometry optimization.[17] The conformational flexibility of the imide tetrahydro ring was studied by scanning the C(Ar)—C(=O)—N—C(=O) torsion angle in the range of ±40° with a step of 10° and with full optimization of the other geometric parameters at each point. The results of calculations are given in Tables 4 and 5.

Results and Discussion

Since there is no substantial steric strain in molecule **1**, it may be suggested that the conformation of the

Table 5. Dependence of the energy (*E*) on the C(Ar)—C(=O)—N—C(=O) torsion angle (φ) in molecules **1—9**

Compound	*E*/kcal mol^{-1} at different φ				
	0°	10°	20°	30°	40°
1	0	0.45	1.80	4.04	7.20
2a	0	0.42	1.65	3.74	6.78
2b	0	0.30	0.80	1.50	2.30
2c	0.52	0.42	0.16	0.08	1.06
3a	0	0.28	1.31	3.32	6.20
3b	0	0.34	1.37	3.12	5.63
3c	0	0.30	1.09	2.53	4.67
4a	0	0.45	1.79	4.04	7.20
4b	0	0.45	1.80	4.03	7.21
4c	0	0.45	1.81	4.07	7.28
5a	0	0.46	1.81	4.06	7.26
5b	0	0.45	1.82	4.07	7.28
5c	0	0.45	1.81	4.07	7.27
6a	0	0.34	1.50	3.55	6.37
6b	0	0.34	1.40	3.17	5.70
7a	0	0.49	1.97	4.44	7.96
7b	0	0.10	0.70	2.10	4.20
8a	0	0.49	1.79	4.03	7.20
8b	0	0.45	1.79	4.02	7.18
9a	0	0.47	1.88	4.22	7.54
9b	0	0.47	1.82	4.05	7.20

imide ring is determined principally by the electronic effects. These effects involve primarily the conjugation between the π-systems of the naphthalene fragment and the carbonyl groups and the lone electron pair of the nitrogen atom, which is maximum in the case of planar molecular geometry. The calculated equilibrium conformation of molecule **1** is planar, which is consistent with the above assumption and agrees with the data[12] obtained previously by the AM1 method. However, X-ray diffraction study of compound **1** (Fig. 1) demonstrated that the imide ring of molecule **1** in the crystal is nonplanar and adopts a strongly flattened boat conformation. The N(1) and C(10) atoms deviate from the plane through the remaining atoms of the ring by 0.06 Å. The nonplanar geometry of the imide ring leads also to the deviation of the O(2) atom from the mean plane of the molecule by 0.11 Å. The N(1) atom has a planar-trigonal configuration (the sum of the bond angles about this atom is 360(3)°). The C(9)—N(1)—C(10) bond angle differs from the ideal trigonal value, which is indicative of the strong electron-withdrawing effect of the carbonyl groups. Previously,[18] this fact has been noted for *N*-alkyl derivatives of **1**. The nonplanar geometry of the imide ring was also observed[19] in the complex of NDCI with nickel dithiocarbamate.

In spite of the fact that the calculated and experimental data on the conformations are somewhat different, the calculated bond lengths and bond angles are in reasonably good agreement with those determined by X-ray diffraction analysis, which confirms that this calculation procedure is applicable for describing the molecules under consideration (see Tables 2—4).

In addition, taking into account that the imide tetrahydro ring in molecule **1** exhibits the high conformational flexibility[12] and that the transition from the planar equilibrium conformation to a sofa conformation with a C(Ar)—C(=O)—NH—C(=O) torsion angle of ±20° leads to an increase in the energy of the molecule by less than 2 kcal mol^{-1} (see Table 5), it may be suggested that the nonplanar geometry of the imide ring in the solid phase is determined by the influence of intermolecular interactions on the geometry of the flexible ring.

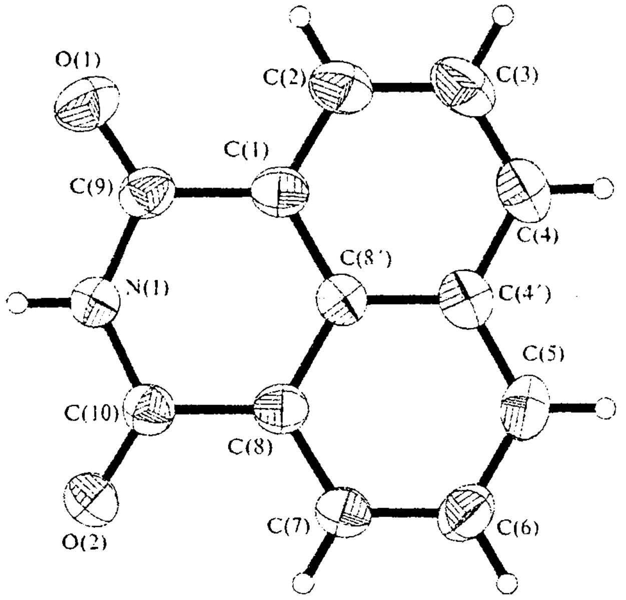
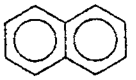


Fig. 1. Structure of compound **1**.

Actually, in the crystal, molecules **1** are linked in centrosymmetrical dimers through the N(1)—H(1)...O(2)' hydrogen bonds (−*x*, 1 − *y*, −*z*) (the H...O distance is 2.02 Å and the N—H...O angle is 173°). These dimers are arranged in stacks along the crystallographic *c* axis. The distance between the adjacent molecules in the stack is ~3.5 Å. There are also shortened intermolecular contacts H(4)...C(4')' (0.5 − *x*, 0.5 + *y*, 0.5 − *z*) and H(4)...C(4)' (0.5 − *x*, 0.5 + *y*, 0.5 − *z*) (2.76 and 2.78 Å, respectively; the sum of the van der Walls radii[20] of the H and C atoms is 2.87 Å) between the molecules of different stacks. This molecular packing is indicative of the presence of rather strong intermolecular interactions, which may lead to a nonplanar conformation of the imide ring in the solid phase.

Previously,[12] the high conformational flexibility of the imide ring has been attributed to the nonaromatic character of its π-system, which is weakly conjugated with the 10π-electron aromatic system of the naphthalene fragment. To test this suggestion, we performed theoretical and experimental analysis of the changes in the bond lengths and bond orders on going from naphthalene (**12**) and diformamide (**13**) to dibenzamide (**14**) and NDCI **1**.



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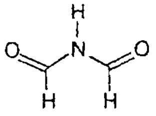

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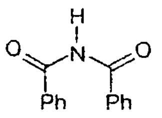
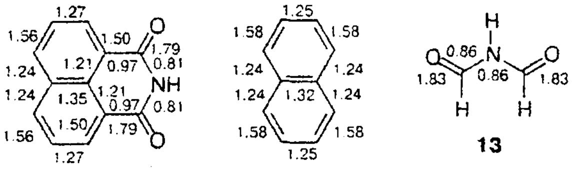


14

A comparison of these values (Scheme 1, where the calculated bond orders in molecules **11**, **12**, and **13** are given; see Table 4) shows that the formation of NDCI leads only to a weak disturbance of the geometry of the naphthalene and imide fragments. As a result, the π-system in molecule **1** may be formally divided into two portions, which are weakly conjugated with each other, *viz*., into the aromatic 10π-electron naphthalene fragment and the 7π-electron imide ring. This scheme suggests that the conformation of the imide ring should be sensitive to the steric effects of the substituents.

However, the results of calculations for molecules **2a—c** demonstrated that the imide ring is noticeably nonplanar only in the case of *tert*-butyl derivative **2c** (its equilibrium conformation can be described as a sofa with a C(Ar)—C(=O)—N—C(=O) torsion angle of 26° and the nitrogen atom deviating from the plane through the remaining atoms of the ring by 0.28 Å). In molecules

Scheme 1



1 **12** **13**

2a,b, the equilibrium conformation of the imide tetrahydro ring remains planar. The phenyl substituent in molecule **2b** is virtually perpendicular to the naphthalimide fragment, which is consistent with the published data for analogous compounds.[5, 21–24]

The introduction of the substituents into the naphthalene fragment (compounds **3**—**5**) does not lead to a change of the planar equilibrium conformation of the imide ring even in the presence of the bulky *tert*-butyl group located in proximity to the carbonyl group in molecule **3c**.

The deformation energy of the imide ring is more sensitive to the steric effects of the substituents (see Table 5). Repulsions between the alkyl and phenyl substituents and the carbonyl groups in molecules **2a**—**c** and **3a**—**c** result in a substantial increase in the conformational flexibility of the imide ring, which is increased as the volume of the substituent increases. In molecules **4a**—**c** and **5a**—**c**, the deformation energy of the tetrahydro ring remains unchanged due to the fact that the substituents are remote from the imide fragment.

According to the results of calculations, the equilibrium conformation of the imide ring remains planar in compounds **6a,b**, which agrees with the experimental data[5] on nitro derivative **6b**, in which the nitro group is rotated virtually perpendicular to the plane of the ring.

X-ray diffraction study of compound **6a** (Fig. 2, see Tables 2 and 3) gave contradictory results. Two symmetrically independent molecules (**A** and **B**) are present in the crystal. The imide ring in molecule **A** adopts a flattened sofa conformation. The N(1A) atom deviates from the plane through the remaining atoms by 0.05 Å and the N(2A) atom deviates from the plane through the remaining atoms by 0.07 Å. In molecule **B**, the imide ring is planar. In addition, molecules **A** and **B** differ in the orientation of the amino groups. Both amino groups have a trigonal-pyramidal configuration (the sums of the bond angles are 313(5)° (**A**) and 317(3)° (**B**)). However, this substituent in molecule **A** is conjugated with the π-system of the imide ring (the H(2NB)—N(2A)—N(1A)—C(9A) torsion angle is −27(2)°). Apparently, this arrangement of the amino group is stabilized by electrostatic interactions between the hydrogen atoms of the substituent and the oxygen atoms of the carbonyl groups (the shortened H(2NA)...O(2A) and H(2NB)...O(1A) intramolecular contacts are 2.33 and 2.20 Å, respectively; the sum of the van der Waals radii[20] of the H and O atoms is 2.45 Å). The amino group in molecule **B** is perpendicular to the plane of the molecule (the H(2ND)—N(2B)—N(1B)—C(9B) torsion angle is 91(2)°). As a consequence, only one shortened intramolecular H(2NC)...O(2B) contact (2.19 Å) is observed. However, the results of calculations demonstrated that this orientation of the amino group is energetically more favorable (by 1.7 kcal mol^{-1}) than that observed in molecule A.

The presence of two molecules per asymmetric unit leads to the formation of a system of shortened intermolecular contacts with the participation of the hydrogen atoms of the amino groups and the oxygen atoms of the C=O groups of the adjacent molecules: H(2NA)...O(2B)′ (1 − x, 1 − y, 1 − z), 2.28 Å; H(2NB)...O(1A)′ (1 − x,

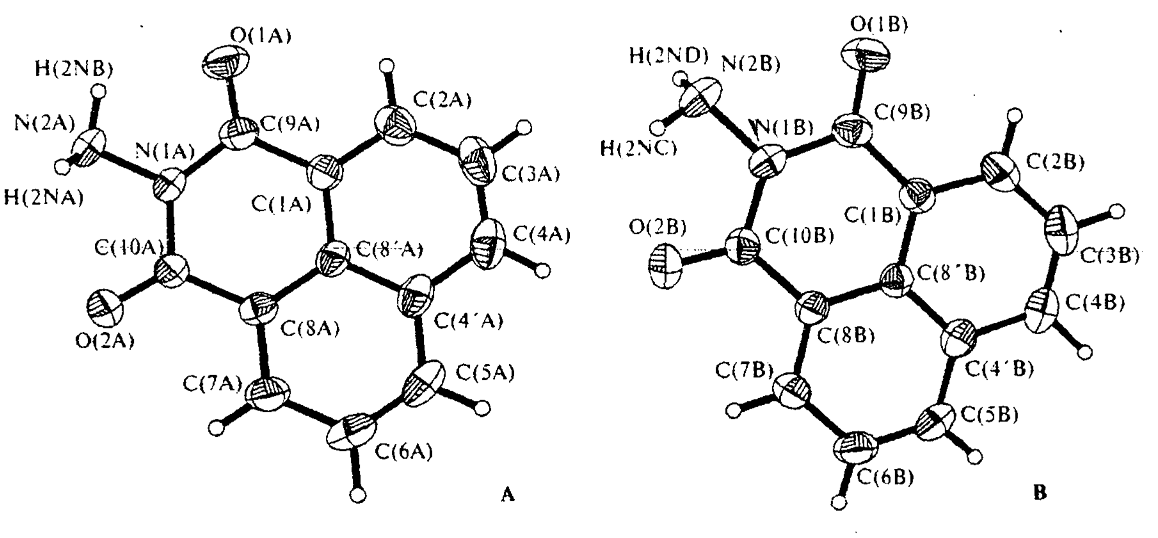


Fig. 2. Structure of compound **6a** (two symmetrically independent molecules **A** and **B**).

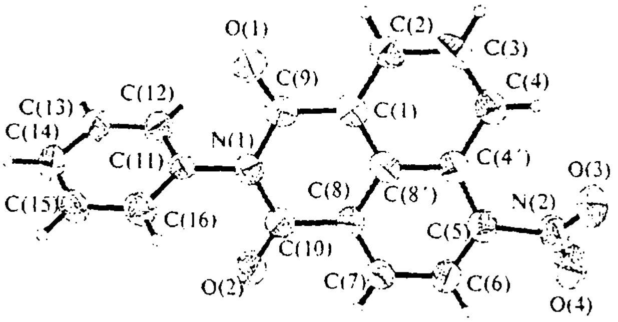


Fig. 3. Structure of compound **10**.

$1 - y$, $2 - z$), 2.21 Å; H(2NC)...O(2A)′ ($1 - x$, $1 - y$, $1 - z$), 2.41 Å; and H(2ND)...O(1B)′ ($1 - x$, $-y - 1$, $1 - z$), 2.22 Å.

According to the results of calculations, the introduction of the electron-releasing and electron-withdrawing substituents at the carbon atoms of the naphthalene fragment (molecules **7**—**9**) does not change the planar equilibrium conformation of the imide ring.

This fact is in good agreement with the results of X-ray diffraction analysis for compound **10** (Fig. 3, see Tables 2 and 3). However, experimental studies of the molecular structure of **11** (Fig. 4) demonstrated that the dicarboximide ring in the crystalline phase adopts a distorted boat conformation. The N(1) and C(9) atoms deviate from the plane through the remaining atoms of the ring by 0.07 and 0.13 Å, respectively. It can be suggested that these deviations are associated with repulsions between the oxygen atoms of the carbonyl groups and the adjacent carbon atoms of the phenyl substituent, which is rotated about the C(Ph)—N bond by only 66.2(5)°. However, in the *N*-phenyl-substituted NDCI derivatives studied previously,[5,22–24] the imide fragment is planar, whereas a virtually identical angle of rotation of the phenyl group (69.4°) is observed in the related *N*-phenylnaphthalenedicarboximide.[23] Therefore, a comparison of the experimental and calculated data provides evidence that the packing effects of the molecules in the crystal substantially affect the geometry of the imide ring in molecule **11**.

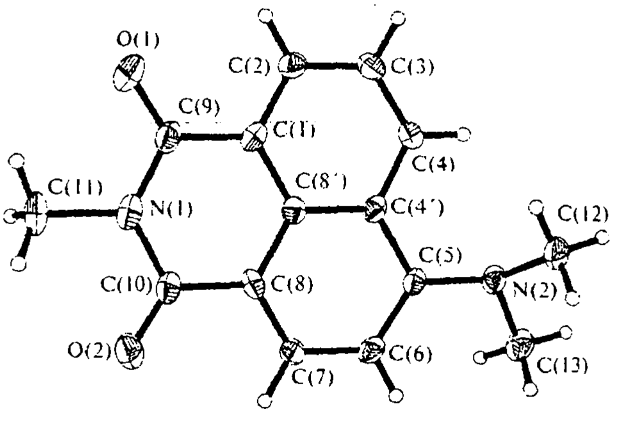


Fig. 4. Structure of compound **11**.

Repulsions between the substituents and the oxygen atoms of the carbonyl groups lead to a noticeable increase in the conformational flexibility of the imide ring in molecules **6a,b** and **7b** (see Table 5). The opposite effect is observed in the case of compound **7a** due, apparently, to the formation of intramolecular N—H...O hydrogen bonds.

The introduction of substituents at other positions of the naphthalene fragment has no effect on the conformational flexibility of the imide ring. A slight increase in the deformation energy of the ring is observed only in molecule **9a** (see Table 5). The insignificant influence of the electronic effects of the substituents on the conformational characteristics of the imide tetrahydro ring confirms the suggestion made previously that conjugation interactions between the naphthalene and imide fragments are weak.

Therefore, the steric effects of the substituents noticeably affect the conformational characteristics of the imide ring, whereas the influence of the electronic factors is insignificant. However, the imide fragment in NDCI as a whole is less sensitive to the effects of the substituents than one would expect based on its high conformational flexibility.

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