

# Unusual behaviour of bis[ $\omega$ -hydroxyalkyl]-1,8,4,5-naphthalenetetracarboxylic bisimides in bisimide–lactam ring contraction: experimental and theoretical study

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## Abstract

A series of novel [ $\omega$ -hydroxyalkyl]-1,8,4,5-naphthalenetetracarboxylic bisimides has been synthesised and tested in the bisimide–lactam ring contraction reaction. It was found that  $N,N'$ -bis[ $\omega$ -hydroxyalkyl]-1,8,4,5-naphthalenetetracarboxylic bisimides with short methylene spacer show unusually low reactivity in bisimide–lactam ring contraction reaction common for six-membered bisimides. The molecular modelling results shows that the reason for such a behaviour is deprotonation of one of the hydroxy groups of bisimides destabilising tetrahedral intermediate — the key intermediate in the ring contraction reaction. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Lactamimides; Ring contraction; Bisimides; Molecular modelling

## 1. Introduction

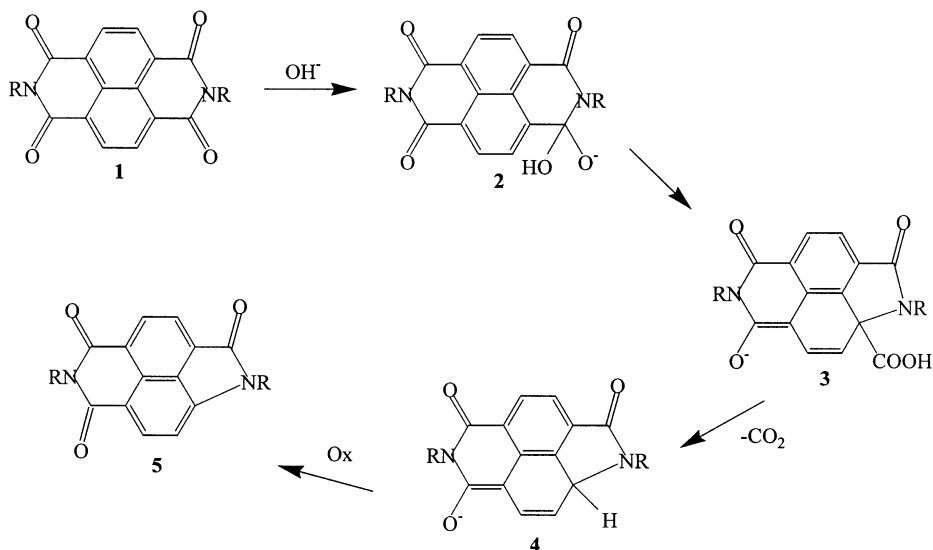
Six-membered ring dicarboximides are commonly viewed as chemically very inert. Strong hydrolysing reagents such as hot, concentrated sulphuric acid or KOH in *tert*-butyl alcohol are required for their saponification [1]. A completely different reaction pathway is observed, however, if under much milder conditions, alkali metal hydroxides in methanol react with six-membered bisimides such as naphthalene-1,8:4,5-tetracarboxylic bisimides producing lactamimides [2] with loss of a C1 fragment from one carboximide. In all cases only one of the imide ring system is transformed to lactam leaving the

second one unchanged and recently the mechanism of this rearrangement has been proposed [3] (Scheme 1; bisimide–lactam ring contraction reaction mechanism). The reaction is initiated by the addition of  $\text{OH}^-$  to one of the imide carbonyl groups. Subsequent ring contraction leads to the formation of a lactam followed by decarboxylation. The decarboxylated product is a dyhydroaromatic species that is oxidised to the aromatic lactamimide. Strong intramolecular charge transfer between lactam and imide groups makes lactamimides good candidates for non-linear optics materials.

The present authors have reported the first synthesis of lactamimide-containing monomers and polymers. Lactamimide-containing monomers were prepared by the ring contraction of the respective six-membered bisimides obtained by the reaction of naphthalene-1,8,4,5-tetracarboxylic dianhydride (**A**) and 6-amino-hexanol and copolymerized with aromatic diacids

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Scheme 1.

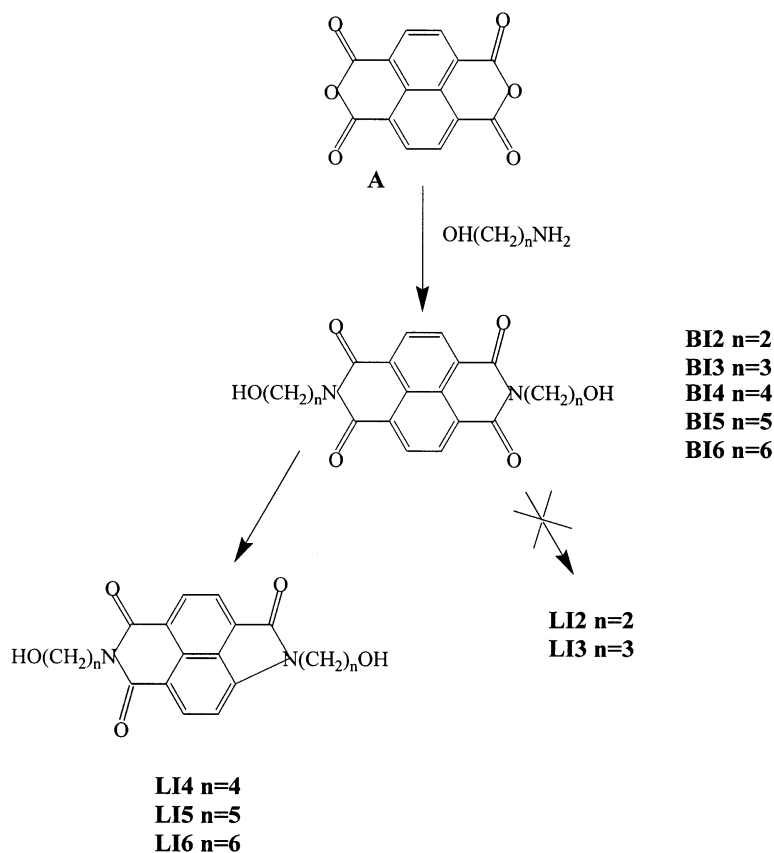
diacetates to give poly lactamimides [4]. To expand a set of available monomers four more bisimides were synthesised starting from **A** and various aminoalcohols such as 4-aminobutanol, 3-aminopropanol and 2-aminoethanol (**BI2–BI6**, Scheme 2; synthetic route to  $N,N'$ -bis( $\omega$ -hydroxyalkyl)-1-amino-4,5,8-naphthalenetetracarboxylic acid-1,8-lactam-4,5-imides) and underwent bisimide–lactam ring contraction to produce the respective monomers. It was found that bisimides **BI4**, **BI5** and **BI6** produce the corresponding lactamimides **LI4**, **LI5** and **LI6** with reasonable yields while **BI2** does not produce **LI2** and **BI3** produces **LI3** with low yield, leaving unchanged significant amount of starting material. To date there have not been reported any specific limitation for bisimide–lactam ring contraction and the goal of this paper is to examine the unusual behaviour of **BI2** and **BI3** bisimides under the ring contraction conditions using the quantum chemistry tools.

## 2. Experimental

A1 reagents were purchased from Aldrich and used without further purification. **BI6** was prepared according to Ref. [4]. The rest of the bisimides were prepared

as follows: a mixture of dianhydride **A** (5 mmol), aminoalcohols (20 mmol) and dioxane (50 ml) was refluxed for 24 h and the reaction mixture was poured into diluted hydrochloric acid. The precipitate was filtered off, and crystallised from *n*-butanol. The m.p. and the mass of molecular ion are listed in Table 1.

*The bisimide–lactam ring contraction.* A mixture of a bisimide (5 mmol), methanol (25 ml), DMSO (25 ml) and KOH (100 mmol) was refluxed for 24 h. In the case of **BI5** and **BI6** the reaction mixture was poured into diluted hydrochloric acid the precipitate was filtered off. In the case of **BI2**, **BI3** and **BI4** the solvent was removed under vacuum. The residue was refluxed with a mixture of ethanol (100 ml) and hydrochloric acid (15 ml). The product was precipitated into water, filtered and dried. The yield of lactamimide was determined by  $^1\text{H-NMR}$  using relation of equivalent naphthalene protons of bisimide to  $\text{H}^2$  proton of lactamimide. NMR spectra were measured on a Varian spectrometer at 300 and 75.5 MHz for H and C nucleus, respectively, in  $\text{DMSO-d}_6$  or  $\text{CDCl}_3$  and mass spectra were taken with JMS-AX505HA (energy 70 eV). A small portion of lactamimides was purified by crystallisation from ethanol to measure m.p. and mass-spectrum (Table 1).



Scheme 2.

Table 1  
The properties of synthesised bisimides and lactamimides

Compound	m.p. (°C) <sup>a</sup>	$M^{+b}$	Yield (%)
<b>BI2</b>	> 300	–	88
<b>BI3</b>	275–276	382	82
<b>BI4</b>	183–185	410	80
<b>BI5</b>	200	438	88
<b>BI6</b>	207	466	83
<b>LI2</b>	–	–	0 <sup>c</sup>
<b>LI3</b>	–	–	65 <sup>c</sup>
<b>LI4</b>	–	–	75 <sup>c</sup>
<b>LI5</b>	120–125	410	> 90 <sup>c</sup>
<b>LI6</b>	132–134	438	> 90 <sup>c</sup>

<sup>a</sup> Melting point (°C).

<sup>b</sup> Mass of molecular ion.

<sup>c</sup> From <sup>1</sup>H-NMR spectra.

### 3. Theoretical methods

All calculations were carried out with GAUSSIAN 98, Revision A.7 program [5]. Firstly, the geometry of all the molecules was optimised to a local minimum in vacuum at HF/6-31 + G level of theory. 6-31G Basis set was augmented with diffuse functions to ensure the correct representation of anionic species. Then the optimisation was repeated at the same level of theory using Onsager's continuum model to take into account the solvent effect. Dielectric constant of 40 was used to model mixture of DMSO–MeOH. To achieve the electron correlation the single point energy was calculated with Becke three parameter hybrid (B3) exchange functional in combination with Lee–Yang–Parr (LYP)

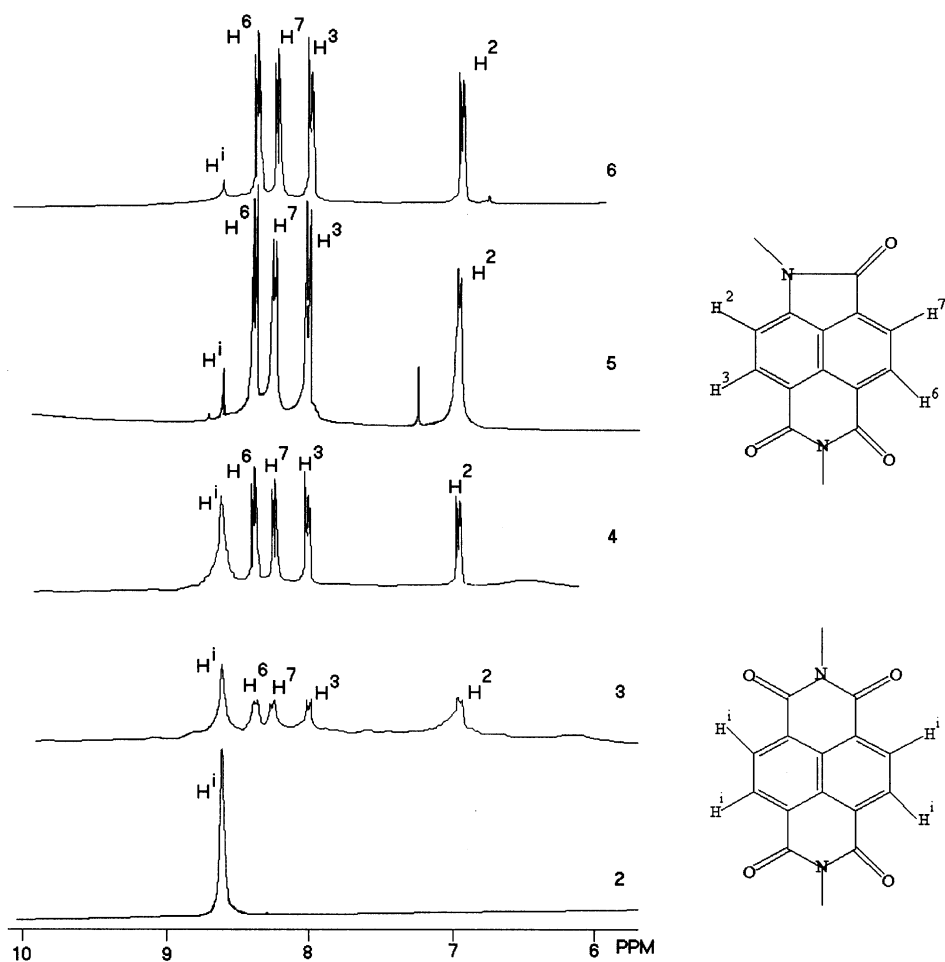


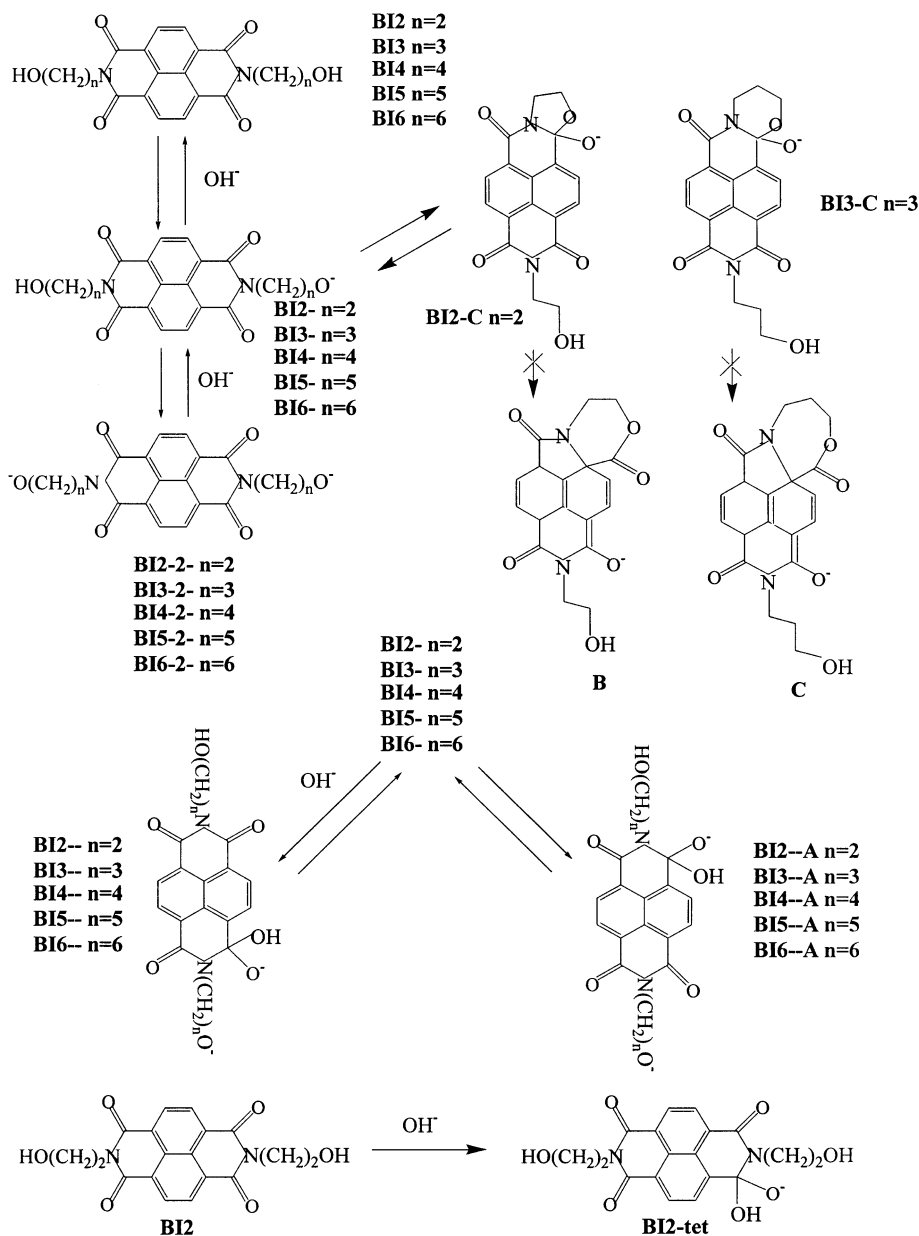
Fig. 1.  $^1\text{H-NMR}$  spectra charts of bisimide–lactamamide ring contraction products (2, 3, 4, 5 and 6 for **BI2**, **BI3**, **BI4**, **BI5** and **BI6** starting materials, respectively).

correlation functional using 6-31 + G(d) basis set and Onsager's continuum model to take into account the solvent effect. Due to the convergence problems existing for negative charged molecules quadratically convergent SCF procedure was requested with SCF=QC keyword when calculating single point energy.

It should be noted that because of long reaction times, irreversible reaction due to the loss of  $\text{CO}_2$  and strong basic conditions the ring contraction reaction is thermodynamically and not kinetically controlled, therefore, the reaction energetics can be used to discuss the reaction paths.

#### 4. Results and discussion

Fig. 1 shows  $^1\text{H-NMR}$  spectra charts of the ring-contraction reaction products of bisimides **BI2**–**BI6**. The relative amount of the starting bisimide in the reaction mixture can be easily determined from the ratio of naphthalenic protons of bisimide (singlet near 8.6 ppm) to four protons of lactamamide (doublets near 8.4, 8.3, 8.0 and 7.0 ppm). As seen from the spectra and Table 1 the conversion for **BI6** and **BI5** is close to 100%, decreasing from **BI4** to **BI2**. It is noteworthy that in the case of **BI2** the starting material was almost quantitatively recovered. To explain such



Scheme 3.

a strong influence of the length of the methylene spacer on the reactivity of bis[ $\omega$ -hydroxyalkyl]-1,8,4,5-naphthalenetetracarboxylic bisimides two hypothesis have been considered. The reaction takes place under strong basic conditions in the presence of excess of KOH. Therefore, there is a possibility of the

abstraction one or two protons from OH groups of bisimides to form charged species (Scheme 3; possible reactions of bisimide containing intermediates) and the acidity of protons should increase with shortening of methylene spacer due to  $-I$  effect of imide nitrogen. The calculations show (Table 2) that

Table 2

The energetics of possible reactions of bisimide containing intermediates

Reaction	$\Delta E$ (kcal/mol)
<b>BI2</b> + OH <sup>-</sup> = <b>BI2-</b> + H <sub>2</sub> O	-86.7
<b>BI3</b> + OH <sup>-</sup> = <b>BI3-</b> + H <sub>2</sub> O	-81.5
<b>BI4</b> + OH <sup>-</sup> = <b>BI4-</b> + H <sub>2</sub> O	-80.3
<b>BI5</b> + OH <sup>-</sup> = <b>BI5-</b> + H <sub>2</sub> O	-78.5
<b>BI2-</b> + OH <sup>-</sup> = <b>BI2(2-)</b> + H <sub>2</sub> O	69.4
<b>BI3-</b> + OH <sup>-</sup> = <b>BI3(2-)</b> + H <sub>2</sub> O	49.1
<b>BI4-</b> + OH <sup>-</sup> = <b>BI4(2-)</b> + H <sub>2</sub> O	48.1
<b>BI5-</b> + OH <sup>-</sup> = <b>BI5(2-)</b> + H <sub>2</sub> O	47.1
<b>BI2</b> = <b>BI2-C</b>	40.3
<b>BI3</b> = <b>BI3-C</b>	31.7
<b>BI2</b> = <b>BI2-tet</b>	-65.7
<b>BI2-</b> + OH <sup>-</sup> = <b>BI2-</b>	18.0
<b>BI2-</b> + OH <sup>-</sup> = <b>BI2-A</b>	24.9
<b>BI3-</b> + OH <sup>-</sup> = <b>BI3-</b>	-18.7
<b>BI3-</b> + OH <sup>-</sup> = <b>BI3-A</b>	6.5
<b>BI4-</b> + OH <sup>-</sup> = <b>BI4-</b>	-44.8
<b>BI4-</b> + OH <sup>-</sup> = <b>BI4-A</b>	-3.4
<b>BI5-</b> + OH <sup>-</sup> = <b>BI5-</b>	-42.0
<b>BI5-</b> + OH <sup>-</sup> = <b>BI5-A</b>	-22.7

anion is easily formed from any bisimide under the reaction condition due to electron-withdrawing imide nitrogen while dianion is already hardly to form, therefore, the main species in the reaction mixture are anions. The ring contraction starts from the attack of OH<sup>-</sup> at carbonyl group of bisimide to produce a tetrahedral intermediate (Scheme 1). Since in the presence of the excess of KOH anions of bisimides dominate in solution, there is a possibility for alkoxide oxygen to attack carbonyl group of the same molecule forming cyclic tetrahedral intermediate. This route is of importance only for **BI2** and **BI3** molecules due to the formation of five and six-membered rings (**BI2-C** and **BI3-C**, Scheme 3). The formation of cyclic intermediates would impede the ring contraction reaction since the next step, the attack of nitrogen at carbon atom of naphthalene ring would produce extremely strained molecules **B** and **C**, respectively (Scheme 3). This mechanism would explain the low reactivity of **BI2** and **BI3** molecules in the ring contraction reaction. The calculations show, however, that **BI2-** and **BI3-** molecules are significantly more stable compared to cyclic intermediates **BI2-C** and **BI3-C** (Table 2), thus showing very low probability of such a mechanism.

Table 3

Total (hartree) and solvation (kcal/mol) energies of studied molecules

Molecule	Total energy (without reaction field)	Total energy (including solvent energy)	Solvation energy
<b>BI2</b>	-1225.273509	-1255.274399	-0.6
<b>BI2-</b>	-1254.501749	-1254.786057	-178
<b>BI3</b>	-1333.901986	-1333.902444	-0.3
<b>BI3-</b>	-1333.210279	-1333.405751	-123
<b>BI4</b>	-1412.509473	-1412.509859	0.24
<b>BI4-</b>	-1411.815277	-1412.007704	-120
<b>BI5</b>	-1491.152271	-1491.153078	-0.5
<b>BI5-</b>	-1490.457559	-1490.636182	-112
<b>BI2(2-)</b>	-1253.985122	-1254.048914	-40.0
<b>BI3(2-)</b>	-1332.632646	-1332.700949	-42.8
<b>BI4(2-)</b>	-1410.764253	-1410.836002	-45
<b>BI5(2-)</b>	-1489.858101	-1489.934595	-48
<b>BI2-C</b>	-1254.713968	-1254.721825	-5.0
<b>BI3-C</b>	-1333.342730	-1333.355243	-7.8
<b>BI2-tet</b>	-1331.159573	-1331.175858	-10.2
<b>BI2-</b>	-1330.362447	-1330.554141	-120
<b>BI2-A</b>	-1330.469719	-1330.543108	-46.1
<b>BI3-</b>	-1408.986806	-1409.232244	-154
<b>BI3-A</b>	-1409.083913	-1409.192115	-67.9
<b>BI4-</b>	-1487.582473	-1487.800324	-136
<b>BI4-A</b>	-1487.640990	-1487.734344	-58.6
<b>BI5-</b>	-1566.241216	-1566.424388	-115
<b>BI5-A</b>	-1566.265748	-1566.393521	-80.2

An alternative explanation of the inhibition of the ring contraction reaction in the case of **BI2** and **BI3** bisimides is the strong positive field effect of alkoxide oxygen formed by proton abstraction destabilising the forming tetrahedral intermediate. It has been found [6,7] that the formation of tetrahedral intermediate is an exothermic process occurring with no activation energy. This is the case for the neutral bisimide molecule. As can be seen from Table 2 the addition of OH<sup>-</sup> to neutral **BI2** molecule to give tetrahedral intermediate **BI2-tet** (Scheme 3) is highly exothermic process with  $\Delta E$  of -65.7 kcal/mol. However, as it was mentioned above under the conditions of the ring contraction reaction the hydroxy-terminated bisimide molecules are in the form of anions. In this case the first step of the ring contraction must be the formation of tetrahedral intermediate which is dianion. Two types of tetrahedral intermediates to be considered are shown in Scheme 3. Table 2 clearly shows that the formation of tetrahedral intermediates for

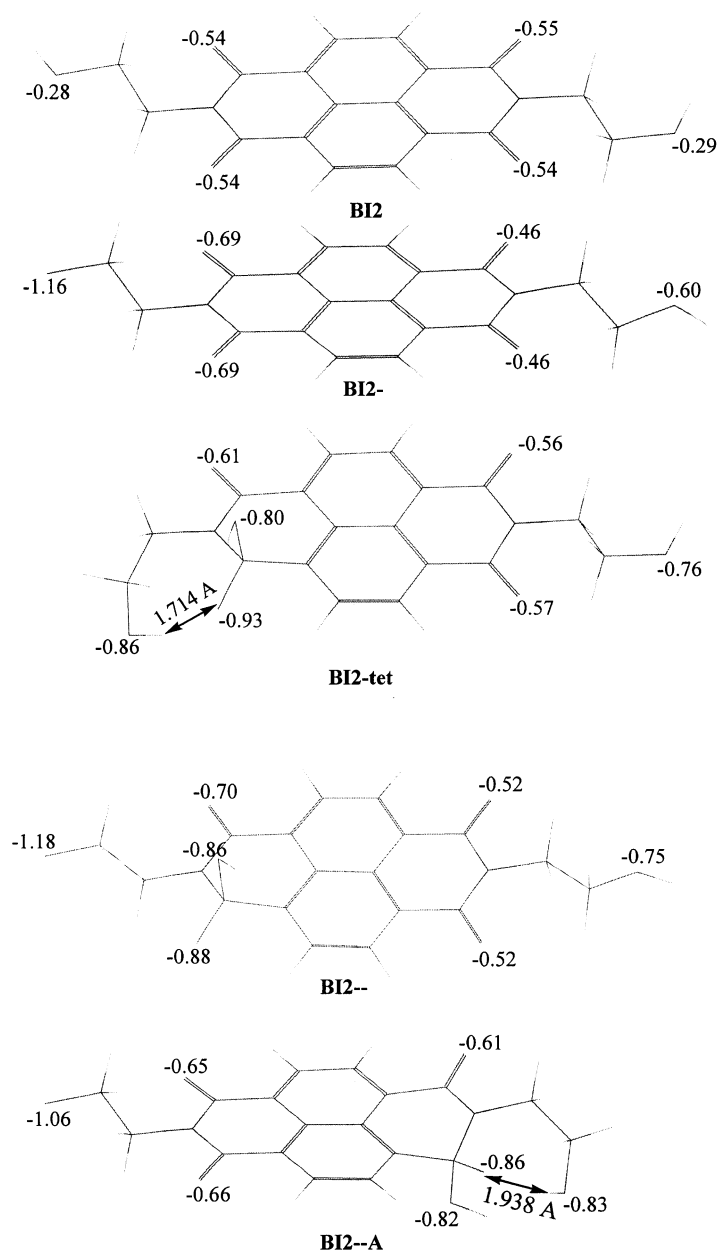


Fig. 2. Equilibrium geometries and Mulliken charges of some molecules calculated at B3LYP/6-31+G(d)//HF/6-31+G level of theory using the Onsager reaction field model.

**BI2-** molecule is hardly possible due positive and large  $\Delta E$  of 18 and 24.9 kcal/mol for **BI2-** and **BI2-A** molecules, respectively. For **BI3-** molecule the formation of tetrahedral intermediates is more favour-

able, as followed from Table 2, however, the formation of **BI3-A** intermediate is still barely possible due to positive  $\Delta E$  of 6.5 kcal/mol. In the case of **BI4-** and **BI5-** molecules the formation of both

types of tetrahedral intermediates becomes thermodynamically favourable, although, the addition of  $\text{HO}^-$  to carbonyl group is a less exothermic process than that for uncharged molecule. As can be expected the destabilisation of tetrahedral intermediates caused by the electrostatic repulsion between two negatively charged oxygen atoms decreases with the length of methylene spacer. It is noteworthy, however, that contrary to the expectations, **A** type of intermediate molecules are not stabilised compared to another one as could be expected from the fact that the separation distance between formal negative charges is always larger in **A** type intermediates. This apparent contradiction can be understood by examining Table 3. When the gas phase energies are considered, **A** type intermediates are always more stable as expected. However, the solvation energies of **A** type intermediates are much lower giving as a result less stable **A** intermediate in solution. The most obvious explanation of this fact is smaller dipole moment of **A** type intermediates leading to their worse solvation, as seen of the electronic density distribution in the molecules of interest.

Fig. 2 represents the optimised geometries and the Mulliken charges on oxygen atoms for **BI2**, **BI2-**, **BI2-tet**, **BI2-** and **BI2-A** as examples. **BI2** molecule the Mulliken charges on hydroxyl oxygens are about  $-0.3e$ . The deprotonation of **BI2** leads to **BI2-** molecule where alkoxide oxygen has negative charge of  $-1.16e$  and the oxygen of other hydroxyl group increase its negative charge by  $-0.3e$  compared to neutral **BI2** molecule. In a similar way the formation of **BI2-tet** intermediate leads to almost equal charges on both hydroxyl oxygens. It means that in spite of methylene spacer the negative charge is delocalised over the entire molecule. As a result of this redistribution of electron density the attack of  $\text{OH}^-$  at any of the carbonyl groups of deprotonated molecules leads to the destabilisation of the formed tetrahedral intermediate. Therefore, the ring contraction reaction is impossible to occur for **BI2** molecule due to positive  $\Delta E$  for any tetrahedral intermediate formation (Table 2). The starting material will be recovered after acidification of reaction mixture (exactly what was observed in practice). In the case of **BI3** molecule the longer methylene spacer favours the formation of tetrahedral intermediate **BI3-**, however  $\Delta E$  of the reaction is only  $-18.7$  kcal/mol, much higher than

for neutral bisimide molecule ( $-65.7$  kcal/mol) and  $\Delta E$  of the formation of **BI3-A** molecule is positive. Therefore, the ring contraction is possible for **BI3** molecule, however due to the strong shielding of carbonyl groups by the negative charge the stability of tetrahedral intermediates is low resulting in relatively low yield of the product. **BI4**, **BI5** and **BI6** compounds produces the corresponding lactamimides with reasonable yields which reflects in negative  $\Delta E$  of the formation of tetrahedral intermediates due to the long methylene spacers decreasing interactions between negative charges. However, even in the cases of **BI5-** anion the addition of  $\text{OH}^-$  is significantly less exothermic than that for the reaction of neutral bisimide molecule with  $\text{OH}^-$  anion (Table 2).

In conclusion, it was found that the reactivity of *N,N'*-bis( $\omega$ -hydroxyalkyl)naphthalene-1,8,4,5-tetracarboxylic bisimides in bisimide–lactam ring-contraction reaction dropped with shortening of methylene spacer. While bisimides **BI5** and **BI6** gave high yields of lactamimides **BI2** does not participate in the ring contraction reaction. The calculation shows that this phenomenon is due to the abstraction of one of the proton from a hydroxyalkyl group by  $\text{OH}^-$  ion. The excessive negative charge on the molecule destabilises the tetrahedral intermediate in the case of short methylene spacers formed by an addition of another  $\text{OH}^-$  to imide carbonyl — the key intermediate in the ring contraction reaction.

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