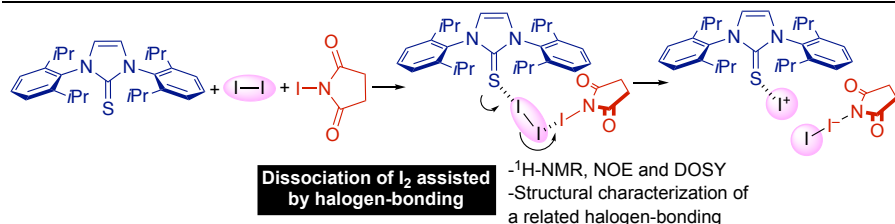# Halogen-Bonding Interaction between I_2 and *N*-Iodosuccinimide in Lewis Base-Catalyzed Iodolactonization

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Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan
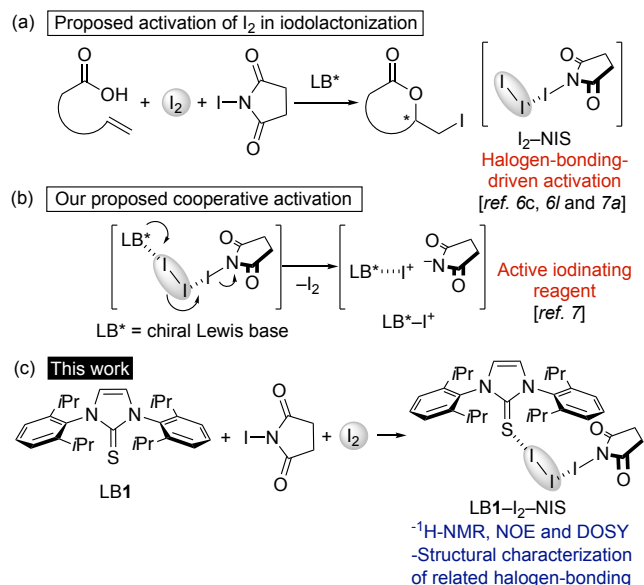*KEYWORDS: halogen-bonding, iodine, N-iodosuccinimide, Lewis base, iodolactonization*

Dissociation of I_2 assisted by halogen-bonding

-^{1}H-NMR, NOE and DOSY
-Structural characterization of a related halogen-bonding

ABSTRACT: Halogen-bonding interaction between I_2 and *N*-iodosuccinimide (NIS) stabilized by a Lewis base (LB) has been explored. ^{1}H-NMR, NOE and DOSY suggest a generation of a 1:1:1 assembly, LB–I_2–NIS. In contrast, when *N*-iodotrifluoromethanesulfonimide (INTf$_2$) is used instead of NIS, LB–I_5^+–LB is generated. Based on these results in combination with DFT calculations, we propose a mechanism for the formation of I_2–NIS and the subsequent generation of an active iodinating species LB–I^+.

Electrophilic iodolactonization has been recognized as a powerful method for constructing various lactones while introducing an iodine atom.[1,2] Therefore, tremendous effort has been devoted to the development of iodolactonization for the synthesis of natural products.[3] In general, an iodinating reagent, such as *N*-iodosuccinimide (NIS), is less reactive than the corresponding brominating reagent.[4,5] To enhance the inherent reactivity of NIS, the combination of NIS with iodine (I_2) has been recently developed for use in enantioselective iodocyclizations (Scheme 1a).[6,7] In more than 10 studies,[6,7] the combination of NIS with I_2 has dramatically improved both the yield and enantioselectivity. This activation is believed to be due to halogen-bonding between I_2 and NIS to provide highly active I_2–NIS, although there has been no structural characterization.[6c,l] Our group has developed an enantioselective iodolactonization catalyzed by a chiral Lewis base in the presence of I_2.[7] We proposed that a chiral Lewis base (LB*) can activate I_2 in cooperation with NIS, to provide LB*–I^+ as a reactive iodinating reagent (Scheme 1b).[7] Even in the case of a weak LB*, the generation of LB*–I^+ is facilitated with cooperative activation by halogen-bonding. In this combination system, the actual iodinating reagent is I_2, not NIS.[7] However, little is known about activation by halogen-bonding between I_2 and NIS.[8] Therefore, it is difficult to clarify the activation of I_2 through the halogen-bonding interaction between I_2 and NIS. To elucidate the details of such halogen-bonding, further studies, such as NMR and structural characterizations, are required

To this end, we were intrigued by the use of a sterically-demanding LB such as thiourea **1** (Scheme 1c).[9] According to our recent report,[10] LB**1** behaves as a sufficient ligand for the isolation of a LB**1**–I_2–I_2 complex. Labile interaction of I_2–I_2 is

enhanced by σ-donation of the thiocarbonyl moiety of LB**1**. Moreover, steric repulsions of LB**1** help to stabilize the halogen-bonding interaction. Based on these findings,[10] we speculated that I_2–NIS would also be stabilized in the presence of sterically-demanding LB**1**. With stabilized I_2–NIS in hand,

Scheme 1. Proposed Activation by I_2 in Iodolactonization

(a) Proposed activation of I_2 in iodolactonization

I_2–NIS
Halogen-bonding-driven activation
[*ref. 6*c, *6l* and *7a*]

(b) Our proposed cooperative activation

LB* = chiral Lewis base

Active iodinating reagent
[*ref. 7*]

LB*–I^+

(c) This work

LB**1**

LB**1**–I_2–NIS
-^{1}H-NMR, NOE and DOSY
-Structural characterization of related halogen-bonding

we began to characterize the chemical and structural features of halogen-bonding interaction.

Initially, we applied ^{1}H-NMR to LB**1**, I$_2$ and NIS in CD$_2$Cl$_2$. When LB**1** was treated with one equivalent of I$_2$, peaks of LB**1** were shifting quantitatively (Table 1, entry 2). Subsequent addition of NIS also facilitated changes of chemical shift of LB**1** and NIS in 5 min (Table 1, entry 3). These quantitative shifts of ^{1}H-NMR suggest an association equilibrium of these three components when 1:1:1 of LB**1**, I$_2$ and NIS are used. On further ^{1}H-NMR studies for LB**1**–I$_2$–NIS at –20 °C, a nuclear Overhauser effect (NOE) was observed between NIS (H^d) and LB**1** (H^a and H^c) (Table 1, LB**1**–I$_2$–NIS). Analysis by diffusion-ordered NMR spectroscopy (DOSY) confirmed the assembly of LB**1**, I$_2$ and NIS, which presumably was LB**1**–I$_2$–NIS (Figure 1); the diffusion coefficients D of NIS [8.94x10^{-10} m^{2}s^{-1}, log D = –9.05] and **A** [6.88x10^{-10} m^{2}s^{-1}, log D = –9.16] decreased in magnitude upon the formation of LB**1**–I$_2$–NIS [5.96x10^{-10} m^{2}s^{-1}, log D = –9.22] (Figure S3).

Table 1. ^{1}H NMR of LB1, LB1–I$_2$, LB1–I$_2$–NIS and NIS in CD$_2$Cl$_2$ at 25 °C^a and NOE of LB1–I$_2$–NIS
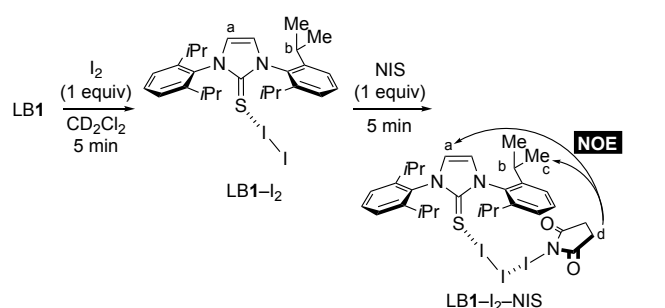
entry	Sample^a	Chemical shift of H^a (ppm)	Chemical shift of H^b (ppm)	Chemical shift of H^d (ppm)
1	LB1	6.87	2.73	–
2	LB1–I$_2$	7.23	2.54	–
3	LB1–I$_2$–NIS	7.29	2.51	2.80
4	NIS	–	–	2.99

^{a} [LB**1**] = 67 mM, [I$_2$] = 67 mM and [NIS] = 67 mM in CD$_2$Cl$_2$ under a nitrogen atmosphere at 25 °C.
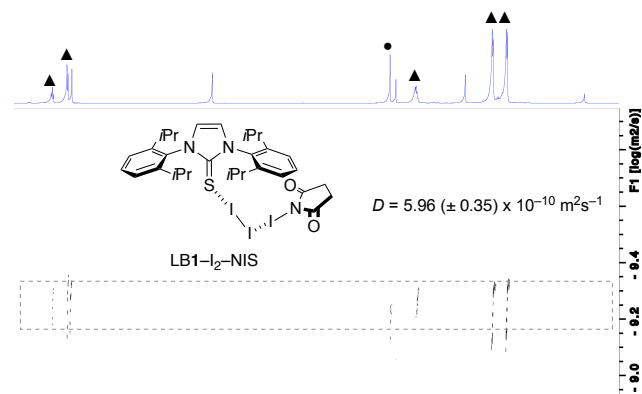
Figure 1. Diffusion coefficients of LB**1**–I$_2$–NIS in CD$_2$Cl$_2$ at –20 °C. Chemical shifts of LB**1** (▲) and NIS (●).

Next, we attempted to isolate LB**1**–I$_2$ and LB**1**–I$_2$–NIS. In the solid-state of LB**1**–I$_2$,[11] the coordination of LB**1** to I$_2$ was observed (Figure 2a). As a result of σ-donation from LB**1**,

elongated I(1)–I(2) (2.879 Å) was observed in comparison with that of free I$_2$ (2.715 Å).[12] In contrast, isolable LB**1**–I$_2$–NIS was not obtained under any condition. Therefore, more electron-deficient iodinating reagent was used in place of NIS. Eventually, instead of LB**1**–I$_2$–NIS, LB**1**–I$_5^+$–LB**1** was obtained when N-iodotrifluoromethanesulfonimide (INTf$_2$) was used (Scheme 2). The structure of LB**1**–I$_5^+$–LB**1** (resting state) can be described as the combined structure of LB**1**–I$_3^+$ (active state) and LB**1**–I$_2$; *i.e.,* after the generation of LB**1**–I$_3^+$ from LB**1**–I$_2$ with INTf$_2$, highly electrophilic LB**1**–I$_3^+$ is immediately captured by another LB**1**–I$_2$. To understand the structure of I$_2$–NIS, we looked at LB**1**–I$_5^+$–LB**1**, which contains I$_3^+$ of LB**1**–I$_3^+$. When we looked at I$_3^+$ [I(3)–I(4)–I(5)] of LB**1**–I$_5^+$–LB**1** (Figure 2b), a bent structure was observed, in accordance with previous studies.[13] In addition, LB**1**–I$_5^+$–LB**1** has highly polarized poly-iodine bonds [I(3)–I(4) (3.183 Å) *vs* I(4)–I(5) (2.902 Å)]. These polarized iodine bonds indicate electron-donation from LB**1** as well as the electron- acceptance from I$^+$ of INTf$_2$. Thus, the elongation of I$_2$ by halogen-bonding interaction suggests the activation of I$_2$ by an iodinating reagent. It is worth mentioning that there have been only two reports on the crystallographic characterization of I$_5^+$.[14,15] The key for the isolation of labile I$_5^+$ of LB**1**–I$_5^+$–LB**1** should be σ-donation to I$_5^+$ and the steric repulsion of LB**1**.
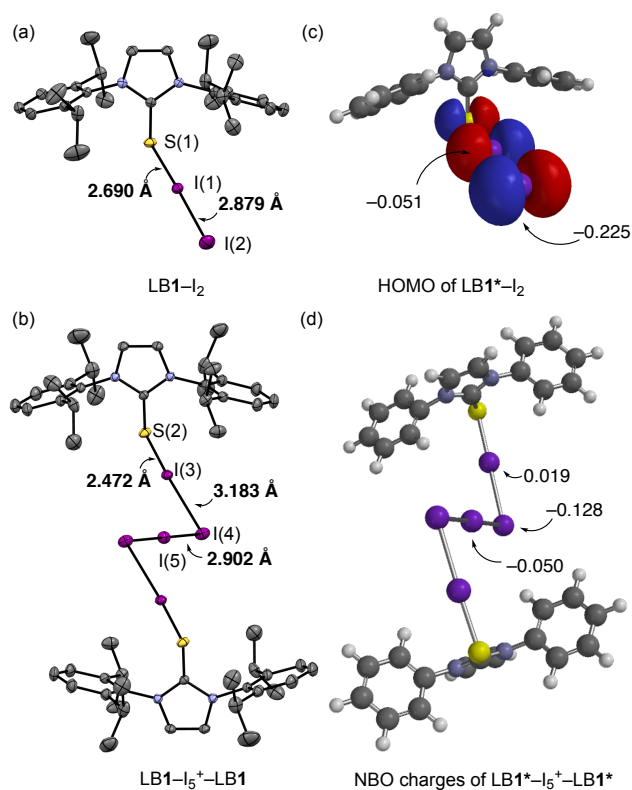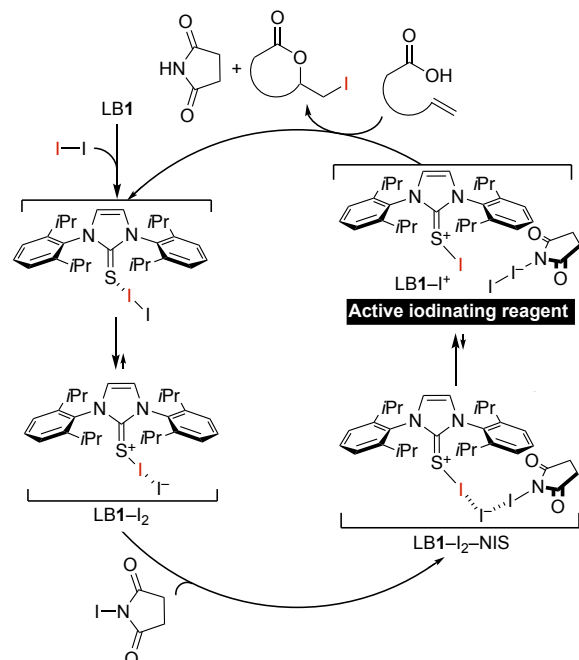

Figure 2. (a) and (b) ORTEP drawings of LB**1**–I$_2$ and LB**1**–I$_5^+$–LB**1** showing the thermal ellipsoids at the 50% probability level (hydrogen atoms and anion have been omitted for clarity). (c) HOMO and NBO charges of LB**1***–I$_2$. (d) NBO charges of LB**1***–I$_5^+$–LB**1***.

Scheme 2. Synthesis of Pentaiodonium Cation
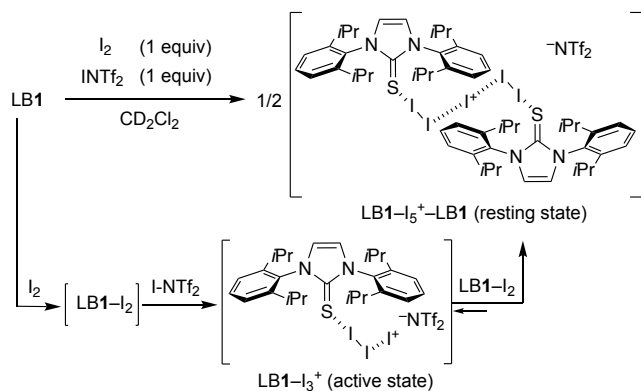
Scheme 3. A Proposed Mechanism

To gain further insight into the generation of halogen-bonding, theoretical calculations were performed on LB**1***–I$_2$ and LB**1***–I$_5^+$–LB**1*** where iPr moiety of LB**1** was removed. The HOMO of LB**1***–I$_2$ was mainly comprised of the p-orbital of the coordinated I$_2$ (Figure 2c). In addition, the NBO charge of I(2) [–0.225] in comparison with that of I(1) [–0.051] indicates that I(2) is nucleophilic iodine (Figure 2a and also see Table S2). This result suggests that LB**1***–I$_2$ has a nucleophilic p-orbital of I(2) toward the iodinating reagent, which also accounts for the bent structure of I$_3^+$. Regarding LB**1**–I$_5^+$–LB**1***, NBO charges of iodine atoms suggest that I(3) [0.019] was more cationic than I(4) [–0.128] and I(5) [–0.050] (Figure 2d). If we consider that I(3)–I(4) is the longest bond [3.183 Å], the dissociation of I(3)–I(4) is more likely than that of I(4)–I(5). Based on structural characterizations and calculations, a proposed mechanism for the generation of I$_2$–NIS by LB**1** is shown in Scheme 3. First, LB**1** coordinates to I$_2$, which gives LB**1**–I$_2$. Subsequent nucleophilic attack occurs by the p-orbital of I$_2$ toward NIS. After generation of LB**1**–I$_2$–NIS, cooperative activation by LB**1** with NIS may facilitate

the bond dissociation of I$_2$. The resulting electrophilic LB**1**–I$^+$ could be a reactive iodonium cation for iodolactonization. In this proposed mechanism, the generation of LB**1**–I$^+$ may be accelerated by cooperative activation in comparison with that without I$_2$. In addition, the resulting iodonium cation has a less-coordinating I$_2$-succinimide anion, which enhances the electrophilicity of I$^+$. These properties of I$_2$ may be the key for boosting the reactivity and selectivity in iodolactonizations.

To check this cooperative activation, we examined the iodolactonization of **2a** with/without I$_2$ in the presence of NIS (Table 2). The corresponding product **3a** was not obtained in the absence of both LB**1** and I$_2$ (entry 1). The addition of 20 mol% of I$_2$ improved the reactivity (entry 2). The yield was further increased when 5 mol% of LB**1** was used in the presence of I$_2$ (entry 3). In contrast, the yield dramatically decreased in the absence of I$_2$ even when LB**1** was used (entry 4).

Table 2. The Effect of I$_2$ and LB1 for Iodolactonization[a]

entry	LB1 (mol%)	I$_2$ (mol%)	yield (%) of 3a
1	0	0	0
2	0	20	20
3	5	20	75
4	5	0	35

[a] The reaction was carried out with LB**1** (5 mol%), I$_2$ (0–20 mol%), **1a** (1 equiv), NIS (1 equiv) in CH$_2$Cl$_2$ at –30 °C

Table 3. The Comparison Experiments[a,b]
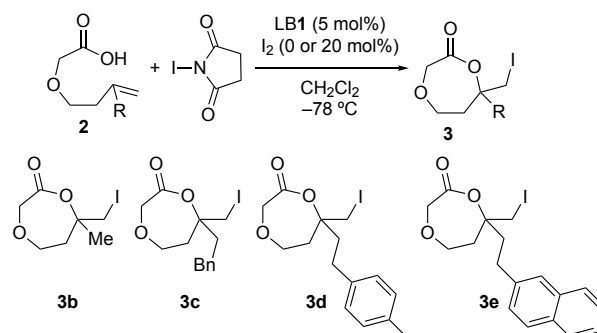
entry	2	3	yield (%) of 3
1	2b	3b	79 [30]
2	2c	3c	78 [14]
3	2d	3d	89 [55]
4	2e	3e	94 [46]
5	2e	3e	91

[a] The reaction was carried out with LB**1** (5 mol %), I$_2$ (20 mol %), **2** (0.12 mmol, 1 equiv) and NIS (1 equiv) in CH$_2$Cl$_2$. [b] The yields of **3** in the absence of I$_2$ are given in brackets. [c] The reaction was conducted at 1.0 mmol scale of **2e**.

Next, we further explored medium-size ring iodolactonization with/without I_2 (Table 3). Although medium-size ring iodolactonizations are presumably slow,[16–18] **3b–3e** were successfully constructed. In contrast, the yield of **3** was decreased in the absence of I_2. These results support the cooperative activation of I_2 by LB**1** and Lewis acidic NIS through halogen-bonding.

In conclusion, halogen-bonding interaction of Lewis base, I_2 and Lewis acidic NIS has been explored by NMR studies, structural characterizations and theoretical calculations. Halogen-bonding interactions between I_2 and NIS and between I_2 and LB may promote the generation of iodonium cation. The results of iodolactonization with/without I_2 support the notion that these halogen-bonding interactions accelerate the rate of the reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental procedures, full spectroscopic data for all new compounds, X-ray data for LB**1**–I_2 and LB**1**–I_5^+–LB**1**, and copies of ^1H, ^{13}C, and ^{19}F NMR spectra (PDF)

Accession Codes

CCDC 1952239 and 1952240 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
The authors declare no competing financial interest.

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