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Preparation of a C_{70} Bis-heterocyclic Derivative with High Chemio- and Regioselectivity

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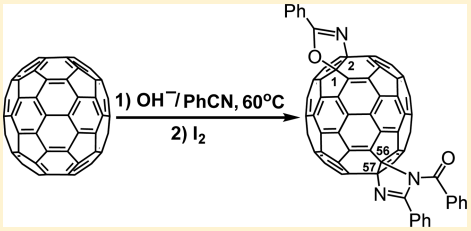
Supporting Information

ABSTRACT: C_{70} bis-heterocyclic derivative (**1**) bearing one oxazoline ring and one imidazoline ring with the 2 o'clock configuration is obtained with high chemio- and regioselectivity via the reaction of C_{70} with hydroxide and benzonitrile quenched with I_2. Further study with benzylation experiment and theoretical calculations indicate that the oxazoline ring is the one first formed on the C_{70} cage, while the imidazoline ring is the one formed after the addition of I_2 via a radical coupling reaction mechanism.



Heterocyclic compounds, which typically have five- or six-membered rings with heteroatom(s) of nitrogen, oxygen, and/or sulfur, constitute an extremely important and diverse group of organic compounds and are of great significance to life and materials science. Accordingly, studies on the preparation of heterocyclic fullerene derivatives are of importance and have attracted intense interest during the exploration of fullerene chemistry, where a large variety of fullerene-fused heterocyclic compounds have been obtained.[1−19] However, studies on the fullerene heterocyclic derivatives are mostly confined to the C_{60} monoheterocyclic derivatives, while reports on C_{60} bis-heterocyclic[19] and C_{70} heterocyclic derivatives[2b,4,8f,j,14b,19] are very limited, and no reports on preparing C_{70} bis-heterocyclic derivatives have appeared so far.

Compared to the preparation of fullerene monoadducts, the achievement of the regiocontrol is crucial in the synthesis of fullerene bis-adducts.[20] Different from the highly symmetrical C_{60} molecule (I_h), the molecule of C_{70} possesses a lowered D_{5h} symmetry, where the [6,6]-double bond in the polar region (α-type bond) is the most reactive due to the highly strained structure in this region.[21] Consequently, the bis-addition reactions of C_{70} would more likely result in the bis-adducts with a configuration of 2, 5, and/or 12 o'clock according to the nomenclature introduced by Diederich and co-workers,[22] where the two addends are positioned at the two distinctive polar regions of the C_{70} cage (Figure 1; there are also bis-adducts with the 10 and 7 o'clock configurations, but they are the enantiomers of the 2 and 5 o'clock regioisomers, respectively, and indistinguishable by MS, NMR, and UV−vis spectral characterizations). The distribution of the 2, 5, and 12 o'clock regioisomers seems to be quite dependent on the specific reactions. The 2, 5, and 12 o'clock regioisomers were obtained with a ratio of roughly 6:1:3 for the Bingel−Hirsch reactions, which is significantly different from the statistical 2:2:1 ratio for the addition site;[21,22] while a high regiocontrol was achieved for the Diels−Alder reaction of C_{70} with molten anthracene, with the formation of only the 12 o'clock regioisomer;[23] however, a mixture of various regioisomers were obtained for the Diels−Alder bisaddition of indene to C_{70}, where the 2 o'clock single regioisomer was isolated and exhibited a superior photovoltaic performance than the mixture of the bis-adducts.[24]

We and several other groups have recently reported the synthesis of the oxazoline and imidazoline derivatives of C_{60}.[8,14] We have extended the work to C_{70} and obtained the respective oxazoline and imidazoline derivatives of C_{70}.[8f,j,14b] Impressively, only monoheterocyclic derivatives are formed, while no bis-heterocyclic products are reported.[8,14] Herein, we report further extension of the work with the production of a C_{70} bis-derivative bearing one oxazoline and one imidazoline heterocycle with the 2 o'clock configuration (compound **1**, Figure 2).

Compound **1** was obtained by reaction of C_{70} with OH^- (TBAOH, tetra-*n*-butylammonium hydroxide) and benzonitrile (PhCN, solvent) at 60 °C quenched with I_2. Table 1 lists the results of reaction screening and the benzylation experiment. The monoheterocyclic compounds bearing an oxazoline or imidazoline ring (compounds **2**, **3**, and **4** in Figure 2) were also obtained during the screening experiment, and their structures were confirmed by comparing with previously reported spectral data.[8a,f,14b] The reaction temperature and the ratio of OH^- to fullerene are important factors affecting the product distribution. Only C_{70} mono-oxazoline (**2**) was obtained when the reaction was carried out at a temperature of 30 °C (entries 1 and 2) or when a small molar ratio of 3:1 between OH^- and C_{70} was used, even though the reaction was carried out at a higher temperature of 60 °C (entry 3). As the molar ratio of OH^- to C_{70} was increased from 3:1 to 6:1, 9:1, and 12:1, and the reaction temperature was elevated to 60 °C, the C_{70} bis-heterocyclic derivative bearing both oxazoline and imidazoline rings with the 2 o'clock configuration (compound **1**) was

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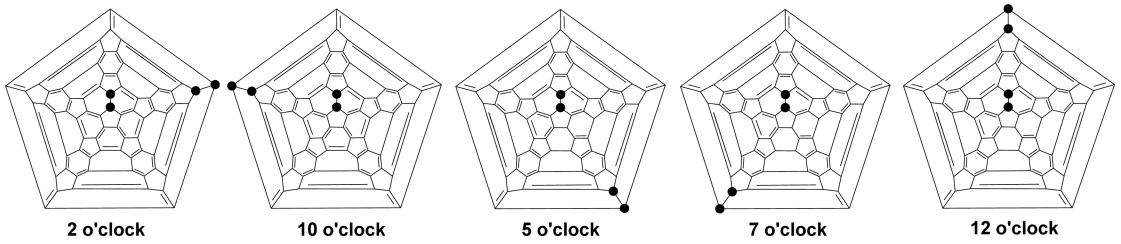

Figure 1. Schlegel diagrams of the 2, 10, 5, 7, and 12 o'clock regioisomers of C_{70} bis-adducts. Adducts with the 10 and 7 o'clock configurations are the enantiomers of the 2 and 5 o'clock regioisomers, respectively.

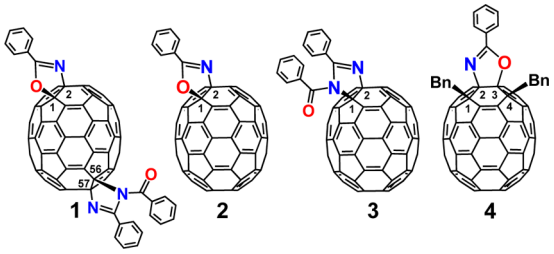

Figure 2. Illustrated structures of compounds **1**–**4**.

Table 1. Results of Reaction Screening[a] and the Benzylation Experiment

entry	fullerene	OH^- (equiv)	temp (°C)	product	% yield[b]
1	C_{70}	3	30	**2**	40
2	C_{70}	9	30	**2**	21
3	C_{70}	3	60	**2**	36
4	C_{70}	6	60	**1**	16
5	C_{70}	9	60	**1**	**28**
6	C_{70}	9	60	**1**	20[c]
7	C_{70}	12	60	**1**	10
8	C_{70}	9	90	**1**	14
9	C_{70}	6	120	**3**	31
10	C_{70}	9	120	**3**	33
11	C_{70}	9	60	**4**	22[d]
12	C_{60}	9	60	mixture	

[a]Reaction conditions: TBAOH (1.0 M in MeOH) and C_{70} or C_{60} (50 mg) were added into PhCN (20 mL) under argon at the preset temperature. The reaction was allowed to proceed under stirring for 50 min before quenching with I_2 (one equiv to TBAOH). [b]Isolated yield. [c]The reaction was allowed to proceed for 90 min. [d]The reaction was quenched with BnBr (Bn = benzyl, 40 equiv to C_{70}).

obtained (entries 4–7). The reaction exhibits very impressive chemio- and regioselectivities as indicated by the approximate 8:1 ratio between compound **1** and two closely eluted small fractions (see Figure S1 (Supporting Information) for the HPLC trace), which are also the C_{70} bis-heterocyclic derivatives as identified by HRMS (Figures S10 and S12, Supporting Information) but not the 5 or 12 o'clock adduct on the basis of UV–vis absorptions (Figures S11 and S13, Supporting Information).[22,25]

A molar ratio of 9:1 between OH^- and C_{70} and a reaction temperature of 60 °C seem to be most appropriate for the generation of the C_{70} bis-heterocyclic compound (entry 5). Less amount of **1** was obtained when a smaller (entry 4) or greater (entry 7) ratio of OH^- to C_{70} was used, due to either the incompletion of the reaction or the overrun side reaction that leads to the formation of more toluene-insoluble polymeric materials. Increase of the reaction time from 50 to 90 min resulted in a lower yield of **1** due to the formation of more toluene-insoluble materials (entry 6). Further increase of the temperature to 90 and 120 °C, however, produced less bis-heterocyclic compound and gradually resulted in C_{70} monoimidazoline (compound **3**, entries 8–10), consistent with previous results that fullerene imidazolines are more preferentially formed at an elevated temperature, likely due to the enhanced reaction between OH^- and PhCN.[14b] Interestingly, dibenzylated C_{70} oxazoline (compound **4**) was obtained when BnBr was used instead of I_2 to quench the reaction at 60 °C (entry 11, see Figure S7 (Supporting Information) for HPLC), while no dibenzylated C_{70} imidazoline, which has been shown to be a stable compound,[26] was detected from the reaction mixture. The result indicates explicitly that the oxazoline heterocycle was first formed on the C_{70} cage, while no imidazolination took place before the addition of I_2, consistent with previous work that a higher temperature (90 °C) is required to accomplish the imidazolination of C_{60} and C_{70}.[14b] Different from the result of C_{70}, the reaction of C_{60} (entry 12) results in a rather complicated product mixture (see Figure S8 (Supporting Information) for HPLC), which is difficult to purify for further characterization, demonstrating the importance of the enhanced reactivity at the two distinctive polar regions of C_{70} in achieving the formation of compound **1**.

The structure of compound **1** is established on the basis of HRMS, UV–vis, ^1H, and ^{13}C NMR spectral characterizations. The protonated molecular ion of the compound ($[M + H]^+$) appears at 1182.12482 in the HRMS spectrum (Figure S3, Supporting Information), in agreement with the theoretical value of the molecule ($[M + H]^+$: $C_{91}H_{16}N_3O_2$, calcd 1182.12370). The UV–vis spectrum of the compound (Figure S4, Supporting Information) shows absorptions at 369, 423, 473, 533, and 653 nm, which are characteristic absorptions for C_{70} bis-adducts with the 2 o'clock configuration,[22,25] indicating unambiguously that compound **1** has the 2 o'clock configuration as the UV–vis absorptions are sensitive toward the structure of the fullerene adducts rather than the type of addends.[27] The ^1H NMR spectrum (Figure S5, Supporting Information) only shows resonances due to the phenyl protons from 6.8 to 8 ppm, confirming the absence of aliphatic protons in the compound. The ^{13}C NMR spectrum (Figure S6, Supporting Information) shows four weak resonances at 93.98, 89.07, 87.90, and 79.34 ppm corresponding to the sp^3 C_{70} carbons bonded to the heteroatoms of the oxazoline and imidazoline rings, which are in good agreement with the chemical shifts of the counterpart carbon atoms in the C_{70} monoadduct bearing the same oxazoline (92.97, 86.67 ppm)[8f] or imidazoline (bound to amino N: 78.22 ppm)[14b] heterocycle in the polar region. In addition, a total of 66 signals are shown for the sp^2 carbons of C_{70} cage of compound **1**, and resonances arising from the two imino carbon atoms are shown at 163.74 and 160.21 ppm, along with the signal corresponding to the

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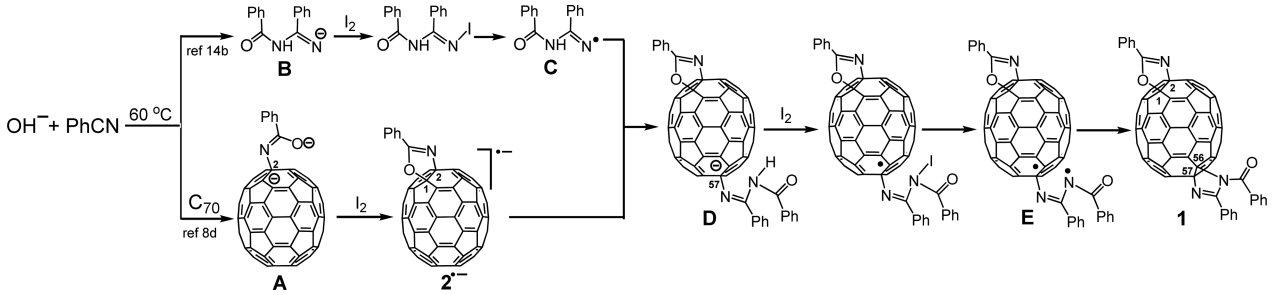
Scheme 1. Proposed Mechanism for the Formation of 1



carbonyl carbon of the benzoyl group at 170.42 ppm, consistent with the structural assignment of compound **1**.

Control experiment starting with compounds **2** (C_{70} monooxazoline) was performed, as the imidazolination occurs in the second step during the formation of **1**. The TBAOH/PhCN solution was first heated to 90 °C in order to convert OH^- to anionic amidine by reacting with PhCN (see Experimental Section),[14b] which would enhance the imidazolination and inhibit the oxazolination of **2**, as the OH^- is required to initiate the oxazolination reaction of neutral fullerene species.[8d,e] The solution temperature was then lowered to 60 °C with the addition of compound **2**, in order to have the imidazolination reaction proceed under conditions similar to that for the formation of **1**. However, a much lower control of the product distribution was shown by the appearance of many partially overlapping peaks in the HPLC trace (Figure S9, Supporting Information), which are difficult to purify for further characterization. Such a discrepancy suggests that the imidazoline heterocycle in compound **1**, which is constituted after the construction of the oxazoline heterocycle, is likely formed via a mechanism different from the typical nucleophilic addition mechanism involved for the imidazolination of a neutral compound,[14b] and that the I_2 is also involved in the reaction rather than just functioning as an oxidant during the formation of **1**.

Scheme 1 shows the proposed mechanism for the formation of **1**. Intermediate **A** ($\mathbf{2}^{2-}$) of the singly bonded C_{70} phenylimidate dianion is first formed via the OH^--initiated nucleophilic addition to C_{70}.[8d] The imino nitrogen atom of the phenylimidate is bound to C_{70} at C2 due to the higher reactivity of the apical carbon atoms with respect to the other C_{70} carbon atoms, and the two electrons are distributed at the C_{70} cage and the unbonded oxygen atom, respectively.[8f,28] Meanwhile, intermediate **B** of monoanionic amidine is formed via the tandem nucleophilic reactions of OH^- with two PhCN molecules at 60 °C,[14b] even though the resulting amidine anion is unable to compete with OH^- to react with C_{70} under the experimental conditions, probably due to the lower reactivity of the intermediate **B**. Direct imidazolination of dianionic intermediate **A** via the nucleophilic addition of anionic amidine intermediate **B** as is the case for imidazolination of neutral fullerenes[14b] is, however, unlikely due to the electron-rich nature of intermediate **A**. Instead, the imidazolination of **A** can be achieved via a radical coupling reaction mechanism after adding I_2 into the reaction system. With the addition of I_2, intermediate **A** can be converted into $\mathbf{2}^{\bullet-}$ by removing one electron accompanied by the ring closure with the formation of the O–C_{70} bond.[28] Simultaneously, the amidine monoanion of intermediate **B** may react with I_2 and form the imino N–I bond,[10b] which would subsequently undergo homolytic cleavage, yielding the amidine radical intermediate **C** with the radical at the imino nitrogen atom.[8g,18,10b] The resulting intermediates $\mathbf{2}^{\bullet-}$ and **C** may then undergo a radical coupling reaction, generating the intermediate **D**, which has one oxazoline ring and a negative charge on the C_{70} cage, and a singly bonded amidine at the apical carbon atom C57 due to its higher reactivity. The intermediate **D** can be further converted into intermediate **E**, where the C_{70} cage bears one radical due to the removal of one electron from the carbon cage by I_2, and the amino nitrogen of the singly bonded amidine bears a radical facilitated by the formation and homolytic cleavage of the amino N–I bond.[10b] The two radicals may then subsequently undergo the coupling reaction, resulting in compound **1** eventually.

Theoretical calculations with Gaussian 09 at the B3LYP/6-311G(d) level were performed to rationalize the unique regioselectivity exhibited during the formation of **1**. Figure 3

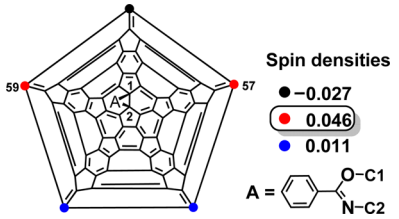


Figure 3. Schlegel diagram of $\mathbf{2}^{\bullet-}$ with partial spin densities on the apical carbon atoms of the pentagon in the unoccupied polar region.

shows the Schlegel diagram of $\mathbf{2}^{\bullet-}$ with partial spin densities on the apical carbon atoms of the pentagon in the unoccupied polar region, which are the typical reaction sites for the subsequent additions.[21] The calculations predict a significant difference of the spin density among these carbon atoms, where C57 and C59 possess the largest spin density of 0.046, while the other three carbon atoms possess a much lower spin density of −0.027 and 0.011, suggesting that the addition of the radical intermediate **C** at C57 or C59 would be more preferential. The addition at C57 and C59 would generate both the 2 and 10 o'clock bis-adducts, which are enantiomers and are indistinguishable under the experimental conditions. The calculations are in good agreement with the experimental result and consistent with the radical coupling reaction mechanism for the imidazolination process during the formation of compound **1**.

The results therefore indicate that the addition of the oxazoline or imidazoline to C_{70} is rather regioselective in compound **1**, with the imino nitrogen atoms of both heterocycles positioned at C2 and C57, and the oxygen and the amino nitrogen atoms at C1 and C56 (Figure 2). Such an orientation is consistent with that of the heterocycle in C_{70}

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mono-oxazoline or imidazoline derivative[8f,14b] and the higher reactivity of the apical C_{70} carbon atoms with respect to the other carbon atoms.

In summary, we have shown a highly chemio- and regioselective synthesis of a bis-heterocyclic C_{70} derivative bearing both oxazoline and imidazoline rings with the 2 o'clock configuration. The reaction takes place via a stepwise manner, where the imidazolination process in the second step occurs via a radical mechanism and is crucial in achieving such selectivity. To the best of our knowledge, this is the first time that a bis-heterocyclic C_{70} derivative with a well-defined structure has been obtained, which has extended the scope of heterocyclic fullerene derivatives.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under an atmosphere of Ar. All reagents were obtained commercially and used without further purification, unless otherwise noted. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. ^{1}H NMR spectra were recorded on a 600 MHz spectrometer, and ^{13}C NMR spectra were recorded on a 150 MHz spectrometer. Accurate MS measurements were performed using an ESI electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI FT-ICR MS).

Preparation of Compound 1. Typically, 535 μL of TBAOH (1.0 M in methanol, 535 μmol) and 50 mg of C_{70} (59.5 μmol) were placed into 20 mL of freshly distilled benzonitrile solution which was heated to 60 °C. The reaction was allowed to proceed for 50 min and was then quenched with I_2 (136 mg, 535 μmol). The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAOH and I_2. The crude product was added to toluene, and the soluble part was purified over a semipreparative HPLC silica column (10 mm × 250 mm) by eluting with a 70:30 v/v mixture of toluene/hexane (flow rate, 3.7 mL/min; detector wavelength, 380 nm), which affords compound **1** as the predominant fraction, along with two closely positioned minor factions (Figure S1, Supporting Information). However, the purification of compound **1** from the two minor fractions cannot be achieved by using the Buckyprep HPLC columns, which are typical for the purification of fullerene derivatives. Compound **1** was obtained as the predominant product with an isolated yield of 28% (19.7 mg), along with about 2 mg of regioisomers of compound **1** as characterized by HRMS and UV−vis.

Spectral Characterization of ***1****.* Positive ESI FT-ICR MS, m/z calcd for $C_{91}H_{16}N_3O_2^+$ $[M + H]^+$, 1182.12370; found, 1182.12482; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 7.94 (*d*, 2H), 7.35 (*m*, 3H), 7.25 (*m*, 4H), 6.96 (*m*, 4H), 6.88 (*t*, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), all signals represent 1C except when noted: δ = 170.42, 163.74, 160.21, 156.37, 156.13, 156.09, 155.44, 155.02, 154.88, 152.80, 152.73, 151.94, 151.90, 151.74, 151.53, 151.49, 151.42, 150.86, 150.84, 150.18, 149.79, 149.75, 149.70, 149.64, 149.62, 149.47, 149.31, 149.28, 148.42, 148.24, 147.99, 147.71, 146.91, 145.97, 145.66, 145.28, 145.23, 144.93, 144.58, 144.38, 144.36, 144.11, 143.95, 143.23, 142.51, 142.45, 141.58, 141.56, 140.70, 140.49, 140.28, 140.20, 139.87, 139.74, 139.58, 138.98, 138.78, 138.55, 135.76, 135.40, 134.59, 134.55, 134.40, 133.86, 133.83, 133.60, 133.19, 132.53 (2C), 132.50, 132.35, 132.28, 130.82, 130.58, 129.55 (2C), 129.30 (2C), 128.88 (2C), 128.80 (2C), 128.36 (2C), 128.33 (2C), 126.62, 93.98, 89.07, 87.90, 79.34. UV−vis (toluene): λ_{max} 369, 423, 473, 533, 653 nm.

Benzylation Experiment. The procedures of the benzylation experiment were similar to those for the preparation of compound **1**, except that BnBr (40 fold) was used instead of I_2. The identity of compound **4** was confirmed by the ^{1}H NMR and UV−vis characterizations as compared with previous work.[8f]

Control Experiment with C_{60} as the Starting Material. The procedures were similar to those for the preparation of compound **1**, except that C_{60} was used instead of C_{70}. The crude product was examined by HPLC using a Buckyprep column eluted with toluene at a flow rate of 3.7 mL/min with the detector wavelength set at 380 nm, which indicated the reaction resulted in a mixture of products that were difficult to purify.

Control Experiment with Compound 2 as the Starting Material. Typically, 95 μL of TBAOH (1.0 M in methanol, 95 μmol) was added into 12 mL of freshly distilled benzonitrile solution, and the solution was stirred for 50 min at 90 °C to afford intermediate **B**. The solution was then cooled to 60 °C, and 11.6 mg of **2** (12.1 μmol) was added. The reaction was allowed to proceed for 45 min and was then quenched with I_2 (24 mg, 95 μmol). The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAOH and I_2. The obtained crude product was subjected to HPLC analysis, which indicated that the reaction resulted in a mixture of products that were difficult to purify.

Computational Methods. The structure of $\mathbf{2}^{\bullet-}$ was optimized with Gaussian 09 at the B3LYP/6-31G level, followed by harmonic frequency calculation at the same level to confirm it as the energy minimum. The spin density of $\mathbf{2}^{\bullet-}$ was obtained with Gaussian 09 at the B3LYP/6-311G(d) level.

ASSOCIATED CONTENT

Supporting Information

HPLC traces of the reaction mixtures, spectral data of new compounds, and computational details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00511.

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Notes

The authors declare no competing financial interest.

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