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An unprecedented [5,6]-open adduct via a direct benzyne- C_{60} cycloaddition

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ABSTRACT

Cycloaddition is one of the best-studied types of reactions in the organic chemistry of fullerenes, engendering [6,6]-closed adducts in the vast majority of cases. Notwithstanding that a formation of open fulleroid structures is undoubtedly of theoretical interest, no one has demonstrated the conformation of [5,6]-open fulleroid via the direct cycloadditions. Here, we establish that cycloaddition between C_{60} and benzyne in situ generated from 2-amino-4,5-dibutoxybenzoic acid affords a new type of elusive [5,6]open structure that is characterized on the basis of NMR, UV–vis spectroscopy, and cyclic voltammetry. Additionally, from density functional theory (DFT) calculations for possible [5,6]-open and [6,6]closed adducts induced of benzyne- C_{60} reaction, as expected, features such as the charge distributions, binding characteristics, and frontier molecular orbital levels, are affected by the different binding modes in C_{60} cage.

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1. Introduction

Among a large variety of protocols developed for chemical modification of buckminsterfullerene,^{1–4} functionalization by addition reactions is one of the most powerful methodologies in fullerene chemistry.^{3–7} In the fullerenes, the kinetic and thermodynamic products are derived from 'localized' addition, that is, 1,2-addition across 6,6-bonds or 1,4-addition across six-membered rings, as well as the halodiester anion⁸ and the azomethine ylide dipolar cycloaddition⁹ to 6,6-bonds of the carbon spheres. Furthermore, despite the fact that benzyne typically reacts with polycyclic aromatic compounds by [4+2] cycloaddition, the cycloaddition of benzyne with C₆₀ favorably occurs at 6,6-ring junctions, resulting in a [6,6]-closed adduct in which benzyne adds across one of the interpentagonal bonds (forming a cyclobutene in the process (see the right of Fig. 1)).^{10–12} One reason for this type of reactivity is certainly due to the fact that in a hypothetical [4+2] adduct one

unfavorable [5,6]-double bond in the lowest energy valence bond (VB) structure is required.⁴ As a result, the synthesis of [5,6]isomers has hitherto proven to be essentially unobserved.^{3,4} Up to now, there are no experimental data available for [5,6]-bridged compounds with an open transannular bond by the direct cycloadditions with C_{60} . In contrast to such principles and results, we found that open [5,6]-bridged fullerene as an atypical result was exclusively obtained by the benzyne- C_{60} reaction (see the left of Fig. 1). Herein, we report on the structural characteristics and









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features of the open [5,6]-structure including density functional theory (DFT) calculations that support the binding modes in the fullerene framework.

2. Results and discussion

With respect to a direct cycloaddition of benzyne to C_{60} , in our initial study, we chose commercially available 2-amino-4,5-dimethoxybenzoic acid as an in situ generated benzyne substrate. A solution of C_{60} in *o*-dichlorobenzene was treated with 2-amino-4,5-dimethoxybenzoic acid and isoamyl nitrite at 100 °C for 24 h. Purification by column chromatography on silica gel afforded a benzyne- C_{60} monoadduct as a major product and a regioisomeric mixture of bisadducts, respectively. The ¹H NMR spectrum of the monoadduct shows a singlet signal at δ 7.57 ppm in the aromatic region and a singlet resonance at δ 3.99 ppm corresponding to the methoxy protons, implying the $C_{2\nu}$ structural conformation (see Supplementary data). These observations well agree with the characterization of the [6,6]-closed adduct previously reported by C_{60} -benzyne reaction.¹¹

In the course of our study on the benzyne- C_{60} reaction, we proceeded to prepare 2-amino-4,5-dibutoxybenzoic acid (4) as a benzyne precursor since the fullerene monoadduct with the methoxy groups on the phenyl ring, after complete drying, possesses only limited solubility in common organic solvents, leading to difficulty in facilitating its spectral characterization. The procedures for the synthesis of the anthranilic acid with two butoxy chains for the generation of benzyne are outlined in Scheme 1. The synthetic procedures and characterization data are described in Supplementary data (e.g., nucleophilic substitution, nitration, reduction, and saponification). The same procedure, above, using 4 instead of 2-amino-4,5-dimethoxybenzoic acid was adopted for the synthesis of fullerene-benzyne monoadduct. Chromatography on silica gel yielded unconverted C₆₀ (first fraction), a monoadduct (second fraction, 15%, m/z 940⁺), and a mixture of bisadducts (third fraction, 12%, m/z 1160⁺). To our surprise, the ¹H NMR spectrum of the monoadduct reveals two singlets of equal intensity at δ 7.69 and 7.64 ppm produced by the phenyl ring (Fig. 2a). Moreover, the resonances related to the butoxy protons appear to be nonequivalent and thus reveal divided peaks, such as two triplets at 4.01 and 3.84 ppm for α -methylene protons ($-OCH_2CH_2CH_2CH_3$), two multiplets at 1.79 and 1.69 ppm for β -methylene protons $(-OCH_2CH_2CH_2CH_3)$, two multiplets at 1.40 and 1.28 ppm for γ methylene protons (-OCH₂CH₂CH₂CH₃), and two triplets at 0.86 and 0.75 ppm for methyl protons (-OCH₂CH₂CH₂CH₂CH₃), respectively.



[5,6]-Open Regioisomer

Scheme 1. Synthesis of [5,6]-open regioisomer via the benzyne-C₆₀ cycloaddition.



Fig. 2. ¹H NMR (a) and ¹³C NMR (b) spectra of [5,6]-open regioisomer in 3:1 CS₂/acetone- d_6 .

Such ¹H NMR patterns suggest that the product has two geometric isomers with different conformations of the dibutoxybenzene moiety, bringing to mind the formation of an open [5,6]-structure.

As shown in Fig. 2b, the ¹³C NMR spectrum shows 28 carbon signals corresponding to fullerene carbons in the sp² region $(\delta = 140 - 160 \text{ ppm})$ and each of four butoxy peaks in the sp³ region $(\delta = 69.55, 69.49, 32.21, 32.09, 20.47, 20.39, 14.80, and 14.72 ppm)$ (see HETCOR and HMBC in Supplementary data for further information). In conjunction with such observations, surprisingly, the resonances at δ 60–80 ppm, assigned to the quaternary bridgehead carbons of the fullerene cage, which are the sites of attachment of the benzyne moiety, were not observed, supporting the open annulene structure. However, the caveat exists that being guaternary carbons, their intensity is expected to be very low. This observation is in opposition to our and other groups' results previously studied of the C_{60} -dimethoxybenzyne reaction, in which even with the good dienophile benzyne, C₆₀ does not react as diene but rather forms a [2+2] cycloadduct¹¹ since the dienes prefer to attack the shorter carbon-carbon bond linking two sixmembered rings, rather than the carbon-carbon bond in the junction between five- and six-membered rings.¹³⁻¹⁵ However, the asymmetry of ¹H NMR and the absence of sp³ carbon atoms in the ¹³C NMR spectrum of the fullerene cage forced us to conclude formation of the elusive [5,6]-open structure.

Assuming that a direct attack on a σ -bond in C₆₀ would be unprecedented, a plausible hypothesis may be formulated (see Scheme 2). The benzyne first forms the [2+2] adduct, which can facilitate the subsequent rearrangement because the butoxy groups are more electron releasing than the methoxy groups. Of course,



Scheme 2. The mechanism proposed to explain the formation of [5,6]-open regioisomer.

one would have to prove this hypothesis, which would make this a much more extended study. For example, how do more electron releasing substituents (dialkylamino) on the benzyne affect this product formation?

To obtain further additional evidence on the assignment of the [5.6]-open structure, we subsequently undertook investigations on its characteristic absorption and electrochemical behavior. Fig. 3 depicts the UV-vis absorption characteristics of C_{60} . (6.6)-phenvl-C₆₁-butyric acid methyl ester (PCBM), and [5,6]-open regioisomer in chloroform solution, where the absorption spectra for the pristine C₆₀ and PCBM obtained in this study are listed for comparison (see Table 1). In the case of the PCBM, the absorption characteristics for the [6,6]-closed fullerene derivatives including the typical band at around 430 nm are observed,^{16–18} reflecting the partially broken symmetry $(C_{2\nu})$ of the fullerene core, relative to pristine C_{60} (I_h) .^{16,4} On the other hand, the similarity of the absorption features between pure C₆₀ and [5,6]-open regioisomer is revealed with particularly the absence of the diagnostic peak at 430 nm for the closed isomers. An immediate consequence, which stems from lifting a carbon-carbon bond, located along a hexagon-pentagon junction, is that 60π -electron nature of the fullerene core is largely conserved in the [5,6]-open isomer.



Fig. 3. UV-vis absorption of C₆₀, PCBM, and [5,6]-open regioisomer in CHCl₃ solution.

Table 1

Optical data

Compound	Absorption (nm)	
C ₆₀	330, 405, 540, 600(sh), 623(sh)	
PCBM	328, 430, 490, 603(sh), 695	
[5,6]-Open regioisomer	319, 417(sh), 540(sh), 600(sh), 690	

The cyclic voltammetry (CV) data are summarized in Table 2 (see Fig. 4). The reduction potentials of PCBM as a [6,6]-closed model are shifted to more negative values with respect to C_{60} due to a decrease in its number of π -electrons and release of strain energy.¹⁹ In contrast, the first reduction values reveal similarities between

Table 2

Electrochemical data^a

Compound	$E_{\rm red}^1$	$E_{\rm red}^2$	$E_{\rm red}^3$
C ₆₀	-1.071	-1.484	-1.969
PCBM	-1.158	-1.540	-2.039
[5,6]-Open regioisomer	-1.036	-1.558	-2.036

^a Experimental conditions: values for 0.5 ($E_{pa}+E_{pc}$) in V versus Fc/Fc⁺; 10⁻⁴ to 10⁻³ mol/L *o*-DCB solution; Bu₄NClO₄ (0.1 M) as supporting electrolyte; Pt wire as counter electrode; 50 mV/s scan rate.



Fig. 4. Cyclic voltammograms of C₆₀, PCBM, and [5,6]-open regioisomer.

[5,6]-open regioisomer and C_{60} , which is not unexpected since it is isoelectronic analogue of C_{60} (60π -electrons).

Quantum-chemical calculations at the density functional theory (DFT) level using B3LYP/6-31G (Gaussian 03 package)²⁰⁻²² were conducted to establish qualitative charge distribution, binding characteristics, and frontier molecular orbital levels of [5,6]-open and [6,6]-closed products. For the [6,6]-closed product (Fig. 5a), two bridgehead sp^3 carbons in the C_{60} cage are negatively charged (-0.188e) and the carbon atoms of the phenyl ring bound to the C₆₀ skeleton are positively charged (+0.072e), clearly showing that a resonance effect is donation of the alkoxy side chains as solubilizers on the phenylene to C₆₀. As shown in Fig. 5b, a similar trend is observed in the [5,6]-open adduct, however, each conjoined carbon between the benzene and C₆₀ exhibits different values in spite of the structurally identical positions, supporting the broken symmetry (see the electrostatic charge distributions in Supplementary data for further information). This notion is completely consistent with the nonequivalent resonances in the ¹H NMR spectrum. In addition, the standard enthalpies of formation (ΔH_f^0) were computed from the enthalpies of reaction (ΔH_r^0) of the each fullerene



Fig. 5. Calculated Mulliken charges (top; red (negative), green (positive)) and optimized structures (bottom; the unit of bonding length is Å (gray: carbon, red: oxygen, and white: hydrogen atoms)). (a) [6,6]-Closed and (b) [5,6]-open products of the benzyne– C_{60} cycloaddition.

reactions. The $\Delta H_{\rm f}^{\rm o}$ were determined 538 kcal/mol for [5,6]open and 614 kcal/mol for [6,6]-closed, while the $\Delta H_{\rm r}^{\rm o}$ were 16 kcal/mol for [5,6]-open and –33 kcal/mol for [6,6]-closed, respectively. Thus, the formation of [6,6]-closed adduct is favored over by approximately 50 kcal/mol. Note that, for both [5,6]-open and [6,6]-closed products with methoxy groups, the charged values of the bridgehead carbons show identity, reflecting the symmetry (see the bottom of Fig. S2 in Supplementary data). It is interesting to note that the charge distribution of [5,6]-open structure is more positively charged when compared to [6,6]closed product (see the range of the scale bar) and its reckoned binding charge (|0.20|e) is somewhat lower than that obtained by the closed product (|0.26|e).

The optimized structures for both the [5,6]-open and [6,6]closed products are shown in the bottom of Fig. 5. In the case of [6,6]-closed junction, the butoxy substituents on the phenyl ring exhibit a planar geometry with the bonds connecting benzyne to C_{60} of 1.53 Å and the sp² bond of 1.37 Å in the cyclobutene formation. An unusually long interior C_{60} bond length of 1.66 Å is noticeable, compared with typical values for benzocyclobutenes (1.58-1.60 Å).²³ The bond lengths in the bridged bicyclic system of the [5,6]-open adduct are 1.37 Å long for the sp² character and 2.46 Å long for the distance between two bridgehead carbons in C₆₀. Interestingly, for the [5,6]-open product, the bridging C–C bond between the fullerene (C^F) and benzyne (C^B) is relatively shorter (1.48 Å) as compared to the [6,6]-closed product (see the above), implying that the binding of the open structure is slightly stronger. Besides, the resultant values by using 6-31G(d) are almost identical to those above (see Fig. S3 in Supplementary data).

In addition, the DFT results reveal considerable dipole moments of 4.01 D and 5.27 D for [6,6]-closed and [5,6]-open products, respectively. These dipole moments are different compared to their counterpart products with methoxy groups ([6,6]-closed=1.48 D and [5,6]-open=1.62 D), respectively, implying the different polarizability of the fullerene derivatives depending on the degree of the chain length of alkoxy groups. The calculated stabilization energies are 476.23 kcal/mol for [6,6]-closed and 596.26 kcal/mol for [5,6]-open. The calculated HOMO energies of -5.78 eV for both the products are essentially the same. However, the LUMOs are estimated to be -3.16 eV and -3.19 eV for [6,6]-closed and [5,6]-open products, respectively (Fig. 6). This suggests that the reduction potentials of the functionalized C₆₀ derivatives are sensitive to the binding mode in fullerene framework. This above study clearly shows the qualitative effects of the bridge modes in a fullerene cage, i.e., [5,6]-open versus [6,6]-closed, as a function of the changed fullerene's π -system.



Fig. 6. HOMOs and LUMOs of (a) [6,6]-closed and (b) [5,6]-open products.

3. Conclusion

In conclusion, we have discovered a novel reaction of C_{60} with in situ generated benzyne from 2-amino-4,5-dibutoxybenzoic acid, which affords one monoadduct identified as a [5,6]-open annulene adduct. The structure of [5,6]-open isomer has been characterized by ¹H NMR and ¹³C NMR spectra, which are supported by additional evidence such as UV–vis spectroscopy and electrochemical

behavior. Additionally, the theoretical study of the possible two [5,6]-closed and [5,6]-open products for the benzyne– C_{60} reaction enables one to access the influence of the binding modes in the fullerene framework. Altogether, the present work provides an example showing a contrast with [6,6]-closed adduct of benzyne– C_{60} previously reported by several research groups. Research in cycloaddition of C_{60} to benzynes with various substitutions is currently under way to help us not only prove the proposed mechanism but also access the correlation of the different formations between C_{60} and benzyne compounds.

4. Experimental section

4.1. Materials and instruments

All starting materials were purchased either from Aldrich or Acros and used without further purification. All solvents are ACS grade unless otherwise noted. Anhydrous THF was obtained by distillation from sodium/benzophenone prior to use. Anhydrous toluene was used as received. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury Vx 200 MHz, Varian Unity Inova 500 MHz, or Varian VNMRS 600 spectrophotometer using CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard and MALDI-MS spectra were obtained from Ultraflex III (Bruker, Germany). UV-vis spectra were taken on Cary 5000 (Varian USA) spectrophotometer. Cyclic voltammetry (CV) measurements were performed on Solartron SI 1287 with a three-electrode cell in a 0.1 M tetra-*n*-butvlammonium perchlorate (Bu₄NClO₄) solution in acetonitrile at a scan rate of 50 mV/s at room temperature under argon. A silver wire, a platinum wire, and a platinum disk were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/Ag⁺ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard.

4.2. Synthesis of methyl-3,4-dibutoxybenzoate (1)

Methyl-3,4-dihydroxybenzoate (10.0 g, 59.4 mmol), n-butylbromide (24.4 g, 178.2 mmol), and K₂CO₃ (28.7 g, 207.9 mmol) were added to methanol (250 ml) and refluxed for 24 h. After evaporating solvent, the mixture was then extracted into ethyl acetate and washed with brine. The crude product obtained was purified by chromatography on silica with 0-10% ethyl acetate in hexane as eluent. Isolated yield=12.8 g (77%) as a colorless liquid. ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.64 (dd, J=8.41, 2.04 Hz, 1H), 7.54 (d, J=2.01 Hz, 1H), 6.87 (d, J=8.44 Hz, 1H), 4.05 (dt, J=6.56, 6.56, 0.98 Hz, 4H), 3.89 (s, 3H), 1.83 (m, 4H), 1.51 (m, 4H), 0.99 (t, *J*=7.31 Hz, 6H). ¹³C NMR (CDCl₃, 50.2 MHz): δ 166.42, 152.61, 147.91, 122.96, 113.56, 111.27, 68.34, 68.08, 51.32, 30.66, 30.55, 18.65, 13.33. ESI-MS (m/z): 280 $((M)^{+})$. Elemental analysis: calculated for C₁₆H₂₄O₄: C, 68.54; H, 8.63; O, 22.83. Found: C, 68.23; H, 8.51; O, 22.53. FTIR (v/cm⁻¹): 3009, 2971, 2841, 1721, 1602, 1519, 1435, 1298, 1275, 1172.

4.3. Synthesis of 2-nitro-4,5-dibutoxy-methylbenzoate (2)

A flask immersed in a room-temperature ice bath was charged with methyl-3,4-dibutoxybenzoate (10 g, 35.7 mmol) and acetic acid (glacial, 52 mL). Over a 15-min period, HNO₃ (70%, 54 mL) was added dropwise with stirring. The orange solution was stirred at room temperature overnight. The reaction was quenched upon addition of ice. The cooled mixture was extracted with diethyl ether, washed with water, NaHCO₃, NaOH, and brine and then dried over MgSO₄. The crude product obtained was purified by chromatography on silica with 0-10% ethyl acetate in hexane as eluent. Isolated yield=10.7 g (93%) as a light yellow liquid. ¹H NMR

 $(200 \text{ MHz}, \text{CDCl}_3) \delta$ (ppm) 7.44 (s, 1H), 7.04 (s, 1H), 4.09 (dt, *I*=6.52, 6.51, 2.55 Hz, 4H), 3.90 (s, 3H), 1.84 (m, 4H), 1.52 (m, 4H), 0.99 (t, *I*=7.44 Hz, 6H). ¹³C NMR (CDCl₃, 50.2 MHz): δ 165.96, 152.01, 140.30, 120.83, 111.28, 107.63, 68.82, 52.62, 30.27, 18.55, 13.21. ESI-MS (m/ z): 325 ((M)⁺•). Elemental analysis: calculated for $C_{16}H_{23}NO_6$: C, 59.06; H, 7.13; N, 4.31; O, 29.50. Found: C, 59.35; H, 7.35; O, 29.73. FTIR (ν/cm^{-1}) : 3043, 2982, 2853, 1727, 1581, 1525, 1475, 1456, 1359, 1270.

4.4. Synthesis of 2-amino-4,5-dibutoxy-methylbenzoate (3)

An round-bottomed flask equipped with a stirring bar was immersed in a room temperature ice bath and charged with SnCl₂·2H₂O (100 g, 441.7 mmol) and HCl (concentrated, 100 mL). A solution of 2-amino-4,5-dibutoxy-methylbenzoate (9.0 g, 27.7 mmol) in EtOH (30 mL) was added and the mixture was stirred at room temperature overnight. The mixture was poured into ice and filtered washed with water. The resulting white solid was taken up in EtOH (30 mL) and poured into aqueous NaOH, filtered and dried. Isolated yield=7.7 g (97%) as a colorless solid. ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.34 (s, 1H), 6.11 (s, 1H), 5.57 (m, 2H), 4.02 (m, 4H), 3.91 (s, 3H), 1.78 (m, 4H), 1.50 (m, 4H), 0.99 (t, J=7.22 Hz, 6H). ¹³C NMR (CDCl₃, 50.2 MHz): 168.35, 155.02, 146.91, 139.57, 116.06, 99.72, 69.78, 67.71, 50.77, 30.98, 30.48, 18.69, 13.41, 13.32. ESI-MS (m/z): 295 $((M)^{+})$. Elemental analysis: calculated for C₁₆H₂₅NO₄: C, 65.06; H, 8.53; N, 4.74; O, 21.67. Found: C, 65.23; H, 8.35; O, 21.55. FTIR (v/cm⁻¹): 3454, 3358, 2997, 2854, 1674, 1598, 1517. 1461. 1390. 1309. 1190.

4.5. Synthesis of 2-amino-4,5-dibutoxybenzoic acid (4)

A round-bottom flask containing 2-amino-4,5-dibutoxy-methylbenzoate (7 g, 23.7 mmol) was mixed with KOH (4.78, 118.5 mmol) and water (15 mL) and EtOH (20 mL). The solution was refluxed overnight to give a clear brown solution. After cooling at ambient temperature for 10 min, water (100 mL) was added to the flask and the solution was titrated to pH 6 with 1 N HCl. The precipitate was filtered and washed with water. The solid was treated with aqueous NaHCO₃, washed again with water, and dried in vacuo over P₂O₅ overnight (Caution: Do not increase temperature, it was decomposed.). Isolated yield=6.3 g (95%) as a colorless solid. ¹H NMR (200 MHz, CDCl₃) δ (ppm) 7.38 (s, 1H), 6.12 (s, 1H), 3.98 (m, 4H), 1.80 (m, 4H), 1.51 (m, 4H), 0.98 (m, 6H). ¹³C NMR (CDCl₃, 50.2 MHz): 172.87, 155.95, 147.87, 139.90, 116.22, 100.60, 99.70, 69.71, 67.95, 21.03, 30.56, 18.83, 13.54, 13.45. ESI-MS (m/z): 281 ((M)⁺•). Elemental analysis: calculated for C₁₅H₂₃NO₄: C, 64.03; H, 8.24; N, 4.98; O, 22.75. Found: C, 63.99; H, 8.15; O, 23.01. FTIR (v/ cm⁻¹): 3489, 3373, 2955, 2925, 2854, 1655, 1586, 1501, 1378, 1309, 1230, 1160, 1036.

4.6. Reaction of C₆₀ with 2-amino-4,5-dimethoxybenzoic acid

A mixture of C₆₀ (720 mg, 1.0 mmol), 2-amino-4,5dimethoxybenzoic acid as an in situ generated benzyne precursor (316 mg, 1.6 mmol), isoamyl nitrite (187 mg, 1.6 mmol), and o-dichlorobenzene (o-DCB) (70 mL) was placed under argon and stirred. The homogenous reaction mixture was heated at 100 °C under argon for 24 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent; tolue $ne\!\rightarrow\!toluene/ethyl$ acetate (9:1(v/v))) to give unreacted C_{60} (100 mg, 14%), monoadduct (150 mg, 17%) as brown-colored powder, and regioisomeric mixture of bisadducts (100 mg, 10%). Then, each solution was concentrated in vacuo, redissolved in a minimal amount of toluene and transferred to a centrifuge tube. The compounds were precipitated with MeOH, centrifuged, decanted, and collected, respectively. The spectral data of monoadduct: ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.57 (s, 2H), 3.99 (s, 6H). ¹³C NMR (150.1 MHz, 3:1 CS_2 /acetone- d_6): After complete drying, the product exhibited only limited solubility, which leads to the difficulty in accessing the proper ¹³C NMR spectrum. MALDI-MS m/z: 856 $((M)^{+})$. Elemental analysis: calculated for C₆₈H₈O₂: C, 95.32; H, 0.94; O, 3.73. Found: C, 95.21; H, 0.85; O, 3.71. FTIR (ν/cm^{-1}): 3068, 2954, 2835, 1596, 1441, 1355, 1234, 1190, 721, 525,

4.7. Reaction of C₆₀ with 2-amino-4,5-dibutoxybenzoic acid

Following the same procedures as the reaction of C₆₀ with 2amino-4,5-dimethoxybenzoic acid, C₆₀ (720 mg, 1.0 mmol), 2amino-4,5-dibutoxybenzoic acid (450 mg, 1.6 mmol), isoamyl nitrite (187 mg, 1.6 mmol), and o-dichlorobenzene (o-DCB, 70 mL) was placed under argon and stirred. The homogenous mixture reaction was heated at 100 °C under argon for 24 h. The residue was chromatographed on silica gel (eluent; toluene \rightarrow toluene/ethyl acetate (9:1(v/v))) to give unreacted C₆₀ (86 mg, 12%), monoadduct (140 mg, 15%) as brown-colored powder, and regioisomeric mixture of bisadducts (140 mg, 12%). Then, each solution was concentrated in vacuo, redissolved in a minimal amount of toluene and transferred to a centrifuge tube. The compounds were precipitated with MeOH, centrifuged, decanted, and collected, respectively. The spectral data of monoadduct ([5.6]-open regioisomer): ¹H NMR (600 MHz, 3:1 CS₂/acetone- d_6): δ (ppm) 7.69 (s, 1H), 7.64 (s, 1H), 4.01 (t, J=6.25 Hz, 2H), 3.84 (t, J=6.25 Hz, 2H), 1.79 (m, 2H), 1.69 (m, 2H), 1.40 (m, 2H), 1.28 (m, 2H), 0.86 (t, J=7.45 Hz, 3H), 0.75 (t, I=7.45 Hz, 3H). ¹³C NMR (150.1 MHz, 3:1 CS₂/acetone- d_6): δ 160.28, 155.51, 154.32, 150.16, 149.55, 149.25, 148.72, 147.30, 147.21, 146.95, 146.90, 146.88, 146.40, 146.98, 145.91, 145.80, 145.50, 145.18, 145.12, 143.68, 146.38, 143.18, 142.85, 142.62, 141.94, 141.79, 140.64, 140.52, 136.18, 135.12, 130.20, 115.78, 114.17, 113.22, 69.55, 69.49, 32.21, 32.09, 20.47, 20.39, 14.80, 14.72. MALDI-MS m/z: 940 ((M)⁺•). Elemental analysis: calculated for C₇₄H₂₀O₂: C, 94.46; H, 2.14; O, 3.40. Found: C, 94.21; H, 2.33; O, 3.52. The bisadducts are characterized by only MALDI-MS m/z: 1160 ((M)⁺•). FTIR (ν/cm^{-1}): 3037, 2959, 2873, 1693, 1604, 1427, 1329, 1067, 734, 573, 511.

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Supplementary data

¹H and ¹³C NMR spectra, HETCOR and HMBC spectra as well as additional calculation studies. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/ 10.1016/j.tet.2013.06.073.

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