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Stereoselective Cycloaddition of Dibenzoxazepinium Ylides to Acetylenes and Fullerene C_{60}. Conformational Behavior of 3-Aryldibenzo-[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepine Systems

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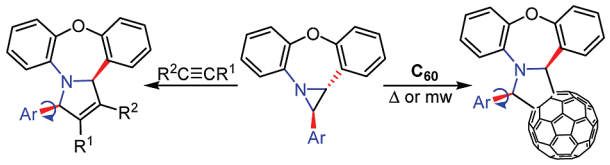

Cycloaddition of dibenzoxazepinium ylides to acetylene carboxylates leads to *cis*-3-aryl-3,13b-dihydrodibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepinecarboxylates, which smoothly dehydrogenate to the corresponding pyrrole derivatives. The *o*-bromophenyl-substituted pyrrole, in contrast to the pyrroline analogue, demonstrates atropoisomerism. Stereoselective cycloaddition of dibenzoxazepinium ylides to fullerene C_{60} gives rise to fulleropyrrolidines with cis-configuration. Restricted Ph group rotation is found in the phenyl derivative. Only one of two possible atropoisomers is formed in the reaction of *o*-bromophenyl-substituted ylide with fullerene C_{60}. Details of cycloaddition and conformational behavior of cycloadducts were studied by DFT computations.

Compounds with nitrogen heterocycles ortho-fused to dibenz[*b*,*f*][1,4]oxazepine exhibit diverse bioactivity.[1] In particular, dibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepines were patented as having valuable antihistamine, sedative, and antidepressive properties.[2] The known methods of synthesis of tetrahydrodibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepines that involved formation of a pyrrole ring via cyclization of precursors with preformed dibenz[*b*,*f*][1,4]oxazepine system[2] or formation of dibenz[*b*,*f*]-[1,4]oxazepine via cyclization of precursors with preformed pyrrole ring[3] did not provide a wide range of this type of heterocycles. In the framework of our research concerning the synthesis of heterocycles via N-ylide reactions,[4] we have recently presented an effective approach to 1-aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines[5] which are excellent precursors of azomethine ylides. These ylides undergo stereoselective 1,3-dipolar

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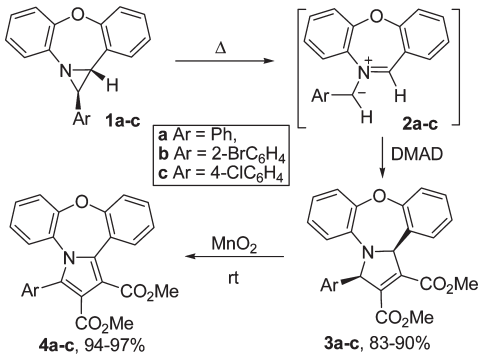
SCHEME 1. Cycloaddition of Ylides 2a−c to DMAD



cycloaddition to C=C dipolarophiles to form dibenzo[*b*,*f*]-pyrrolo[1,2-*d*][1,4]oxazepine derivatives containing a pyrrolidine moiety. Cycloaddition of the ylides to C≡C dipolarophiles can provide access to the corresponding pyrroline and pyrrole derivatives. 1,3-Dipolar cycloaddition of azomethine ylides across the [6,6] ring juncture in C_{60} is widely used to functionalize fullerenes.[6] This method led to an important class of fullerene derivatives, pyrrolidino[3′,4′:1,2][60]fullerenes, having useful applications in materials science and medicinal chemistry.[6,7] The approach generally involves in situ generation of azomethine ylides from aldehydes and amines followed by their cycloaddition to fullerenes.[6−8] Cycloaddition of azomethine ylides generated by ring-opening of aziridines to C_{60} is much less studied,[9] but this method can be expected to provide a stereoselective route to fulleropyrrolidine derivatives.

In this note, we report the cycloaddition of azomethine ylides generated from 1-aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines to C≡C dipolarophiles and to fullerene C_{60}. Heating aziridines **1a−c** in the presence of acetylenes leads to products formed by 1,3-dipolar cycloaddition of the corresponding iminium ylides **2a−c** to the triple bond. Thus, from aziridines **1a−c** in refluxing toluene, in the presence of dimethyl acetylenedicarboxylate (DMAD) as a dipolar trap, cycloadducts **3a−c** were obtained in high yields (Scheme 1). Compounds **3a−c** can be easily dehydrogenated with active MnO_2 for 30 min at rt to give compounds **4a−c** in 94−97% yield.

The NMR spectra demonstrated different conformational behavior of *o*-Br-phenyl-substituted pyrroline **3b** and pyrrole **4b**. Pyrroline **3b**, according to ^{1}H NMR and X-ray analysis,

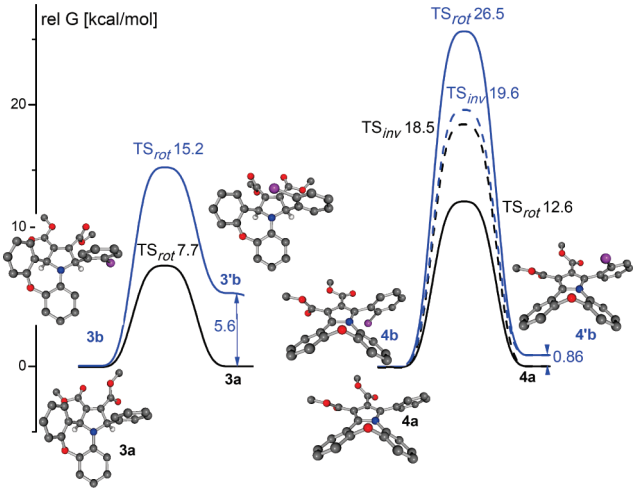


FIGURE 1. Energy profiles for conformational transformations of adducts **3a**,**b** and **4a**,**b**. Relative free energies [kcal·mol^{-1}, 298 K] computed at the B3LYP/6-31G(d) level. Hydrogen atoms on aromatic rings and methyl groups are omitted for clarity.

exists in both solution and the solid state as a single conformational isomer, while the corresponding dehydrogenated compound **4b** is present as a mixture of atropoisomers **4b** and **4′b** (ratio at 25 °C in $CDCl_3$ 0.6:0.4, in DMSO-d_6 0.7:0.3, in crystal ca. 0.8:0.2). The ratios of atropoisomers in solutions were unchanged after keeping the solutions for 3 days at rt. The observation of a sole set of signals in the NMR spectra of pyrroline **3b** can be explained by either the low rotation barrier of the aryl group or the high free energy difference of rotational isomers. According to DFT B3LYP/6-31G(d) calculations (Figure 1), the degenerate rotation barrier ($\Delta G^{\ddagger}$) of the Ph-ring in **3a** equals 7.7 kcal·mol^{-1}. Once the hydrogen in the ortho-position of the phenyl ring is substituted by a bromine the barrier to rotation rises to 15.2 kcal·mol^{-1}. This is not enough to prevent interconversion of rotamers at rt. On the other hand, the free energy difference between atropoisomers **3b** and **3′b** is sufficiently large ($\Delta\Delta G$ = 5.6 kcal·mol^{-1}) for only one, the most stable isomer **3b**, to be observed in the NMR spectra and in the solid state.

Dehydrogenation of pyrroline **3a** to pyrrole **4a** changes the molecular shape, resulting in an increase of the rotational barrier to degenerate rotation of the Ph ring from 7.7 to 12.6 kcal·mol^{-1}. In pyrrole **4a**, in contrast to pyrroline **3a**, one more topomerization process can be observed, namely oxazepine ring inversion ($\Delta G^{\ddagger}$ = 18.5 kcal·mol^{-1}). Substitution of the hydrogen in the ortho-position of the phenyl ring with a bromine causes a sharp increase of the barrier of rotation of the aryl group from 12.6 (**4a**) to 26.5 (**4b**) kcal·mol^{-1}, whereas the barrier to inversion of the oxazepine ring changes only slightly from 18.5 to 19.6 kcal·mol^{-1}. The free energy difference between atropoisomers **4b** and **4′b**, in contrast to compounds **3b** and **3′b**, is only 0.86 kcal·mol^{-1}, and this leads to the detection of both atropoisomers in the crystal (see the Supporting Information (SI)) and solutions. The equilibrium in solution is established fast enough, probably via inversion of the oxazepine ring, which has a lower activation barrier than aryl rotation.

Heating aziridine **1a** with unsymmetrical acetylenes **5a−c** leads to mixtures of the regioisomeric cycloadducts **6a−c** and **7a−c** in 73−93% overall yields (Scheme 2). The major isomers **7a**,**c** and **6b** were isolated pure and their structure

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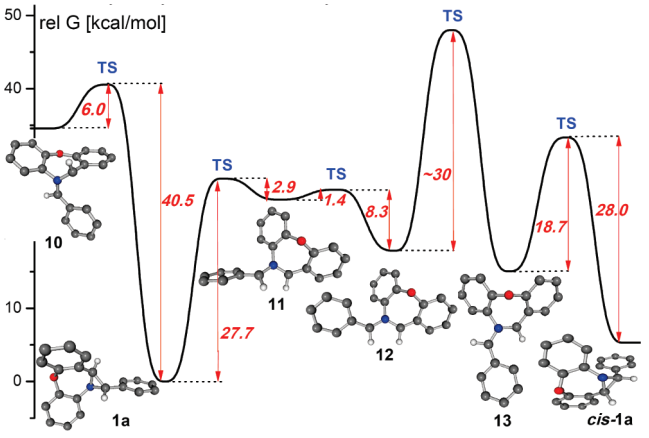
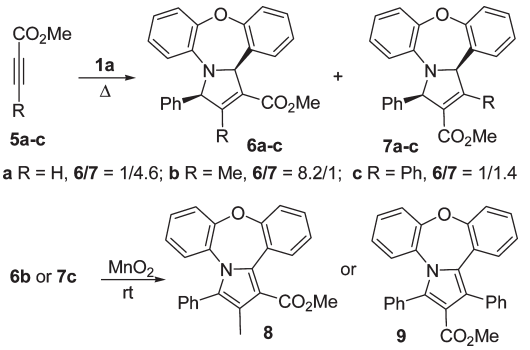


FIGURE 2. Reaction profiles for transformations of aziridines and ylides. Relative free energies [kcal·mol^{-1}, 373 K] computed at the B3LYP/6-31G(d) level. Hydrogen atoms on aromatic rings are omitted for clarity.

SCHEME 2. Cycloaddition of Ylides 2a−c to Acetylenes 5a−c



was proved by X-ray analysis. Dehydrogenation of compounds **6b**,**7c** proceeds smoothly with active MnO_2 at rt to give compounds **8**,**9** in 97−99% yields.

The primary cycloadducts **3**, **6**, and **7** proved to be stable under the reaction conditions. ^{1}H NMR analysis of the reaction mixtures showed no other stereoisomers of compounds **3**, **6**, and **7**. It can be concluded, therefore, that cycloaddition of ylides **2** to substituted acetylenes proceeds with complete stereoselectivity. According to calculations (Figure 2), the ring-opening of aziridine **1a** occurs conrotatory with the formation of either the nonplanar U-ylide **10** or W-ylide **11**.[10] The barrier to formation of the first one is 12.8 kcal·mol^{-1} higher than that of the latter, and the W-ylide **11** is more stable than the U-ylide **10** by 15.7 kcal·mol^{-1}. Ylide **11** can be converted to the more stable planar W-ylide **12** by rotation of the Ph-ring through a 1.4 kcal·mol^{-1} activation barrier. Ylide **12** in turn can be transformed to an even more stable S-ylide **13** by rotating the PhCH group around the ylide C−N bond.

We were unable to find the transition state for the transformation of ylides **12** → **13** because of an extraordinary complexity of the potential energy surface. To evaluate the barrier to *Z*,*E*-isomerization of the iminium ylide, calculations were performed of simpler ylides: $^-CH_2—N^+H=CH_2$ (**14**), $^-CH_2—N^+Ph=CH_2$ (**15**), $^-CHPh—N^+H=CH_2$ (**16**), and 1,4-oxazepinium-methanide (**17**). Both restricted and unrestricted B3LYP/6-31G(d) calculations showed that the barriers to *Z*,*E*-isomerization change only a little in the row of model ylidic structures **14**−**17** (32.5−35.2 kcal·mol^{-1}). This result allows the estimation of the barrier to transformation of ylides **12**→**13** to be at least ~30 kcal·mol^{-1}. The stereochemistry of cycloadducts **3**, **6**, and **7** and calculated energy parameters testify to the participation of only W-ylide **12** in the cycloaddition.

One can also conclude from the results obtained that the observed stereoselectivity is due to the lower barrier to cycloaddition of ylide **12** to the C≡C bond, compared with the barrier to transformation of ylides **12**→**13**. The results of the calculations of transition states of cycloaddition of ylide **12** to butynedioic acid do not contradict this conclusion. Eight possible transition states were found (see the SI). The lowest barrier to cycloaddition corresponds to the *anti*-approach of butynedioic acid relative to the oxygen of the oxazepine ring ($\Delta G^{\ddagger}$ = 13.7 kcal·mol^{-1}).

The calculated barrier to cycloaddition of ylide **12** to methyl propiolate and tetrolate (eight possible transition states were found in each case, see the SI) is much higher than those to butynedioic acid, but nevertheless lower than the barrier to transformation of ylides **12**→**13**. This finding is in agreement with the cis-stereochemistry of the cycloadducts. The experimentally found regioselectivity of cycloaddition of ylide **12** to methyl propiolate (1/4.6 ratio of regioisomers **6a**, **7a**) is in accordance with calculated barrier values for cycloaddition: $\Delta G^{\ddagger}$ = 16.5 and 15.9 kcal·mol^{-1}, respectively. The computed barriers to cycloaddition of ylide **12** to methyl tetrolate leading to regioisomers **6b** and **7b** are practically equal ($\Delta G^{\ddagger}$ = 23.1 and 23.0 kcal·mol^{-1}). Calculations, therefore, predict a change of regioselectivity on passing from **5a** to **5b**, but do not correspond to the experimentally found 8.2/1 isomer ratio.

We succeeded in performing stereoselective cycloaddition of ylides **2a**−**c** to fullerene C_{60}. The reactions were carried out either in boiling toluene or *o*-dichlorobenzene at 100 °C, as well as in toluene or chlorobenzene under microwave irradiation. Fulleropyrrolidines **18a**−**c** with cis-orientation of pyrrolidine hydrogens were obtained (Scheme 3). Conventional heating and microwave irradiation gave comparable yields, but in the last case the reaction times were significantly shorter (see the SI).

The cis-orientation of the pyrrolidine protons of the products **18a**−**c** was confirmed by the presence of a through-space interaction between them. Complete assignment of the signals in ^{1}H NMR spectra of **18a**,**b** was achieved by COSY and NOESY experiments (see the SI). Analysis of the NOESY spectrum of **18a** (measured at 22 °C) revealed the existence of an interchange of chemical shifts for H-7, H-10 and H-8, H-9. Positive cross-peaks (7/10 and 8/9) between signals of proton pairs were found, as opposed to the rest of the interacting protons. These remaining protons give negative cross-peaks due to through-space interaction in the extreme-narrowing limit: $\omega_o\tau_c < 1$. In this condition the existence of positive cross-peaks having the same sign as diagonal peaks in a phase-sensitive EXSY-NOESY experiment can be a consequence of some dynamic phenomena (slow on the NMR time scale) which affect the mentioned protons.[11] The suggestion is further supported by the observation that the signals of H-7 and H-10

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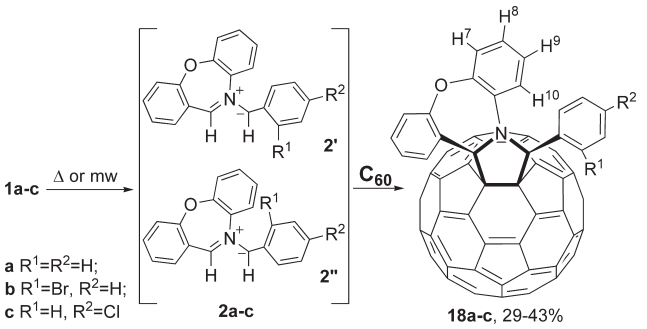
SCHEME 3. Cycloaddition of Ylides 2a−c to Fullerene C_{60}

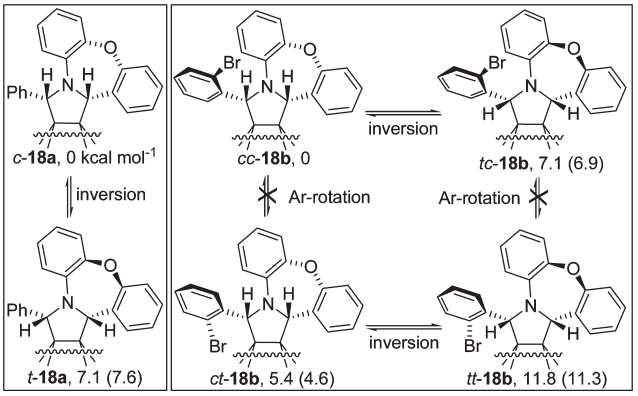


of the adduct **18a** are broadened in the ^{1}H NMR spectrum. The confirmation of the existence of dynamic phenomena was obtained by variable-temperature spectra. When heating the sample from 22 to 74 °C these signals broaden and their fine structure disappears at ca. 70 °C (see the SI). To disclose the conformational structure of the cycloadducts **18a−c** and the nature of dynamic phenomena found for **18a**, the computations of conformers of **18a**,**b** were performed at the B3LYP/6-31G(d) level, whereas the energy profiles for their conformational transformations were computed at the ONIOM B3LYP/6-31G(d):B3LYP/STO-3G level.[12] According to the calculations, there are two conformers of adduct **18a**, due to the conformational flexibility of the oxazepine ring (*c*-**18a** and *t*-**18a**).

In the case of adduct **18b**, computations recognize four conformers. Two of them arise from inversion of the oxazepine ring whereas the other two arise from a rotation of the 2-bromophenyl ring (*cc*-, *ct*-, *tc*-, and *tt*-**18b**). The conformers with the Ph group and oxygen oriented in the same direction are much more stable. In these conformers pyrrolidine C−H bonds are practically parallel and the pyrrolidine ring is significantly less planar than in conformers with the Ph group and oxygen oriented in the opposite direction. Earlier it was established by X-ray analysis that both types of conformations are really realized in adducts of ylide **2a** to C═C dipolarophiles.[5] Two conformational processes are possible in compounds **18a**,**c**, namely inversion of the oxazepine moiety and rotation of the aryl ring. The ONIOM simplification for the fullerene moiety, excepting common atoms of fullerene and pyrrolidine rings, is valid because this approach reproduces well the relative energy of conformers, computed at the B3LYP/6-31G(d) level (Scheme 4). The values of the calculated barrier to transformation *c*-**18a** → *t*-**18a** via inversion ($\Delta G^{\ddagger}$ = 12.5 kcal·mol^{-1}), the barrier to Ph group rotation in *c*-**18a** (23.8 kcal·mol^{-1}), the barrier to Ph group rotation in *t*-**18a** (8.2 kcal·mol^{-1}), as well as the higher stability of *c*-**18a** compared with *t*-**18a** ($\Delta\Delta G$ = 6.9 kcal·mol^{-1}), lead to the conclusion that the dynamic phenomenon observed in NMR spectra of **18a** is the restricted rotation of the Ph group in conformer *c*-**18a**. Restricted rotation of aryl groups has been observed earlier in 2-aryl-substituted nonfused fulleropyrrolidines.[13]

In contrast, once the hydrogen in the ortho-position of the Ph group is substituted with a bromine (**18b**), the rotational energy barrier becomes high enough to prevent interconversions of *cc*-**18b** ↔ *ct*-**18b** and *tc*-**18b** ↔ *tt*-**18b** via rotation of the Ar group. On the other hand, the barriers to the transformations of *cc*-**18b** → *tc*-**18b** ($\Delta G^{\ddagger}$ = 12.8 kcal·mol^{-1}) and *ct*-**18b** → *tt*-**18b** (13.7 kcal·mol^{-1}) via inversion of the dibenzoxazepine moiety are too low for the observation of any dynamic exchange at 22−74 °C in the ^{1}H NMR spectrum of **18b**. (See the graphic representation of the discussed transformations in the SI.)

SCHEME 4. Relative Total Energies of Conformers of Fulleropyrrolidines 18a,b Computed at the ONIOM B3LYP/6-31G(d): B3LYP/STO-3G (or B3LYP/6-31G(d)) Level



Although two pairs of diastereoisomeric conformers *cc*-**18b**/*ct*-**18b** and *tc*-**18b**/*tt*-**18b** can in principle exist, taking into account the low barriers to inversion of the dibenzoxazepine moiety, we could observe only the most stable *cc*-**18b**/*ct*-**18b** atropoisomers under the conditions used. The detection of only one atropoisomer leads to a conclusion that the reaction of ylide **2b** with C_{60} is completely diastereoselective, affording only one of the two possible atropoisomers. The ylide **2b** formed via conrotatory aziridine ring-opening of **1b** can exist in two conformations **2′b** and **2″b** (Scheme 3), the first one being much more stable ($\Delta\Delta G$ = 3.8 kcal·mol^{-1}). The barrier to the transformation of **2′b** to **2″b** by Ar-ring rotation is $\Delta G^{\ddagger}$ = 9.8 kcal·mol^{-1}. The cycloaddition of ylide **2′b** to C_{60} leads to *cc*-**18b**, whereas cycloaddition of ylide **2″b** to C_{60} leads to *ct*-**18b**. The calculation of the barriers to cycloaddition of the conformers **2′b**, **2″b** to ethylene showed that the first is much lower than the second ($\Delta\Delta G^{\ddagger}$ = 8.6 kcal·mol^{-1}), explaining the formation of only *cc*-**18b** atropoisomer in the reaction of **1b** with C_{60}.

In summary, heating azirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines with C≡C dipolarophiles leads to dibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepinecarboxylates in high yields via stereoselective 1,3-dipolar cycloaddition of W-ylides. Primary pyrrolidine cycloadducts smoothly dehydrogenate under mild conditions to pyrrole derivatives. The change of rigidity of the substituted 5-membered ring fragment in compounds **3**, **4**, and **18** dramatically influences the conformational behavior of 3-aryldibenzo[*b*,*f*]pyrrolo[1,2-*d*][1,4]oxazepine systems.

Experimental Section

General Procedures (GP1) for Cycloaddtion of Ylides from *trans*-1-Aryl-1,11b-dihydroazirino[1,2-*d*]dibenz[*b*,*f*][1,4]oxazepines (6a−c) to Acetylenes. A solution of compound **1a−c** (0.351 mmol) and dipolarophile (0.351−0.701 mmol) in anhyd toluene (5 mL) was heated at 90−100 °C in an inert atmosphere. The reaction was monitored by TLC. The solvent was removed in vacuo and the residue was purified by crystallization or flash chromatography.

General Procedures (GP2) for the Dehydrogenation of Pyrrolines 3a−c, 6b, and 7a,c. A mixture of pyrrolines **3a−c**, **6b**, and **7a**,**c** (0.06−0.26 mmol) and active MnO_2 (0.100 g, 1.15 mmol) in

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(13) Ajamaa, F.; Figueira Duarte, T. M.; Bourgogne, C.; Holler, M.; Fowler, P. W.; Nierengarten, J.-F. *Eur. J. Org. Chem.* **2005**, 3766.

anhyd toluene (4 mL) was vigorously stirred at rt for 30−40 min. The solid was filtered off and washed with dichloromethane (3 × 20 mL). The solvent was evaporated and the residue was crystallized from an appropriate solvent.

Compound 18a. A mixture of compound **1a** (10 mg, 0.03 mmol) and fullerene C_{60} (38 mg, 0.055 mmol) in *o*-dichlorobenzene (2 mL) was subjected to microwave irradiation (160 W) for 2 h. The temperature reached at the end of the process was 65 °C. Column chromatography (silica, benzene−hexane) gives 10 mg of cycloadduct **18a** (28% yield based on **1a**). Brown solid; ^{1}H NMR (C_6D_6) δ 5.81 s (1H, CHN), 5.91 s (1H, CHN), 6.72−6.82 m (3H), 6.85−6.95 m (2H), 6.95−7.00 m (2H), 7.25−7.32 m (1H), 7.35−7.40 m (1H), 7.50−7.55 m (1H), 7.63−7.70 m (1H), 7.77−7.83 m (1H); ESI-HRMS calcd for $C_{80}H_{15}NO$ $[M + H]^+$ 1006.1226, found 1006.1227.

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Supporting Information Available: General experimental methods, detailed experimental procedures, additional tables and graphs, as well as characterization data and ^{1}H and ^{13}C NMR spectra for all new compounds, 2D NMR data for compounds **18a**,**b**, crystallographic data for compounds **3a**,**b**, **4b**, **6b**, **7a**,**b**, and **8** (CIFs), computation details and energies of the reactants, transition states, and their Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.