The Syntheses of Pyrazino-Containing Sultines and Their Application in Diels−Alder Reactions with Electron-Poor Olefins and [60]Fullerene

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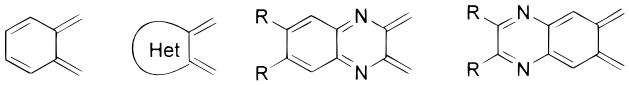
The Diels−Alder reactions of heterocyclic *o*-quinodimethanes, generated in situ from 6,7-disubstituted quinoxalino[2,3-*d*]-[1,2λ^4]oxathiine 2-oxides (**6a**−**c**), 2,3-disubstituted-8,9-dihydro-6*H*-8λ^4-[1,2]oxathiino[4,5-*g*]quinoxalin-8-one (**7a**−**c**) (sultines), and pyrazinosultine (**22**), with electron-poor olefins and [60]fullerene are described. The heterocyclic-fused sultines **7a**−**c** and **22** are readily prepared from the corresponding dibromides **9a**−**c** and **24** with the commercially available Rongalite (sodium formaldehyde sulfoxylate). When heated in the presence of electron-poor dienophiles and [60]fullerene, all of the sultines underwent extrusion of SO_2, and the resulting heterocyclic *o*-quinodimethanes (**3a**−**d**, **4a**−**c**, and **25**) were intercepted as the 1:1 adducts in good to excellent yields. The temperature-dependent ^{1}H NMR spectra of fullerene derivatives **31**−**38** show a dynamic process for the methylene protons. The activation free energies ($\Delta G_c^{\ddagger}$) determined for the boat-to-boat inversion of these pyrazino-containing C_{60} compounds (**31**−**34** and **38**) are found to be in the range of 14.1−14.8 kcal/mol, but they are in the range of 15.2 to >17.1 kcal/mol for adducts **35**−**37**. The activation free energies ($\Delta G_c^{\ddagger}$) are significantly affected by (1) the orientations and (2) the substituents of the quinoxaline rings and (3) the extended benzannulation in the arenes of C_{60} adducts (see Table 2), which implies that both *electronic interactions* and *steric effects* between the aromatic addends and C_{60} are important. Tautomerization of methylquinoxaline to its enamine is invoked as a rationalization for the lowering of $\Delta G_c^{\ddagger}$ in some of the fulleroadducts.

Derivatives of [60]fullerene have become the current focus of research in biological and material science because of the unique spherical structure of this molecule and its feasibility for bulk production.[1] Among the many derivatization methods available, cycloaddition reactions have played an important role, with the Diels−Alder reaction being particularly useful.[1] In the pioneering stage, many of the cycloadducts to C_{60} were found to be thermally unstable because they undergo cycloreversion to give the component molecules.[1] Stable Diels−Alder adducts of C_{60} were first explored by Müllen[2a−d] and Rubin[2e−g] in their pioneering work using *o*-quinodimethane (**1**) and its analogues as reactive dienes. These highly reactive species, generated in situ from a variety of precursors,[2,3] are efficiently trapped by [60]fullerene, which gains extra stabilization because of the restoration of the aromatic system.



1 **2** **3a** R = H, **3b** R = Me, **3c** R = Cl **4a** R = H, **4b** R = Cl, **4c** R = Ph

Although *o*-quinodimethane **1** has frequently been used for the derivatization of [60]fullerene, its heterocyclic analogues **2** have been recognized only recently.[4] Various

(1) For recent reviews, see: (a) Hirsch, A. *Synthesis* **1995**, 895. (b) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme Medical Publishers: New York, 1994. (c) Diederich, F.; Isaacs, L.; Philip, D. *Chem. Soc. Rev*. **1994**, 243. (d) Averdung, J.; Torres-Garcia, G.; Luftmann, H.; Schlachter, I.; Mattay, J. *Fullerene Sci. Tech*. **1996**, *4*, 633. (e) Diederich, F.; Kessinger, R. *Acc. Chem. Res*. **1999**, *32*, 537. (f) Wudl, F. *Acc. Chem. Res*. **1992**, *25*, 157. (g) Da Ros, T.; Prato, M. *Chem. Commun*. **1999**, 663. (h) Kräutler, B.; Maynollo, J. *Tetrahedron* **1996**, *52*, 5033.

(2) (a) Gügel, A.; Belik, P.; Water, M.; Kraus, A.; Harth, E.; Wagner, M.; Spickermann, J.; Müllen, K. *Tetrahedron* **1996**, *52*, 5007. (b) Belik, P.; Gügel, A.; Kraus, A.; Water, M.; Müllen, K. *J. Org. Chem*. **1995**, *60*, 3307. (c) Gügel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 559. (d) Belik, P.; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 78. (e) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc*. **1993**, *115*, 344. (f) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc*. **1993**, *115*, 4919. (g) Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y.-Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganapathi, P. S.; Shephard, M. J.; Paddon-Row, M. N.; Rubin, Y. *J. Org. Chem*. **1996**, *61*, 5032−5054 and references therein.

(3) For reviews of *o*-quinodimethanes, benzocyclobutenes, and related chemistry, see: (a) Oppolzer, W. *Synthesis* **1978**, 793; *Heterocycles* **1980**, *14*, 1615. (b) Kametani, T. *Pure Appl. Chem*. **1979**, *51*, 747. (c) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev*. **1980**, *9*, 41. (d) Martín, N.; Seoane, C.; Hanack, M. *Org. Prep. Proced. Int*. **1991**, *23*, 237. (e) Chou, T.-S. *Rev. Heteroat. Chem*. **1993**, *8*, 65. (f) Ando, K.; Kankake, M.; Suzuki, T.; Takayama, H. *Tetrahedron* **1995**, *51*, 129. (g) Collier, S. J.; Storr, R. C. *Prog. Heterocycl.c Chem*. **1998**, *10*, 25. (h) Segura, J. L.; Martín, N. *Chem. Rev*. **1999**, *99*, 3199.

(4) For recent works on heterocyclic *o*-quinodimethanes, see: (a) Tomé, A. C.; Enes, R. F.; Cavaleiro, J. A. S.; Elguero, J. *Tetrahedron Lett*. **1997**, *38*, 2557. (b) Tomé, A. C.; Cavaleiro, J. A. S.; Storr, R. C. *Tetrahedron* **1996**, *52*, 1723; **1996**, *52*, 1735; **1993**, *34*, 6639. (c) Boulle, C.; Cariou, M.; Bainville, M.; Gorgues, A.; Hudhomme, P.; Orduna, J.; Garín, J. *Tetrahedron Lett*. **1997**, *38*, 81. (d) Ohno, M.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron Lett*. **1996**, *37*, 9211; **1995**, *36*, 6899. (e) Fernández-Paniagua, U. M.; Illescas, B. M.; Martín, N.; Seoane, C. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1077 and reference cited therein. (f) Ohno, M.; Koide, N.; Eguchi, S. *Heterocycl. Commun*. **1995**, *1*, 125. (g) Ohno, M.; Kojuma, S.; Eguchi, S. *J. Chem. Soc., Chem. Commun*. **1995**, 565. (h) Carly, P. R.; Compernolle, F.; Hoornaert, G. J. *Tetrahedron Lett*. **1995**, *36*, 2113. (i) Carly, P. R.; Cappelle, S. L.; Compernolle, F.; Hoonaert, G. J. *Tetrahedron* **1996**, *52*, 11889. (j) Al Hariri, M.; Jouve, K.; Pautet, F.; Domard, M.; Fenet, B.; Fillion, H. *J. Org. Chem*. **1997**, *62*, 405.

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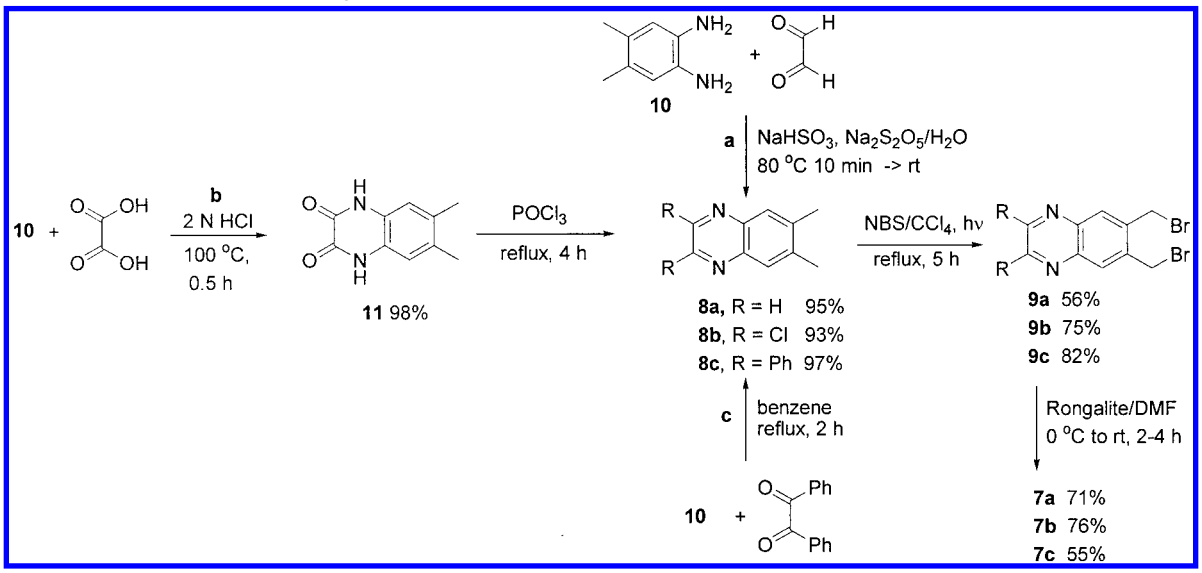
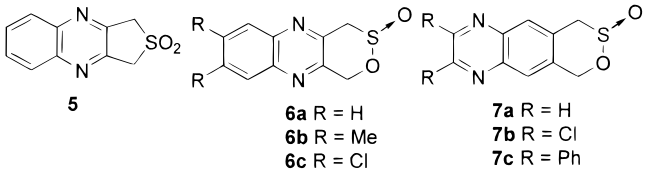
Scheme 1. Syntheses of 2,3-Disubstituted Quinozalinosultines 7a−c



methods for generating these highly reactive dienes have been developed. Among them, cheletropic elimination of SO_2 from heteroaromatic-fused 3-sulfolenes and 1,4-elimination from the corresponding α,α′-dihalides have drawn the most attention.[3,4] Quinoxalines are important naturally occurring heterocycles and are usually found to have biological and pharmaceutical activity.[5] Although Chou et al. reported[6a] the generation of quinoxalino-*o*-quinodimethane **3a** from SO_2 extrusion of the corresponding sulfolene **5**, all of their attempts to isolate the Diels−Alder adducts failed. To our surprise, the 1,4-elimination from 2,3-bis(bromomethyl)quinoxaline by NaI in DMF also failed to give the expected Diels−Alder adducts when strong dienophiles such as *N*-methyl and *N*-phenylmaleimide were applied,[6b] even though this method is generally assumed to give the heterosubstituted *o*-quinodimethane **3a**. Thus, finding an easy and high-yield method for generating quinoxalino-2,3- and quinoxalino-6,7-quinodimethanes **3** and **4** is of particular interest.

Recently, we reported a high-yield method for the generation and trapping of quinoxalino-2,3-quinodimethanes **3a**−**c** from thermolysis of the corresponding sultines **6a**−**c**.[7]



The sultines prove to be excellent precursors for heterocyclic *o*-quinodimethanes **2** and can react with many good dienophiles under mild conditions. Interestingly, Mattay et al.,[8a] Martín et al.,[8b] and Eguchi et al.[8c] have independently reported the syntheses of quinoxalino-fused [60]-fullerene. The latter two groups both used the iodide-induced 1,4-elimination method to generate reactive **3a** from corresponding 2,3-bis(bromomethyl)quinoxaline and then trapped it with C_{60}; however, Mattay et al. prepared the quinoxalino-fused fullerene by condensation of C_{60}-fused diketone with *o*-diaminoarenes. We report here the synthesis of several novel nitrogen-containing heterocyclicfused sultines **7a**−**c** and **22**, sulfolenes **13a**−**c**, and cyclobutenes **18a**−**c** and their application in Diels−Alder reactions with electron-poor olefins and C_{60}.[9]

Results and Discussion

Previously unknown quinoxalino-fused sultines **7a**−**c** were readily synthesized from the reactions of Rongalite (sodium formaldehyde sulfoxylate) with the corresponding 2,3-disubstituted 6,7-dibromomethylquinoxalines **9a**−**c** (where R = H, Cl, and phenyl)[5] in 55−76% yields (Scheme 1). The 6,7-dibromomethylquinoxaline **9a** was obtained from NBS bromination of 6,7-dimethylquinoxaline **8a**,[5b] which, in turn, was obtained from the condensation of 4,5-dimethyl-1,2-phenylenediamine (**10**) with glyoxal (process a) in aqueous sodium hydrogen sulfite at 80 °C. The preparation of 2,3-dichloro-6,7-bis(bromomethyl)-quinoxaline **9b** followed a method developed by Leeson et al.,[5c,d] which also started from **10** but in which **10** was reacted with oxalic acid to give 1,4-dihydro-6,7-dimethylquinoxaline-2,3-dione **11** in 98% yield (process b). Refluxing **11** in $POCl_3$ for 4 h gave the desired 2,3-dichloro-6,7-

(5) (a) Villemin, D.; Martin, B. *Synth. Commun.* **1995**, *25*, 2319. (b) Baudy, R. B.; Greenblatt, L. P.; Jirkovsky, I. L.; Conklin, M.; Russo, R. J.; Bramlett, D. H.; Emrey, T. A.; Simmonds, J. T.; Kowal, D. M.; Stein, R. P.; Tasse, R. P. *J. Med. Chem.* **1993**, *36*, 331. (c) Leeson, P. D.; Baker, R.; Carling, R. W.; Crutis, N. R.; Moore, K. W.; Williams, B. J.; Foster, A. C.; Donald, A. E.; Kemp, J. A.; Marshall, G. R. *J. Med. Chem.* **1991**, *34*, 1243. (d) Cai, S. X.; Kher, S. M.; Zhou, Z.-L.; Ilyin, V.; Espitia, S. A.; Tran, M.; Hawkinson, J. E.; Woodward, R. M.; Weber, E.; Keana, J. F. W. *J. Med. Chem.* **1997**, *40*, 730. (e) Anderson, L. M.; Butler, A. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 323.

(6) (a) Chou, T.-S.; Ko, C.-W. *Tetrahedron* **1994**, *50*, 10721. (b) Alexandrou, N. E.; Mertzanos, G. E.; Stephanidou-Stephanatou, J.; Tsoleridis, C. A.; Zachariou, P. *Tetrahedron Lett.* **1995**, *36*, 6777. (c) Chou, T.-S.; Ko, C.-W. *Molecules* **1996**, *1*, 93.

(7) (a) Chung, W.-S.; Liu, J.-H. *Chem. Commun.* **1997**, 205. (b) Chung, W.-S.; Lin, W.-J.; Liu, W.-D.; Chen, L.-G. *J. Chem. Soc., Chem. Commun.* **1995**, 2537 and references therein.

(8) Different methods in the synthesis of **31** have been reported, see: (a) Torres-Garcia, G.; Luftmann, H.; Wolff, C.; Mattay, J. *J. Org. Chem.* **1997**, *62*, 2752. (b) Fernández-Paniagua, U. M.; Illescas, B. M.; Martín, N.; Seoane, C.; de la Cruz, P.; de la Hoz, A.; Langa, F. *J. Org. Chem.* **1997**, *62*, 3705. (c) Ohno, M.; Koide, N.; Sato, H.; Eguchi, S. *Tetrahedron* **1997**, *53*, 9075,

(9) Part of this work has already been presented as follows: (a) In *Book of Abstracts*; 16th International Congress of Heterocyclic Chemistry, Bozeman, MT, 1997; OP-V-13. (b) Presented at the 216th National Meeting of American Chemical Society, Boston, MA, August 23−27, 1998; Paper 139.

Scheme 2. Sealed-Tube Pyrolysis of Sultines 7a−c, Sulfolenes 13a−c, and Cyclobutenes 18a−c in Toluenes

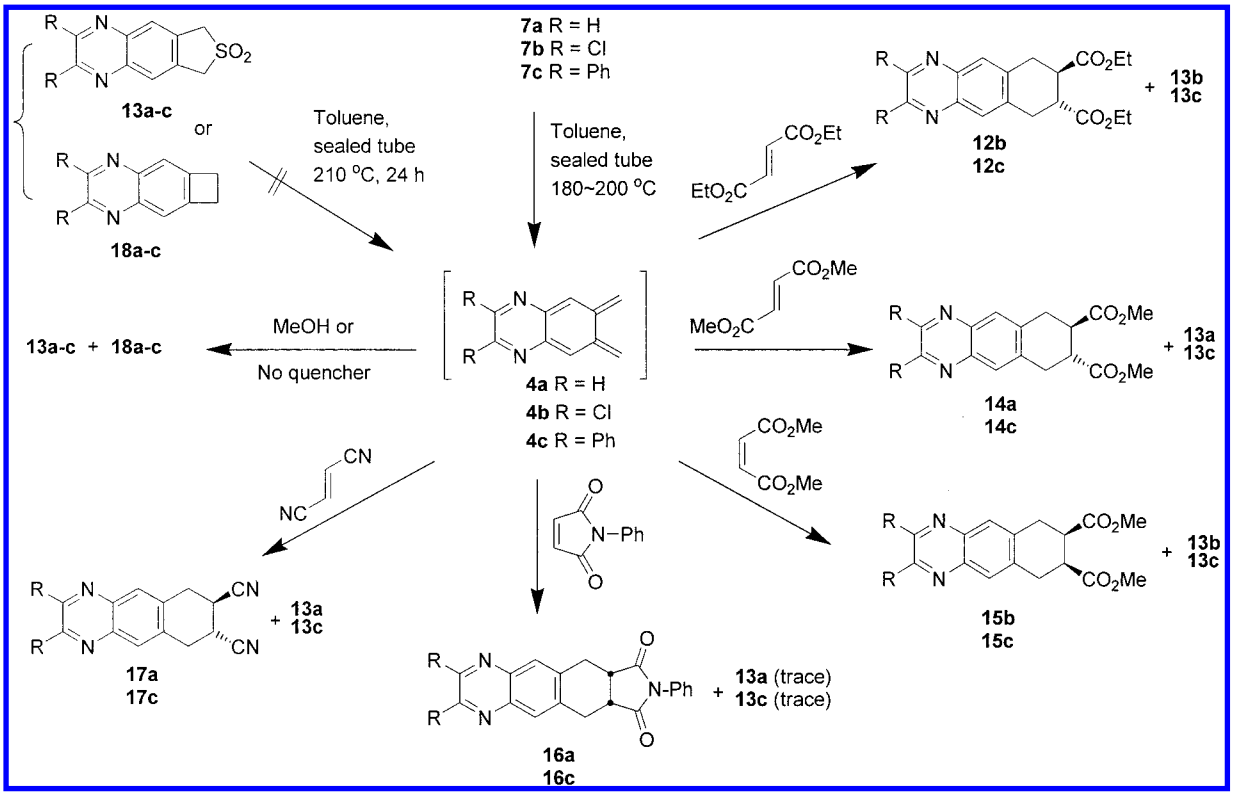


Table 1. Formation and Trapping of *o*-QDM 4a−c with Various Dienophiles (3 equiv) in a Sealed Tube in Toluene

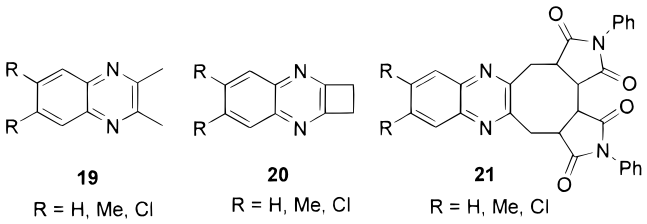
entry	precursor to *o*-QDM **4a−c**	quencher	reaction conditions[a]	products (yield)
1	**7a**	dimethyl fumarate	A	**14a** (75%) + **13a** (6%)
2	**7a**	*N*-phenylmaleimide	A	**16a** (87%) + **13a** (trace)
3	**7a**	fumaronitrile	A	**17a** (75%) + **13a** (trace)
4	**7a**	MeOH	A	**13a** (57%) + **18a** (31%)
5	**7a**	—[b]	A	**18a** (63%) + **13a** (28%)
6	**13a**	*N*-phenylmaleimide	D	no reaction
7	**18a**	*N*-phenylmaleimide	D	no reaction
8	**7b**	diethyl fumarate	B	**12b** (82%) + **13b** (6%)
9	**7b**	dimethyl maleate	B	**15b** (62%) + **13b** (15%)
10	**7b**	*N*-phenylmaleimide	B	**16b** (93%) + **13b** (trace)
11	**7b**	MeOH	B	**13b** (45%) + **18b** (42%)
12	**7b**	—[b]	B	**18b** (55%) + **13b** (35%)
13	**13b**	*N*-phenylmaleimide	D	no reaction
14	**18b**	*N*-phenylmaleimide	D	no reaction
15	**7c**	diethyl fumarate	C	**12c** (92%) + **13c** (trace)
16	**7c**	dimethyl fumarate	C	**14c** (83%) + **13c** (trace)
17	**7c**	dimethyl maleate	C	**15c** (60%) + **13c** (20%)
18	**7c**	*N*-phenylmaleimide	C	**16c** (98%) + **13c** (trace)
19	**7c**	fumaronitrile	C	**17c** (60%) + **13c** (10%)
20	**7c**	MeOH	C	**13c** (45%) + **18c** (16%)
21	**7c**	—[b]	C	**13c** (74%) + **18c** (12%)
22	**13c**	*N*-phenylmaleimide	D	no reaction
23	**18c**	*N*-phenylmaleimide	D	no reaction

[a] Reaction conditions: A, 180 °C for 4 h; B, 200 °C for 4 h; C, 200 °C for 24 h; and D, 210 °C for 24 h. [b] No quencher was added.

dimethylquinoxaline **8b** in 93% yield, which, after NBS bromination, gave the dibromide **9b** in 75% yield. Similarly, refluxing **10** with benzil in benzene (process c) led to the formation of 2,3-diphenyl-6,7-dimethylquinoxaline **8c** in 97% yield, which, after NBS bromination, gave the desired 2,3-diphenyl-6,7-bisbromomethylquinoxaline **9c**.

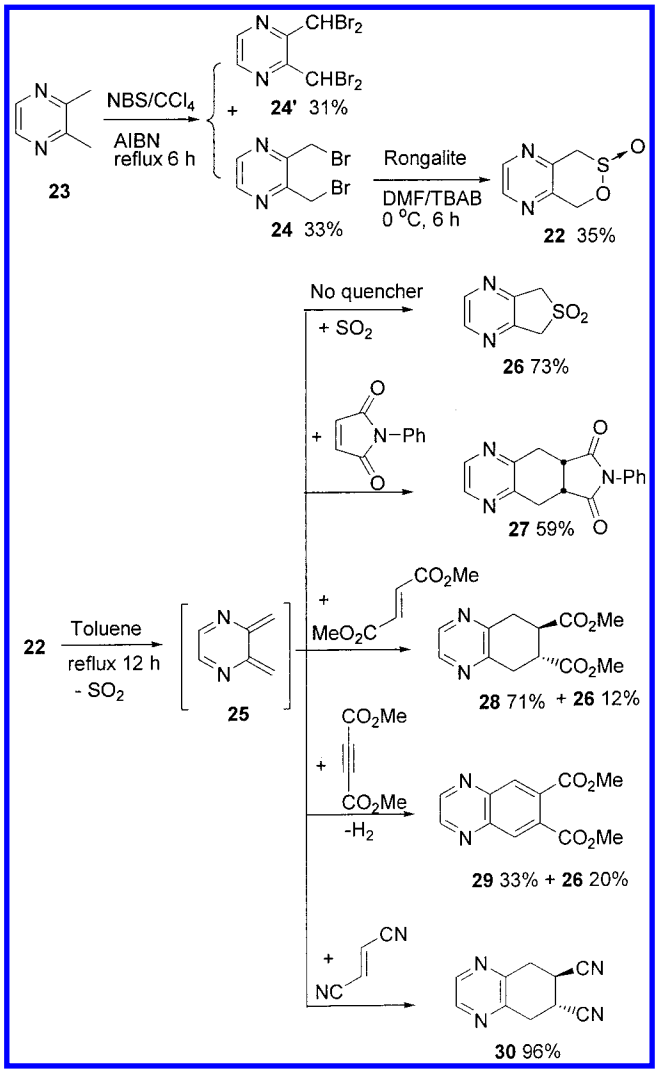
The Diels−Alder reactions of these sultines (**7a−c**) with typical dienophiles are presented in Scheme 2 and Table 1. For example, when heated in toluene (sealed tube; 4 h for **7a**,**b**; 24 h for **7c**) in the presence of 3 equiv of diethyl fumarate, dimethyl fumarate, dimethyl maleate, fumaronitrile, or *N*-phenylmaleimide, the sultines **7a−c** all underwent extrusion of SO_2, and the resulting quinoxalino-6,7-quinodimethanes **4a−c** were intercepted as the 1:1 adducts (**12−17**) in 60−98% yields (entries 1−3, 8−10, and 15−19 of Table 1). Small amounts (≤20%) of sulfolenes **13a−c** were also formed; however, they did not react with any of these dienophiles even at 210 °C (entries 6, 13, and 22), in contrast with the high reactivities of sultines **6a−c**[7a] and **7a−c**. The low reactivity of sulfolenes **13a−c** is consistent with that reported by Chou et al. in the pyrolysis of sulfolene **5**.[6a]

Although the structure and reactivity of 2,3-disubstituted quinoxalinosultines **7a**−**c** are very similar to those of 6,7-disubstituted quinoxalinosultines **6a**−**c**,[7a] there are three major differences in their reaction products. In the absence of a dienophile, sultines **7a**−**c** underwent thermal extrusion of SO_2 to form the cyclobuta[6,7-*g*]quinoxalines **18a**−**c** and the rearranged sulfolenes **13a**−**c** in various ratios depending on the substituents (entries 5, 12, and 21). The same mixtures (**13** and **18**) were formed in the pyrolysis of sultines **7a**−**c** in toluene with added MeOH (entries 4, 11, and 20). This is in contrast to our previous observation on the thermolysis of sultines **6a**−**c**, in which the corresponding 2,3-dimethylquinoxalines **19a**−**c** were the only products when hydrogen donors such as MeOH or 1,4-cyclohexadiene were present. The second important difference between the thermal reaction of sultines **7a**−**c** and **6a**−**c** is in their trapping behavior with NPM. The reaction of **6a**−**c** with excess NPM at 200 °C gave mixtures of *cis*- and *trans*-quinoxalinocyclooctenes **21**, but the reaction of **7a**−**c** with excess NPM gave only the 1:1 Diels−Alder adducts **16a**−**c**.[10] The third surprise is that the cyclobuta[6,7-*g*]quinoxalines **18a**−**c** did not react with any dienophiles (e.g., NPM; entries 7, 14, and 23) even at 210 °C for 24 h, but their analogues, cyclobuta[1,2-*b*]quinoxalines **20a**−**c**, reacted smoothly at 180 °C with all of the dienophiles listed above.[7a] As a matter of fact, the cyclobutapyrimidines have been successfully applied as *o*-QDM precursors in syntheses of Diels−Alder adducts and fullerene derivatives.[13b,c]



The pyrazino-fused sultine **22** can also be prepared similarly from corresponding bisbromide **24**, which was prepared by bromination of commercial available 2,3-dimethylpyrazine **23**. When sultine **22** was refluxed in toluene in the presence of 1.2 equiv of dienophiles (e.g., *N*-phenylmaleimide, dimethyl fumarate, etc.), the 1:1 Diels−Alder adducts (**27**-**30**) were obtained in good to excellent yields (Scheme 3). Without any quencher, sulfolene **26**[6c] was obtained in 73% yield. It is important to note that the reaction temperature decreased from 180−200 °C in quinoxalinosultines **6a**−**c** and **7a**−**c** to 110 °C in pyrazinosultine **22**; however, the corresponding pyrazino sulfolene **26** was reported[6c] to react with dienophiles only at 300 °C!

Scheme 3. Synthesis of Pyrazinosultine and its Trapping Reactions



The quinoxalinosultines **6a**−**c** reported[7a] previously and all of the sultines prepared in this work were tested for their reactivity with [60]fullerene. When C_{60} (50 mg, 0.069 mmol) was refluxed in *o*-dichlorobenzene (in toluene for **22**) with a slight excess (1.2 equiv) of the pyrazino-containing sultines **6**, **7**, and **22** for a variable period of time (24 h for **6** and **7**, 6 h for **22**), the 1:1 cycloadducts were obtained in moderate to good yields as follows: **31**, 66%; **32**, 78%; **33**, 53%; **34**, 51%; **35**, 84%; **36**, 10%; **37**, 29%; and **38**, 75% (all based on consumed C_{60}, Scheme 4). The yield for adduct **36** was very poor because of the difficulty in finding a proper solvent to dissolve both sultine **7b** and C_{60}. The isolation of cycloadducts **31**−**38** was accomplished by column chromatography on silica gel using hexane/toluene (4:1) to toluene as the eluent. Interestingly, the mono-addition product of C_{60} is predominantly formed in these pyrazino-containing sultines without detection of appreciable amounts of bis-addition products. The reactivity of fullerene double bonds (at the 6,6-ring junction) is probably decreased by a significant amount after the first addition of a quinoxaline group on C_{60}, which permits the obtainment of high yields of mono adducts.[2g] The structures of the cycloadducts **31**−**38** were elucidated by spectral inspections. First, FAB-MS confirmed the presence of the 1:1 cycloadducts by the molecular ion peaks (M + 1) at the following *m*/*z* values:

(10) In a recent review, Storr[3g] revised his assignments[5a,b] of the eight-membered ring to an ene-reaction-type product. Our results,[7a] however, seemed to fit with the *cis*- and *trans*-cyclooctenes.

(11) (a) Ref 2e. (b) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, Germany, 1993; p 293.

(12) The T_c and $\Delta G_c^{\ddagger}$ values of naphthaleno-fused [60]fullerene were reported by Najanyram, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351.

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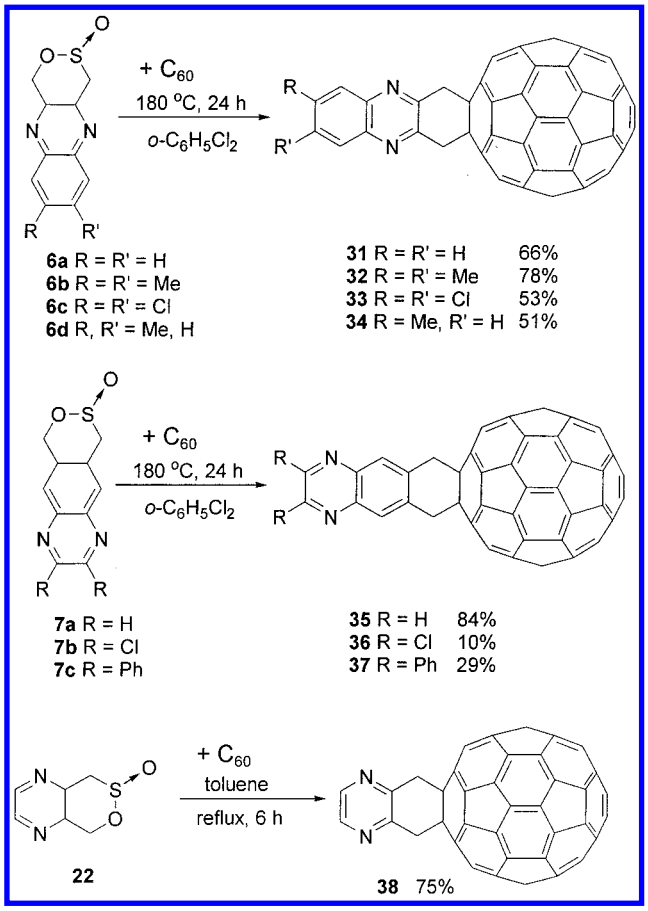
Scheme 4. Diels–Alder Reactions of Sultines with [60]Fullerene



31, 877; **32**, 905; **33**, 944; **34**, 891; **35**, 877; **36**, 939; **37**, 1029; and **38**, 827. The base peaks were at *m*/*z* 720 in most cases. In the UV/vis spectra of **31**–**38**, a new sharp band with λ_{max} near 434 nm appeared, which is very characteristic of the Diels–Alder monoadducts of [60]-fullerene at the 6,6-ring junction.[1]

In ^{1}H NMR spectra measured at 22 °C, the two methylene protons show two broadened signals (δ 4.8–4.9 and 5.1–5.2) for adducts **31**–**34**. In contrast, they show two well resolved AB quartets for adducts **35**–**37** and a singlet for adduct **38** (see Experimental Section). The two diastereotopic methylene protons are separated by 0.27 ± 0.01 ppm for adducts **31**–**34**, but are further separated by 0.38 ± 0.02 ppm for adducts **35**–**37**. Variable-temperature NMR measurements (vide infra) imply that the Diels–Alder adducts **31**–**38** involve some flipping motion of the cyclohexene rings and that the inversion rates of the cyclohexene rings are clearly different among these adducts. Calculations[8,13,14b] and X-ray structural analysis[2e,f] of many Diels–Alder adducts of C_{60} have shown that the most stable conformation of the cyclohexene ring is the boat form and that the inversion occurs between the two equivalent boat conformations. To estimate the difference in the inversion rates among these adducts, variable-temperature ^{1}H NMR measurements[11] were carried out, and the coalescence temperatures for the two doublet signals of the methylene protons were measured. On the basis of the coalescence temperatures of these heteroaromatic-fused fullerene adducts **31**–**38**, the activation free energies of inversion $\Delta G_c^{\ddagger}$ at the corresponding temperatures were calculated and are summarized in Table 2. For example, variable-temperature experiments of **31** revealed that the ring inversion was in the slow exchange region below 0 °C, giving a well-resolved AB quartet with a chemical shift difference of 0.25 ppm, and an activation energy $\Delta G_c^{\ddagger}$ of 14.5 ± 0.2 kcal/mol was calculated (Figure 1). Similar activation energies were obtained for adducts **32** and **34** (Table 2). The value for adduct **33** was not measured because of its poor solubility in most organic solvents. Interestingly, compound **35** showed a larger chemical shift difference (0.38 ppm), a higher coalescence temperature (55 °C), and hence, a larger $\Delta G_c^{\ddagger}$ (15.2 ± 0.2 kcal/mol), even though its structure is very similar to those of **31**–**34**. The activation energies $\Delta G_c^{\ddagger}$ were astonishingly high for 2,3-dichloroadduct **36** (a low limit of 17.2 kcal/mol was estimated) and 2,3-diphenyladduct **37** (17.1 kcal/mol). The bulky dichloro and diphenyl substituents should have lowered the activation energy barriers in adducts **36** and **37** if steric hindrance were the only factor affecting the boat-to-boat conformation transitions. Although steric effects have been proposed[12] as the main factor in a study of a series of aromatic attached fullerene adducts, other factors such as π–π and n–π electronic interactions are needed to explain the current results.

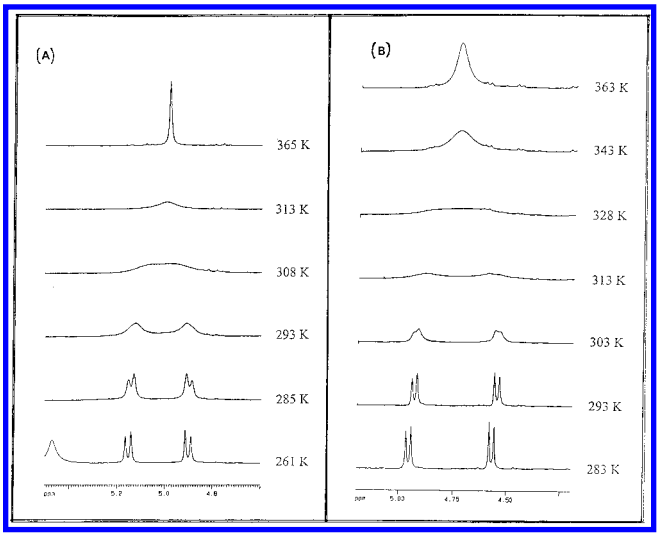
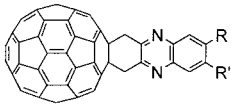
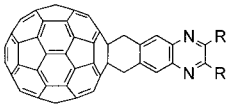
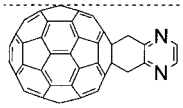
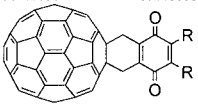
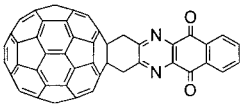
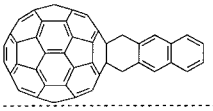
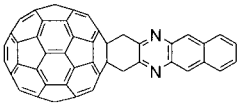


Figure 1. Various temperature measurements of ^{1}H NMR spectra (600 MHz, 1:3 $CDCl_3/CS_2$) of Diels–Alder adducts: (A) **31**, for which T_c is 308 K; and (B) **35**, for which T_c is 328 K.

Based on their semiempirical PM3 calculations,[8b] Martín et al. have found a linear correlation between the activation energy barriers and the length of the C62–C63 bond in aromatic-fused fullerenes, i.e., as the bond length increases the barrier also increases.[13a,b] They therefore proposed that the geometrical features, but not the electronic properties, of the organic addend are responsible for the activation energy barriers. Scrutinizing the activation energy barriers in Table 2, one may suspect that some kind of "electronic interactions" are involved, because quite different activation energy barriers were obtained for quinoxalino heterocycles of similar sizes but different orientations with respect to C_{60}. For example, the activation energy barrier $\Delta G_c^{\ddagger}$ of fullerene adduct **31** was found to be smaller (14.5 kcal/mol) than

(14) For strong evidence of through-space orbital interactions in fulleroids, see: (a) Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q. C.; Maggini, M.; Martín, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591. (b) Iyoda, M.; Sultana, F.; Sasaki, S.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1929.

Table 2. Activation Free Energies ($\Delta G_c^{\ddagger}$) of Fullerene Adducts 31−42 from Dynamic ^{1}H NMR[a]

structures of adducts		T_c, °C	$\Delta\delta_{AB}$, ppm[c]	$\Delta G_c^{\ddagger}$, kcal/mol	Reference
	**31** R = R' = H	35	0.25	14.5±0.2	this work
		34	0.30[b]	14.8±0.1	8a
	32 R = R' = Me	40	0.27	14.8±0.2	this work
	34 R = Me, R' = H	40	0.27	14.6±0.2	this work
	**35** R = H	55	0.38	15.2±0.2	this work
	36 R = Cl	>95	0.36	>17.2±0.2	this work
	37 R = Ph	95	0.40	17.1±0.2	this work
	**38**	25	0.23	14.1±0.2	this work
	**39a** R = H	-30	0.69	11.3±0.2	13a, 14b
	39b R = Br	-18	0.74	11.5±0.2	13a
	39c R + R = Ph	-21	1.56	11.6±0.2	13a
	**40**	<-60	-	<10.5±0.2	this work
	**41**	73	0.47[b]	16.4±0.2	this work
		80	0.46[d]	16.6±0.2	12
	**42**	45	0.36	16.1±0.2	8a
		60		15.8±0.2	8b

[a] Various temperature measurements were taken in a Bruker 600 MHz NMR, unless otherwise specified, and the solvents used were either $CDCl_3/CS_2$ = 3:1 or d_4-*ortho*-dichlorobenzene (for T_c higher than 55 °C). The activation free energies were obtained using equations from ref 11. $k_c = 2.22(\Delta\nu_{AB}^2 + 6\ J_{AB}^2)^{1/2}$, $\Delta G_c^{\ddagger} = 4.58\ T_c\ (10.32 + \log\ (T_c/k_c)) \times 10^{-3}$ kcal/mol. [b] Recorded in a 300 MHz NMR. [c] Data are reported at the highest temperature that affords well-separated quartets. For example, −12 °C for **31** and **32**, −5 °C for **34**, 10 °C for **35**, and −60 °C for **38**. [d] Recorded in a 500 MHz NMR.

that of adduct **35** (15.2 kcal/mol), even though their sizes are exactly the same except that the pyrazine ring is closer to C_{60} framework in the former. We also noted a general trend in our data that supports the notion of electronic $\pi-\pi$ interactions: the activation energy barrier is larger with increased benzannulation. For example, a comparison of the $\Delta G_c^{\ddagger}$ values of **38** (14.1 kcal/mol), **31** (14.5 kcal/mol), and **42** (15.8 kcal/mol) shows that 0.4 kcal/mol is added for the first benzannulation and an additional 1.3 kcal/mol is added for naphthoannulation. Such a difference has been observed previously by Nishimura et al.[12] and Martín et al.[13a] for carbocyclic analogues and was partly assigned to electronic-π interactions between the C_{60} framework and the overlying aromatic ring.

It is, however, a surprise to note that pyrazino annulation between C_{60} and the aromatic ring leads to a decrease in $\Delta G_c^{\ddagger}$ of at least 0.5−0.6 kcal/mol (cf. **39c** and **40**, **41**, and **42**). In the latter cases, nonbonded repulsion between the lone-pair electrons of the nitrogens and the C_{60} framework is probably involved and, thus, may decrease the activation energy barriers. Alternatively, the lowering of the activation energy barriers in the adducts **31**−**34** compared with those of adducts **35**−**37** can be explained by the tautomeric equilibrium between dimethylquinoxaline and its enamine tautomers. That is, the planarity of the cyclohexene ring, caused by the tautomerization, may stabilize the transition state energy and, thus, decrease the boat-to-boat inversion barriers.[15] Interestingly, fulleroadducts with benzoquinone and naphthoquinone addends (**39a**−**c**), have the smallest $\Delta G_c^{\ddagger}$ reported thus far for the series of Diels−Alder adducts of C_{60} (see Table 2). In adducts **39a**−**c** and **40**, the repulsion between the lone-pair electrons of quinone and the π-electrons of C_{60} could conceivably play an important role in lowering the transition state energy during the ring-inversion processes.

Finally, the ^{13}C NMR spectroscopy also provides important information about the structure of cycloadducts **31**−**38**. The position of attack of these heterocyclic *o*-quinodimethanes (**3**, **4**, and **25**) on a double bond between two annelated six-membered rings of the fullerene is shown by the number of ^{13}C NMR signals. Seventeen such signals of fullerene indicate a C_{2v} symmetry for the molecule (resulting from rapid ring inversion of the cyclohexene unit if measured above the coalescence temperature T_c).[2d] However, if the spectrum is taken at a temperature below T_c, one sees a well-resolved AB quartet in the ^{1}H NMR for cycloadducts **31**−**38**. The conformation is frozen, and one expects to observe 32

(15) For tautomerization of quinoxaline, see: (a) Aumiller, W. D.; Dalton, C. R.; Czarnik, A. W. *J. Org. Chem.* **1995**, *60*, 728. (b) Pohmer, J.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1995**, *60*, 8283. (c) Schönberg, A.; Mostafa, A. *J. Chem. Soc.* **1943**, 654.

signals of the fullerene because of its C_s symmetry. Indeed, we have observed that the peak numbers in ^{13}C NMR and the symmetry of **31**, **32**, and **35** are dependent on measuring temperatures (see Experimental Section). This explains why some of the reported ^{13}C NMR signal numbers were less than expected if they were run in a slow exchanging mode.[4c, 8a]

Summary and Conclusions

We report here a convenient, high-yield method for the syntheses of quinoxalinosultines **7a**−**c** and pyrazinosultine **22** and their application in Diels−Alder reactions with electron-poor olefins and C_{60}. Although the structures of 2,3-quinoxalinosultines **7a**−**c** are very similar to those of 6,7-quinoxalinosultines **6a**−**c**,[7a] their reaction products are different in three respects. Among the other reported syntheses of quinoxalino-fused [60]fullerenes,[8] our methods give the best yields. Quinoxalinosultines, pyrazinosultine, and other heterocyclic analogues[7] are thus useful synthons of heterocyclic *o*-quinodimethanes **2**.

Dynamic NMR spectra were recorded for the heterocyclic-fused [60]fullerenes (**31**−**38**), and their boat-to-boat inversion energy barriers ($\Delta G_c^{\ddagger}$) were determined. Our results indicate that the $\pi-\pi$ and $n-\pi$ electronic interactions and the "tautomerization-induced planar effects" are three important factors in determining the activation free energy barriers. However, how they correlate with the "bond-length effect of C62−C63" is not yet fully understood and will be the subject of further theoretical calculations. Work is in progress in this direction.

Experimental Section

General. Melting points were determined on a Yanaca MP-500D melting point apparatus and are uncorrected. ^1H NMR spectra were recorded at either 300 or 600 MHz, ^{13}C and DEPT NMR spectra were recorded at either 75.4 or 150.9 MHz, and the chemical shifts are reported in parts per million (δ) relative to $CDCl_3$ (δ = 7.25 for a proton and 77 ppm for carbon) or tetramethylsilane as the internal standard. Coupling constants are reported in hertz (Hz). The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol. C, H, and N combustion analysis was performed on a Heraeus analyzer, and all analyzed compounds are within ±0.4% of the theoretical value unless otherwise indicated. Column chromatography was performed on silica gel 70−230 or 230−400 mesh; thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254}. The preparations of 1,4-dihydro-6,7-dimethylquinoxaline-2,3-dione **11**,[5d] 6,7-bis(bromomethyl)-quinoxaline **9a**,[5b] 6,7-dibromomethyl-2,3-dichloro-quinoxaline **9b**,[5c,d] and 6,7-dibromomethyl-2,3-diphenylquinoxaline **9c**[5e] all followed literature procedures.

General Procedures for the Synthesis of Quinoxalinosultines 7a−c. A solution of **9a**−**c**[5b,c] (e.g., for **9a**, 1.40 g, 4.43 mmol) and Rongalite (3.41 g, 22.2 mmol) in DMF (20 mL) was stirred at room temperature for 2 h. The mixture was diluted with H_2O (40 mL) and extracted three times (20 mL) with CH_2Cl_2. The organic layer was dried over $MgSO_4$, concentrated, and purified by column chromatography (4:1 hexane/ethyl acetate) to give 0.69 g (3.14 mmol, 71%) of **7a** as a pale gray solid. For the synthesis of **7b**, a longer reaction time (4 h) was needed, and the yield was 76%. The reaction for **7c** was carried at 0 °C for 4 h, and the eluent was 5:1 hexane/ethyl acetate, with 26−55% yield.

2,3-Disubstituted 8,9-dihydro-6*H*-8λ^4-[1,2]oxathiino[4,5-*g*]quinoxalin-8-one, Sultine 7a: an off-white solid; mp 161−162 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (2H, s), 8.00 (2H, s), 5.54 (1H, AB, J = 13.8 Hz), 5.21 (1H, AB, J = 13.9 Hz), 4.69 (1H, A′B′, J = 15.6 Hz), 3.85 (1H, A′B′, J = 15.5 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.55 (CH), 145.44 (CH), 142.37 (C_q), 141.85 (C_q), 135.54 (C_q), 130.20 (CH), 128.95 (C_q), 126.18 (CH), 62.79 (CH_2), 57.15 (CH_2); MS (EI) *m*/*z* 220 (M^+, 1), 156 ($M^+ - SO_2$, 100); HRMS calcd for $C_{10}H_8N_2O_2S$ 220.0306, found 220.0304.

2,3-Dichloro-8,9-dihydro-6*H*-8λ^4-[1,2]oxathiino[4,5-*g*]quinoxalin-8-one, Sultine 7b: a pale gray solid; mp 182−186 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (2H, s), 5.50 (1H, AB, J = 14.1 Hz), 5.19 (1H, AB, J = 14.1 Hz), 4.63 (1H, A′B′, J = 15.6 Hz), 3.80 (1H, A′B′, J = 15.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.40 (C_q), 140.14 (C_q), 139.64 (C_q), 136.93 (C_q), 130.47 (C_q), 129.24 (C_q), 129.16 (CH), 125.05 (CH), 62.52 (CH_2), 57.07 (CH_2); MS (EI) *m*/*z* 288 (M^+, 7), 224 ($M^+ - SO_2$, 100), 189 (28); HRMS calcd for $C_{10}H_6Cl_2N_2O_2S$ 287.9527, found 287.9520. Anal. Calcd for $C_{10}H_6Cl_2N_2O_2S$: C, 41.54; H, 2.09; N, 9.69. Found: C, 41.35; H, 2.29; N, 9.46.

2,3-Diphenyl-8,9-dihydro-6*H*-8λ^4-[1,2]oxathiino[4,5-*g*]quinoxalin-8-one, Sultine 7c: a pale yellow solid; mp 219−223 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08−8.07 (2H, d, J = 4.4 Hz), 7.52−7.50 (4H, m), 7.39−7.26 (6H, m), 5.55, 5.21 (2H, AB_q, J = 13.7 Hz), 4.71, 3.82 (2H, A′B′$_q$, J = 15.4 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.29 (C_q), 154.18 (C_q), 140.85 (C_q), 140.31 (C_q), 138.58 (C_q), 135.64 (C_q), 129.95 (CH), 129.76 (CH), 129.08 (CH), 128.89 (C_q), 128.29 (CH), 126.12 (CH), 63.16 (CH_2), 57.75 (CH_2); MS (EI) *m*/*z* 372 (M^+, 6), 309 (27), 308 ($M^+ - SO_2$, 100), 307 (56), 102 (24); HRMS calcd for $C_{22}H_{16}N_2O_2S$ 372.0934, found 372.0941. Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.97; H, 4.30; N, 7.53. Found: C, 70.18; H, 4.54; N, 7.58.

General Procedure for the Trapping Experiments of Quinoxalinosultines 7a−c with Dienophiles such as Diethyl Fumarate, Dimethyl Fumarate, Dimethyl Maleate, *N*-Phenylmaleimide, and Fumaronitrile. A solution of quinoxalinosultines **7a** (50 mg, 0.23 mmol), with or without their respective dienophiles (3 equiv vs **7**), in toluene (4 mL) was sealed in a 20-mL Pyrex tube by three cycles of the freeze−pump−thaw method and was heated at 180 °C for 4 h. (The solutions for **7b** were also heated at 200 °C for 4 h, but those for **7c** were heated for 24 h.) After the solution cooled to room temperature, the solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 1:1 to 1:4) as the eluent. Respective yields for the trapping experiments with or without dienophiles are summarized in Scheme 2 and Table 1.

Diethyl-(7*R*,8*R*)-2,3-dichloro-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (12b): 82% yield, a pale yellow solid; mp 151−152 °C; δ_H 7.75 (2H, s), 4.18 (4H, q, J = 7.2 Hz), 3.38−3.12 (6H, m), 1.27 (6H, t, J = 7.2 Hz); δ_C 173.62 (C_q), 144.89 (C_q), 139.53 (C_q), 139.32 (CH), 126.62 (CH), 61.18 (CH_2), 41.45 (CH), 31.58 (CH_2), 14.12 (CH_3); MS (EI) *m*/*z* 396 (M^+, 13), 322 (39), 249 (71), 238 (100); HRMS (EI) calcd for $C_{18}H_{18}Cl_2N_2O_4$ 396.0643, found 396.0635.

Diethyl-(7*R*,8*R*)-2,3-diphenyl-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (12c): 92% yield, a white solid; mp 141−143 °C; δ_H 7.91 (2H, s), 7.48−7.45 (4H, m), 7.33−7.28 (6H, m), 4.19 (4H, q, J = 6.9 Hz), 3.42−3.18 (6H, m), 1.28 (6H, t, J = 6.9 Hz); δ_C 174.03 (C_q), 153.20 (C_q), 140.01 (C_q), 139.09 (C_q), 137.61 (C_q), 129.77 (CH), 128.70 (CH), 128.21 (CH), 127.57 (CH), 61.08 (CH_2), 41.91 (CH), 31.88 (CH_2), 14.18 (CH_3); MS (EI) *m*/*z* 480 (M^+, 33), 406 (43), 333 (100); HRMS (EI) calcd for $C_{30}H_{28}N_2O_4$ 480.2050, found 480.2040. Anal. Calcd for $C_{30}H_{28}N_2O_4$: C, 75.00; H, 5.83; N, 5.83. Found: C, 74.63; H, 5.99; N, 6.10.

7,8-Dihydro-6*H*-7λ^6-thieno[3,4-*g*]quinoxaline-7,7-dione (13a): a brown solid; mp 257−258 °C; δ_H 8.90 (2H, s), 8.11 (2H, s), 4.61 (4H, s); δ_C 145.89 (CH), 142.57 (C_q), 133.66 (C_q), 127.17 (CH), 56.38 (CH_2); MS (EI) *m*/*z* 220 (M^+, 18), 156 ($M^+ - SO_2$, 100); HRMS calcd for $C_{10}H_8N_2O_2S$ 220.0306, found 220.0315.

2,3-Dichloro-7,8-dihydro-6*H*-7λ^6-thieno[3,4-*g*]quinoxaline-7,7-dione (13b): a pale yellow solid; δ_H 8.00 (2H, s), 4.56 (4H, s); δ_C 142.05 (C_q), 140.63 (C_q), 135.04 (C_q), 126.01 (CH), 56.37 (CH_2); HRMS calcd for $C_{10}H_6N_2O_2\,S^{35}Cl_2$ 287.9527, found 287.9528.

2,3-Diphenyl-7,8-dihydro-6*H*-7λ^6-thieno[3,4-*g*]quinoxaline-7,7-dione (13c): a pale yellow solid; mp > 290 °C, dec;

δ_H 8.13 (2H, s), 7.53−7.50 (4H, m), 7.38−7.35 (6H, m), 4.61 (4H, s); δ_C 154.44 (C_q), 140.78 (C_q), 138.46 (C_q), 133.27 (C_q), 129.78 (CH), 129.22 (CH), 128.34 (CH), 126.71 (CH), 56.50 (CH_2); MS (EI) *m*/*z* 372 (M^+, 62), 308 ($M^+ - SO_2$, 100), 307 (73), 154 (33); HRMS calcd for $C_{22}H_{16}N_2O_2S$ 372.0934, found 372.0921. Anal. Calcd for $C_{22}H_{16}N_2O_2$ S: C, 70.97; H, 4.30; N, 7.53. Found: C, 70.92; H, 4.55; N, 7.58.

Dimethyl-(7*R*,8*R*)-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (14a): 75% yield, a pale yellow solid; mp 142−143 °C; δ_H 8.77 (2H, s), 7.85 (2H, s), 3.77 (6H, s), 3.44−3.36 (2H, m), 3.33−3.17 (4H, m); δ_C 174.25 (C_q), 144.63 (CH), 141.69 (C_q), 137.57 (C_q), 127.79 (CH), 52.20 (CH_3), 41.54 (CH), 31.53 (CH_2); MS (EI) *m*/*z* 300 (M^+, 23), 240 (51), 181 (100); HRMS (EI) calcd for $C_{16}H_{16}N_2O_4$ 300.1110, found 300.1115.

Dimethyl-(7*R*,8*R*)-2,3-diphenyl-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (14c): 83% yield, a pale yellow solid; mp 199−202 °C; δ_H 7.91 (2H, s), 7.48−7.45 (4H, m), 7.34−7.24 (6H, m), 3.75 (6H, s), 3.43−3.23 (6H, m); δ_C 174.49 (C_q), 153.25 (C_q), 140.03 (C_q), 139.08 (C_q), 137.46 (C_q), 129.78 (CH), 128.74 (CH), 128.23 (CH), 127.60 (CH), 52.31 (CH_3), 41.80 (CH), 25.88 (CH_2); MS (EI) *m*/*z* 452 (M^+, 87), 392 (70), 333 (100); HRMS (EI) calcd for $C_{28}H_{24}N_2O_4$ 452.1737, found 452.1739. Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.34; H, 5.31; N, 6.20. Found: C, 73.79; H, 5.51; N, 6.37.

Dimethyl-(7*R*,8*S*)-2,3-dichloro-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (15b): 62% yield, a pale yellow solid; mp 178−179 °C; δ_H 7.76 (2H, s), 3.74 (6H, s), 3.53−3.30 (6H, m); δ_C 172.69 (C_q), 144.77 (C_q), 139.15 (C_q), 138.92 (C_q), 127.20 (CH), 52.21 (CH_3), 40.17 (CH), 30.03 (CH_2); MS (EI) *m*/*z* 368 (M^+, 14), 308 (61), 249 (100), 57 (33); HRMS (EI) calcd for $C_{16}H_{14}Cl_2N_2O_4$ 368.0331, found 368.0338. Anal. Calcd for $C_{16}H_{14}Cl_2N_2O_4$: C, 52.05; H, 3.82; N, 7.59. Found: C, 51.79; H, 3.49; N, 7.57.

Dimethyl-(7*R*,8*S*)-2,3-diphenyl-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarboxylate (15c): 60% yield, a pale yellow solid; mp 143−146 °C; δ_H 7.95 (2H, s), 7.49−7.46 (4H, m), 7.35−7.26 (6H, m), 3.72 (6H, s), 3.55−3.37 (6H, m); δ_C 172.99 (C_q), 153.15 (C_q), 139.83 (C_q), 139.15 (C_q), 137.25 (C_q), 129.76 (CH), 128.66 (CH), 128.19 (CH), 52.13 (CH_3), 40.48 (CH), 30.04 (CH_2); MS (EI) *m*/*z* 452 (M^+, 60), 392 (54), 333 (100). Anal. Calcd for $C_{28}H_{24}N_2O_4$: C, 74.34; H, 5.31; N, 6.20. Found: C, 73.97; H, 5.71; N, 6.19.

8-Phenyl-6a,7,8,9,9a,10-hexahydro-6*H*-isoindolo[5,6-*g*]-quinoxaline-7,9-dione (16a): 87% yield, a light yellowish solid; mp 244−245 °C; δ_H 8.81 (2H, s), 7.96 (2H, s), 7.30−7.24 (3H, m), 6.89−6.83 (2H, m), 3.58−3.48 (4H, m), 3.28−3.18 (2H, m); δ_C 177.71 (C_q), 144.83 (CH), 142.38 (C_q), 137.84 (C_q), 131.35 (C_q), 128.93 (CH), 128.55 (C_q), 127.84 (CH), 126.05 (CH), 39.66 (CH), 29.98 (CH_2); MS (EI) *m*/*z* 329 (M^+, 100), 182 (70), 181 (63); HRMS (EI) calcd for $C_{20}H_{15}N_3O_2$ 329.1164, found 329.1159.

2,3-Dichloro-8-phenyl-6a,7,8,9,9a,10-hexahydro-6*H*-isoindolo[5,6-*g*]quinoxaline-7,9-dione (16b): 93% yield, a pale yellow solid; mp 294−297 °C; δ_H 7.79 (2H, s), 7.30−7.17 (3H, m), 6.90−6.60 (2H, m), 3.50−3.10 (6H, m); δ_C 177.43 (C_q), 145.35 (C_q), 139.96 (C_q), 139.32 (C_q), 131.28 (C_q), 129.04 (CH), 128.69 (CH), 126.68 (CH), 126.04 (CH), 39.50 (CH), 30.09 (CH_2); MS (EI) *m*/*z* 397 (M^+, 100), 250 (54); HRMS (EI) calcd for $C_{20}H_{13}N_3Cl_2O_2$ 397.0384, found 397.0378.

2,3,8-Triphenyl-6a,7,8,9,9a,10-hexahydro-6*H*-isoindolo-[5,6-*g*]quinoxaline-7,9-dione (16c): 98% yield, a pale yellow solid; mp > 270 °C dec; δ_H 8.00 (2H, s), 7.53−7.50 (4H, m), 7.36−7.27 (9H, m), 6.92−6.89 (2H, m), 3.57−3.22 (6H, m); δ_C 172.84 (C_q), 153.17 (C_q), 140.50 (C_q), 138.85 (C_q), 137.64 (C_q), 131.39 (C_q), 129.77 (CH), 128.94 (CH), 128.81 (CH), 128.53 (CH), 128.21 (CH), 127.51 (CH), 126.13 (CH), 39.75 (CH), 30.07 (CH_2); MS (EI) *m*/*z* 481 (M^+, 100), 480 ($M^+ - 1$, 15); HRMS (EI) calcd for $C_{32}H_{23}N_3O_2$ 481.1792, found 481.1794.

(7*R*,8*R*)-6,7,8,9-Tetrahydrobenzo[*g*]quinoxaline-7,8-dicarbonitrile (17a): 75% yield, a pale yellow solid; mp 268−270 °C; δ_H 8.84 (2H, s), 7.96 (2H, s), 3.70−3.59 (2H, m), 3.48−3.37 (4H, m); δ_C 145.62 (CH), 141.93 (C_q), 132.92 (C_q), 129.33 (CH), 118.06 (C_q), 30.55 (CH_2), 28.40 (CH); MS (EI) *m*/*z* 234 (M^+, 100), 156 (87); HRMS calcd for $C_{14}H_{10}N_4$ 234.0905, found 234.0903.

Because of a solubility problem, the trapping of **12b** with fumaronitrile was not carried out.

(7*R*,8*R*)-2,3-Diphenyl-6,7,8,9-tetrahydrobenzo[*g*]quinoxaline-7,8-dicarbonitrile (17c): 60% yield, a white solid; mp 261−263 °C; δ_H 7.97 (2H, s), 7.49−7.46 (4H, m), 7.36−7.28 (6H, m), 3.68−3.41 (6H, m); δ_C 154.14 (C_q), 140.11 (C_q), 138.70 (C_q), 132.66 (C_q), 129.74 (CH), 129.01 (CH), 128.85 (CH), 128.27 (CH), 118.17 (C_q), 30.72 (CH_2), 28.55 (CH); MS (EI) *m*/*z* 386 (M^+, 100), 385 (24); HRMS calcd for $C_{26}H_{18}N_4$ 386.1533, found 386.1534. Anal. Calcd for $C_{26}H_{18}N_4$: C, 80.83; H, 4.66; N, 14.51. Found: C, 79.99; H, 4.84; N, 14.17.

6,7-Dihydrocyclobuta[*g*]quinoxaline (18a): a brown solid; mp 107−109 °C; δ_H 8.75 (2H, s), 7.71 (2H, s), 3.43 (4H, s); δ_C 149.50 (C_q), 143.95 (C_q), 142.99 (CH), 122.21 (CH), 29.45 (CH_2); MS (EI) *m*/*z* 156 (M^+, 100), 111 (28), 97 (45), 85 (59), 71 (55), 57 (70); HRMS calcd for $C_{10}H_8N_2$ 156.0687, found 156.0689.

2,3-Dichloro-6,7-dihydrocyclobuta[*g*]quinoxaline (18b): a pale yellow solid; mp 157−160 °C; δ_H 7.73 (2H, s), 3.40 (4H, s); δ_C 150.98 (C_q), 142.12 (C_q), 138.42 (C_q), 121.42 (CH), 29.60 (CH_2).

2,3-Diphenyl-6,7-dihydrocyclobuta[*g*]quinoxaline (18c): a pale yellow solid; mp 113−118 °C; δ_H 7.76 (2H, s), 7.50−7.47 (4H, m), 7.32−7.30 (6H, m), 3.34 (4H, s); δ_C 151.37 (C_q), 149.38 (C_q), 142.11 (C_q), 139.31 (C_q), 129.83 (CH), 128.47 (CH), 128.19 (CH), 121.98 (CH), 29.55 (CH_2); MS (EI) *m*/*z* 308 (M^+, 100), 309 ($M^+ + 1$, 21), 307 ($M^+ - 1$, 82), 154 (23), 102 (21); HRMS calcd for $C_{22}H_{16}N_2$ 308.1315, found 308.1304.

Synthesis of Pyrazinosultine 22. A solution of **24** (1 g, 3.79 mmol) and Rongalite (0.86 g, 5.68 mmol) in DMF (10 mL) was stirred at 0 °C for 6 h. The mixture was diluted with H_2O (10 mL) and extracted three times (5 mL) with CH_2Cl_2. The organic layer was dried over $MgSO_4$, concentrated, and purified by column chromatography (3:2 hexane/ethyl acetate) to give 0.223 g of **22** as a gray solid (34.6%). **22**: a gray solid; mp 59−61 °C; δ_H 3.95 (1H, AB, J = 16.4 Hz), 4.38 (1H, AB, J = 16.5 Hz), 5.15 (1H, A′B′, J = 15.9 Hz), 5.43 (1H, A′B′, J = 15.8 Hz); δ_C 56.23 (CH_2), 61.32 (CH_2), 141.69 (C_q), 143.47 (CH), 144.44 (CH), 147.33 (C_q); MS (EI) *m*/*z* 170 (M^+, 15), 106 ($M^+ - SO_2$, 100).

General Procedure for the Trapping Experiments of Pyrazinosultine 22 with Dienophiles such as *N*-Phenylmaleimide, Dimethyl Fumarate, Dimethyl Acetylenedicarboxylate, and Fumaronitrile. A solution of pyrazinosultine **22** (50 mg, 0.294 mmol), with or without the respective dienophiles (0.353 mmol), in toluene (3 mL) was refluxed under N_2 for 12 h. The solvent was evaporated under vacuum, and the residue was subjected to silica gel chromatography using hexane/ethyl acetate (from 3:1 to 1:1) as the eluent. Slightly lower yields were obtained in each case when the reactions were carried out in a sealed tube at 180 °C for 24 h. Sulfolene **26** was obtained in 73% yield (no quencher). For the trapping of dienes, the respective yields are: *N*-phenylmaleimide, 59% of dimethyl fumarate, 71% of **28**, and 12% of **26**; dimethyl acetylenedicarboxylate, 33% of **29** and 20% of **26**; and fumaronitrile, 96% of **30**.

Pyrazinosulfolene 26: a white solid; mp 196−198 °C (lit.[6c] 188−189 °C); δ_H 4.60 (4H, s), 8.58 (2H, s); δ_C 58.01 (CH_2), 145.22 (CH), 147.69 (C_q); MS (EI) *m*/*z* 170 (M^+, 25), 106 ($M^+ - SO_2$, 100); HRMS calcd for $C_6H_6O_2N_2S$ 170.01500, found 170.01474.

Adduct 27: a white solid; mp 186−189 °C; δ_H 3.28−3.33 (2H, m), 3.42−3.57 (4H, m), 7.04 (2H, d, J = 7.5 Hz), 7.32−7.39 (3H, m), 8.41 (2H, s); δ_C 31.84 (CH_2), 39.36 (CH), 126.06 (CH), 128.7 (CH), 129.02 (CH), 131.35 (CH), 143.20 (CH), 151.13 (C_q), 177.08 (C_q); MS (EI) *m*/*z* 279 (M^+, 77), 132 [$M^+ - (PhNC_2O_2)$, 96], 131 [$M^+ - (PhNC_2O_2 + H)$, 100]; HRMS calcd for $C_{16}H_{13}O_2N_3$ 279.1001, found 279.10089. Anal. Calcd for $C_{16}H_{13}O_2N_3$: C, 68.81; H, 4.69; N, 15.04. Found: C, 68.87; H, 4.71; N, 15.02.

Cycloaddition Reactions of C_{60} with Pyrazinosultine 22. A solution of C_{60} (105 mg, 145 mmol) and pyrazinosultine **22** (30 mg, 176 mmol) in toluene (20 mL) was refluxed for 6 h. The resulting brown reaction mixture was evaporated to dryness under reduced pressure. The residue was subjected

to silica gel chromatographywith toluene as the eluent, recovering 35 mg of unreacted C_{60} and 62 mg of adduct **38** (52% yield, 78% based on consumed C_{60}).

Adduct 38: a brown solid; mp > 460 °C; δ_H (measured at 25 °C) 4.87 (4H, s), 8.73 (2H, s); δ_C 46.70 (CH_2), 64.70 (aliph. C of C_{60}), 135.14, 140.03, 141.45, 141.73, 141.82, 142.35, 142.86, 143.73, 144.37, 144.68, 145.19, 145.33, 145.41, 146.01, 146.24, 147.40, 153.10, 155.23 [where 20 peaks are expected (C_{2v}) and 20 carbons observed]; MS (EI) *m*/*z* 827 ($M^+ + 1$, 12), 720 (100); HRMS $(M + H)^+$ calcd for $C_{66}H_7N_2$ 827.0610, found 827.0610.

General Procedures for the Cycloaddition Reactions of C_{60} with Quinoxalinosultines 6a−c and 7a−c. A solution of C_{60} (50 mg, 69 mmol) and quinoxalinosultines **6a−d** and **7a−c** (83 mmol) in *o*-dichlorobenzene (20 mL) was refluxed under nitrogen for variable periods of time (24 h for **6a−c, 7b** and **7c**; 4 h for **7a**). The resulting brown reaction mixture was evaporated to dryness under reduced pressure. The residue was subjected to silica gel chromatography with hexane/toluene (2:1 to 1:1) as the eluent, recovering various amount of unreacted C_{60} and the adducts **31−37**.

31: 51% yield, 66% based on consumed C_{60}; a brown solid; mp > 495°C; ^{1}H NMR (22 °C, 300 MHz, 1:3 $CDCl_3/CS_2$) δ_H 8.28−8.22 (2H, m), 7.89−7.83 (2H, m), 5.18 (2H, br AB), 4.93 (2H, br AB); ^{13}C NMR (0 °C, 150 MHz, 1:3 $CDCl_3/CS_2$) δ_C 47.09* (CH_2), 64.14 (aliph. C_q of C_{60}), 129.15* (CH), 129.64* (CH), 134.86, 135.19, 139.81, 140.00*, 141.24, 141.38, 141.43, 141.63 (b, 2C), 141.70, 142.16, 142.22, 142.31, 142.59, 142.76, 144.18, 144.21, 144.29, 144.83, 144.99, 145.05, 145.06, 145.23, 145.33 (b, 2C), 145.79, 145.91, 146.06, 146.09, 147.24, 152.85*, 154.77, 154.82 (30 fullerene signals and * denotes peaks from quinoxaline); ^{13}C NMR (92 °C, 150 MHz, $C_6D_4Cl_2$) δ_C 47.67* (CH_2), 64.80 (aliph. C_q of C_{60}), 130.15* (CH), 130.19* (CH), 135.12, 140.05*, 141.43, 141.76, 141.82, 142.32, 142.80, 143.12, 144.37, 144.69, 145.21 (b, 2C), 145.43, 146.01, 146.22, 147.46, 153.42,* 155.42; FAB-MS $(M + H)^+$ *m*/*z* 877 ($M + 1$, 31), 720 (100); UV (THF) λ_{max}, nm (log ϵ) 434 (3.18), 322 (4.25), 256 (4.61), 244 (4.66).

32: 66% yield, 78% based on consumed C_{60}; a brown solid; mp > 495 °C; ^{1}H NMR (22 °C, 300 MHz, 1:3 $CDCl_3/CS_2$) δ_H 7.98 (2H, s), 5.15 (2H, br AB), 4.88 (2H, br AB); 2.61 (6H, s); ^{13}C NMR (0 °C, 150 MHz, 1:3 $CDCl_3/CS_2$) δ_C 20.41* (CH_3), 47.10* (CH_2), 64.34 (aliph. C_q of C_{60}), 128.32* (CH), 134.89 (CH), 135.21, 139.82, 139.95*, 140.01, 141.26, 141.36, 141.43, 141.45*, 141.66, 141.68, 141.73, 142.18, 142.23, 142.61, 142.78, 144.22, 144.25, 144.40, 144.92, 145.01, 145.06, 145.08, 145.25, 145.33, 145.37, 145.81, 145.93, 146.07, 146.11, 147.26, 151.77*, 154.99, 155.10 (32 fullerene signals and * denotes 6 peaks from quinoxaline); FAB-MS (MNB) *m*/*z* 905 ($M + 1$, 17), 720 (78), 663 (100); UV (THF) λ_{max}, nm (log ϵ) 434 (3.15), 326 (4.28), 248 (4.70), 216 (4.66).

35: 63% yield, 84% based on consumed C_{60}; a brown solid; mp > 495 °C; ^{1}H NMR (22 °C, 300 MHz, 1:3 $CDCl_3/CS_2$) δ_H 8.91 (2H, s), 8.37 (2H, s), 5.09 (2H, AB, $J = 14.1$ Hz), 4.71 (2H, AB, $J = 14.0$ Hz); ^{13}C NMR (22 °C, 150 MHz, 1:3 $CDCl_3/CS_2$) δ_C 44.90* (CH_2), 64.96 (aliph. C_q of C_{60}), 128.03* (CH), 135.11, 135.81, 139.95, 140.17, 140.26,* 141.36, 141.55, 141.69, 141.81, 141.91, 142.37, 142.40, 142.83, 142.93,* 142.97, 144.42, 144.44, 144.63, 144.66* (CH), 145.15, 145.21 (b, 2C), 145.25, 145.40, 145.45, 145.57, 145.98, 146.08, 146.24, 146.27, 147.44, 155.50, 155.63; ^{13}C NMR (95 °C, 150 MHz, $C_6D_4Cl_2$) δ_C 45.10* (CH_2), 65.29 (aliph. C_q of C_{60}), 128.04* (CH), 135.37, 140.03, 140.32,* 141.39, 141.81, 141.84, 142.30, 142.79*, 143.34, 144.40, 144.57* (CH), 144.92, 145.19 (b, 2C), 145.45, 145.98, 146.20, 147.44, 155.85; FAB-MS (MNB) *m*/*z* 877 ($M + 1$, 35), 720 (100); UV (THF) λ_{max}, nm (log ϵ) 434 (3.35), 322 (4.27), 310 (4.25), 254 (4.67), 242 (4.70), 214 (4.83).

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Supporting Information Available: ^{1}H and ^{13}C (or DEPT) NMR spectra for compounds **7a**, **12b**, **13a, 14a**, **16a−18a**, **16c**, **18c**, **22**, and **26−38** and synthetic procedures and spectral data for **8a−c**, **9a−c**, **24**, **28−30**, **33**, **34**, **36**, and **37**. This material is available free of charge via the Internet at http://pubs.acs.org.

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