J. Org. Chem. **1997,** *62,* 3705−3710

Thermal and Microwave-Assisted Synthesis of Diels−Alder Adducts of [60]Fullerene with 2,3-Pyrazinoquinodimethanes: Characterization and Electrochemical Properties

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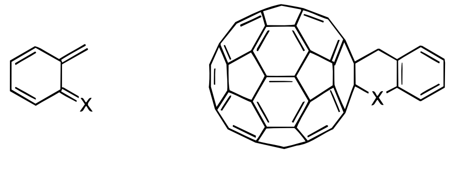
Received January 24, 1997[⊗]

[4+2] Cycloaddition reactions of six-membered heterocyclic *o*-quinodimethanes, generated “in situ” from pyrazine derivatives, to [60]fullerene, either under thermal or microwave irradiation are described. Other microwave assisted cycloadditions involving *o*-quinodimethanes derived from thiophene were also performed. A comparative study of the activation energy for the boat-to-boat conformational inversion has been carried out by dynamic NMR experiments, the $\Delta G^{\ddagger}$ values being highly dependent on the nature of the covalently attached heterocyclic systems. Theoretical calculations predict a more planar cyclohexene ring for the five member containing cycloadducts. The cycloaddition process is controlled by the HOMO of the heterocyclic *o*-quinodimethanes showing a LUMO(C_{60})-HOMO(diene) energy differences typical for favoured cycloadditions. The redox properties of the novel organofullerenes have been determined by cyclic voltammetry in solution, showing a cathodically shifted first reduction potential values, related to [60]fullerene. Compound **15c** bearing two cyano groups exhibited an opposite trend which was accounted for by the lower LUMO energy determined by semiempirical calculations.

Introduction

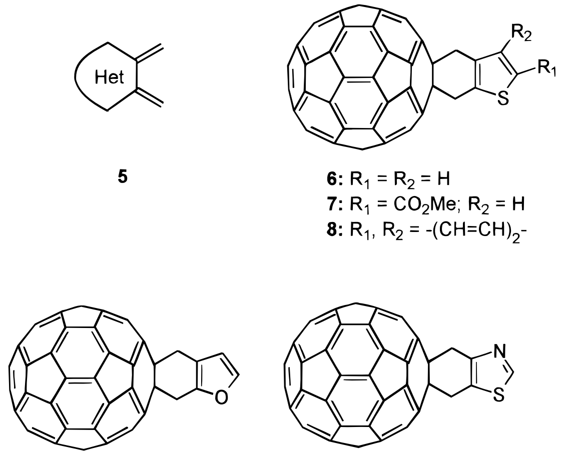
Cycloaddition reactions are among the most outstanding and expeditious methods for the derivatization of [60]fullerene, which behaves as a good dienophile reacting with a large variety of dienes.[1] In particular, [4 + 2] cycloaddition reactions afford selectively the adducts on 6,6-ring junctions which, in some cases, undergo a facile retro-Diels−Alder reaction as a consequence of the low thermodynamic stability of the adduct formed.[2] Very stable Diels−Alder cycloadducts have been, however, prepared by using different substituted *o*-quinodimethanes[3] due to the stabilization by aromatization of the resulting products. Thus, Diels−Alder and hetero-Diels−Alder cycloadditions of C_{60} with *o*-quinodimethane (**1**) and related heterodienes (**2**) have been previously reported to yield the respective carbo[4] and heterocycle-fused[5] fullerenes (**3** and **4**) (Figure 1).



1: X = CH_2
2: X = O, S

3: X = CH_2
4: X = O, S

Figure 1.



5

6: $R_1 = R_2 = H$
7: $R_1 = CO_2Me$; $R_2 = H$
8: R_1, R_2 = -(CH=CH)$_2$-

9

10

Figure 2.

[4 + 2] Cycloaddition reactions of heteroaromatic analogues of *o*-quinodimethane (**5**) (Figure 2) as dienes and [60]fullerene have been much less studied due to the synthetic difficulties in the preparation of the specific

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

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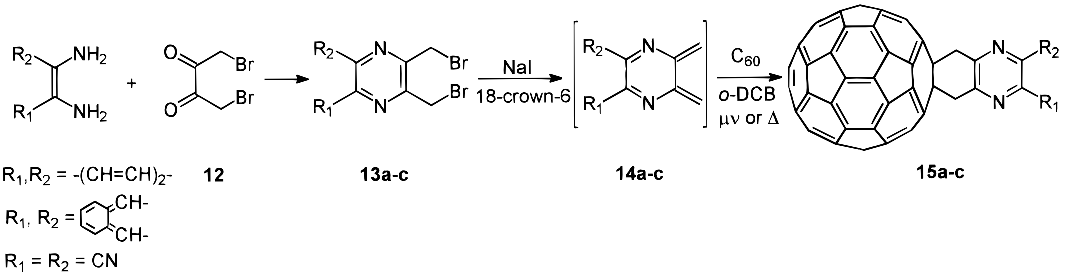
S0022-3263(97)00134-5 CCC: $14.00

Scheme 1



heterocyclic precursors needed for the generation "in situ" of the corresponding heteroaromatic *o*-quinodimethanes.[6] Although this methodology results very appropriate for the covalent attachment of heterocycles to the C_{60} core connected through two methylene units, it is synthetically restricted to the generation of these reactive intermediates, some of which have not yet been reported.[6]

Consequently, only a quite limited number of heterocyclic systems, not directly fused to the C_{60} cage, are known. To the best of our knowledge, only the thiophene-containing derivatives **6**−**8**,[7,8] the very light sensitive in oxygen atmosphere furan-linked derivative **9**,[9] and the thiazole ring containing cycloadduct **10**[9] have been reported. Indole and quinoxaline derivatives have also been recently described by Eguchi *et al.*[9] Other attempts to prepare cycloadducts with the oxazolidine ring attached to the C_{60} core were unsuccessful.[5]

On the other hand, microwave irradiation has shown to be a very useful alternative to conventional heating as source of energy for chemical reactions.[10] In this regard, significative reduction of reaction times and improved yield of products are generally achieved. Sometimes, microwave irradiation is crucial, because the reaction fails under conventional heating.[11]

We have recently reported that the Diels−Alder reaction of *o*-quinodimethane and its derivatives with [60]fullerene can be advantageously carried out by using sultines as precursors of *o*-quinodimethane under microwave irradiation due to the observed accelerating effect of microwaves.[12] In fact, a wide variety of cycloaddition reactions can be successfully performed on [60]fullerene under microwave conditions.[13]

In this paper we report [4 + 2] cycloadditions of a series of six-membered heteroaromatic *o*-quinodimethanes to [60]fullerene together with other cycloadditions of five-membered sulfur containing *o*-quinodimethanes to C_{60} obtained by microwave irradiation in comparison with thermal conditions. The C_{60}−pyrazine and thiophene-containing adducts are readily prepared in moderate yields, thus providing an expeditious access to [6,6]-closed fullerene derivatives covalently attached to different heterocycles.

Dynamic behavior of the different adducts has also been investigated by using variable-temperature NMR studies. Considering the electroactive character of these novel organofullerenes, we have carried out their electrochemical characterization by cyclic voltammetry in solution. PM3 theoretical calculations were also performed in order to gain some understanding of the experimental findings.

Results and Discussion

The novel pyrazine-containing cycloadducts (**15a**−**c**) were synthesized by Diels−Alder reaction of [60]fullerene with the corresponding 2,3-bis(bromomethyl)pyrazine derivatives (**13a**−**c**), which can be easily prepared, in a one-step procedure, by condensation of 1,4-dibromo-2,3-butanedione (**12**) with 1,2-phenylenediamine (**11a**), naphthalenediamine (**11b**), and 2,3-diaminobutenedinitrile (**11c**)[14] (Scheme 1). 2,3-Pyrazinoquinodimethane derivatives (**14a**−**c**) were generated "in situ" by treatment of 2,3-bis(bromomethyl)pyrazine derivatives (**13a**−**c**) with sodium iodide in *o*-dichlorobenzene (ODCB) at 130 °C, according to the method recently reported for the generation of 2,3-quinoxalinoquinodimethane.[15] These reactive intermediates (**14a**−**c**) were easily trapped as the respective Diels−Alder adducts by reaction with [60]fullerene acting as the dienophile (see the Experimental Section) (Table 1).

An alternative procedure for the preparation of pyrazine-containing cycloadducts (**15a** and **15b**) has been recently reported by Mattay *et al.*[16] In this synthetic approach the pyrazine ring is generated in the last synthetic step by condensation of *o*-phenylenediamine with the appropriate fullerocyclohexanedione.[17]

In this work we have used a focused microwave reactor (Maxidigest MX350 from Prolabo).[18] The novel results, together with those obtained for the cycloaddition of

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Table 1. Comparative Results in Cycloadditions Using Classical and Microwave Procedures

	microwave[a]		classical heating		
compd	time (h)	yield (%)	T (°C)	time (h)	yield (%)
7	1.25	16 (21)[b]	reflux[c]	72	25 (42)[b,7]
8	1.16[e]	23 (28)[b]	reflux[c]	17	43 (70)[b,7]
15a	0.50	26 (37)[b]	reflux[d]	24	13 (22)[b]
15b	0.50	22 (52)[b]	reflux[d]	24	5 (14)[b]
15c	0.33	9 (42)[b]	reflux[d]	5	16 (43)[b]

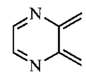
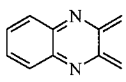
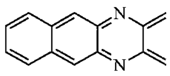
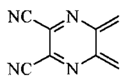
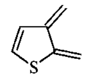
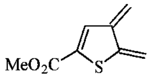
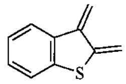
[a] Power 60 W. [b] Based on recovered C_{60}. [c] Toluene. [d] ODCB. [e] Power 70 W.

substituted thieno-*o*-quinodimethanes to [60]fullerene, previously reported under thermal conditions,[7] are shown in Table 1.

Thermally activated cycloadditions were accomplished by carrying out these reactions in refluxing ODCB under argon atmosphere and using the stoichiometry C_{60}:**13a**−**c**:NaI:18-crown-6 (1:1.1:4:3). It is interesting to note that only compound **15c** was optimized in the pyrazine series by monitoring of the thermal reaction by TLC. The reaction was concluded when the presence of regioisomeric bisadducts could be detected. This result is in good agreement with the remarkable higher yield obtained based on recovered C_{60}. Longer reaction times as in **15a,b** result in lower yields due to the formation of nonisolated higher adducts (see Table 1). Microwave-assisted cycloadditions were performed under the same experimental conditions for the preparation of cycloadducts **7** and **8** (105 W, monomode) and different experimental conditions for cycloadducts **15a**−**c** (C_{60}:**13a**−**c**, 2:1 or 4:1; TBAB as phase transfer catalyst; 60 W monomode) were used. Both different microwave-assisted experimental conditions were used for the preparation of organofullerene **7** without significative change in the obtained yields, although shorter times and lower power were needed when TBAB was used (see the Experimental Section). Interestingly, the use of microwave irradiation led to lower yield with five-membered *o*-quinodimethanes (**18**, **19**), and higher yields were obtained when six-membered 2,3-pyrazinoquinodimethanes were used as dienes, related to the classical heating. Only compound **15c** was obtained in a lower yield although in this case large amounts of polyadducts were observed by TLC. The yields of pyrazine cycloadducts obtained by thermal activation are comparatively lower than those of thiophene cycloadducts. In this regard, in addition to the formation of higher adducts and possible dimerization of the generated *o*-quinodimethane, the reaction of the bromomethyl groups with the heterocyclic nitrogen yielding a pyridinium salt cannot be ruled out.

In order to rationalize these experimental findings we have carried out PM3 quantum-chemical calculations (Hyperchem from Autodesk) on the heterocyclic *o*-quinodimethanes used as dienes in the preparation of cycloadducts **7**, **8**, and **15a**−**c**, in addition to the parent unsubstituted pyrazino- and thienoquinodimethanes (**16** and **17**) (Table 2). From these data it is observed that the cycloaddition is controlled by the HOMO of the heterocyclic *o*-quinodimethanes. The LUMO(C_{60})−HOMO(diene) energy differences are clearly in the range of energetically favored cycloadditions. On the other hand, no significative differences were observed from the distance (r_{1-4}) between the C_1 and C_4 carbon atoms of the respective dienes (Table 2). Consequently, cycloaddition reactions using 2,3-thienoquinodimethanes and 2,3-pyrazinoquinodimethanes are both favored from the orbital term point of view.

Table 2. PM3 Calculated HOMO and LUMO Levels of C_{60} and Heterocyclic *o*-Quinodimethanes

	Compound	$r_{1\text{-}4}$ (Å)	E (eV)	ΔE
	C_{60}	-	LUMO: -2.89 HOMO: -9.49	-
16		2.872	LUMO: -1.12 HOMO: -9.16	6.27
14a		2.939	LUMO: -1.65 HOMO: -8.58	5.69
14b		2.923	LUMO: -1.96 HOMO: -8.13	5.24
14c		2.923	LUMO: -2.10 HOMO: -9.83	6.94
17		3.027	LUMO: -0.53 HOMO: -8.42	5.53
18		3.030	LUMO:-1.11 HOMO:-8.63	5.74
19		2.998	LUMO: -0.61 HOMO: -8.40	5.51

ΔE = $LUMO_{C60}$ - $HOMO_{DIENE}$

The UV−vis spectra of compounds **15a**−**c** exhibit a typical weak absorption band at around 430 nm, characteristic for a dihydrofullerene structure. The ^{13}C NMR spectra of **15a** and **15c** showed 22 and 19 lines, respectively, consistent with a C_{2v} symmetry for these molecules. Cycloadduct **15a** showed the quaternary sp^3-hybridized carbon atoms of attachment to the substituent at δ 64.52 and the CH_2 groups at δ 47.46. The quinoxaline carbons appear together with the remaining C_{60} sp^2-carbon atoms between 155 and 127 ppm. Analogously, cycloadduct **15c** showed the quaternary carbons at δ 64.02 and 46.82 with the cyano group at δ 112.85, thus confirming the 6,6-ring junction on the C_{60} cage. The lower solubility of adduct **15b** prevented the registration of its ^{13}C NMR spectrum.

Compared to the previously reported thiophene-containing cycloadducts (**7**, **8**)[7] in which the methylene protons appear as two singlets at around δ 4.6−4.8, the pyrazine analogues (**15a,b**) present two broad doublets as a consequence of the restricted conformational inversion of the ring at room temperature, and **15c** shows a broad singlet.

The cyclohexene ring has a boat conformation, and the activation free energy for the boat-to-boat inversion has been determined by DNMR experiments for the cycload-

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(18) In the early experiments, domestic microwave ovens were used; this hardware had several limitations for using in laboratory. Home-made modifications were first performed, and specific designed apparatus have appeared later.

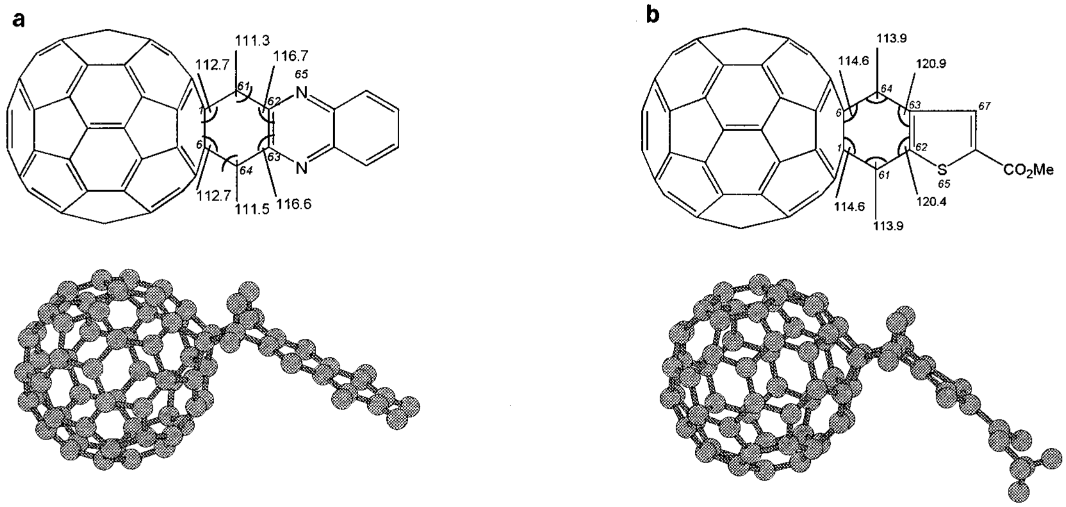

Figure 3.

Table 3. Activation Free Energies Determined for the Novel Heterocyclic Cycloadducts

compd	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kJ mol^{-1})[a]	J_{AB} (Hz)	$\Delta G^{\ddagger}$ (kJ mol^{-1})[b]
15a	323	104.4	64.7	14.4	64.5
15b	333	126.1	66.2	14.4	66.1
7	245	26.2	51.3	14.7	50.2
7	241	14.8	51.6	13.9	49.8
8	223	51.0	45.3	15.4	44.9
8	231	86.7	45.9	15.4	45.8

[a] Activation free energies at the coalescence temperatures according to $\Delta G^{\ddagger} = aT[9.972 + \log(T+\Delta\nu)]$ (ref 20). $a = 1.914 \times 10^{-2}$ kJ mol^{-1}. [b] Activation free energies at the coalescence temperatures according to $\Delta G^{\ddagger} = aT[9.972 + \log(T+(\delta\nu^2+6J^2_{AB})^{1/2}]$ (ref 20).

dition with carbocyclic *o*-quinodimethanes.[19] However, this is the first study on cycloadducts derived from C_{60} and heterocyclic *o*-quinodimethanes. The coalescence temperature and $\Delta G^{\ddagger}$ values show a great dependence on the nature of the heterocyclic system (Table 3).

The ^{1}H-NMR spectra of **15a** and **15b** at 293 K in $CDCl_3$ solution display a broad double doublet, indicative of a dynamic process. At 253 K a sharp AB system is observed in both compounds ($\delta_B = 5.29$, $\delta_A = 4.94$, $J_{AB} = 14.4$ Hz for compound **15a**; and $\delta_B = 5.36$, $\delta_A = 4.94$, $J_{AB} = 14.4$ Hz for compound **15b**). These AB quartets coalesce at 323 K for **15a** and 333 K for **15b**.

The ^{1}H-NMR spectrum of **7** at 293 K in $CDCl_3$ solution displays two broad singlets which become sharp at 323 K ($\delta = 4.76$ for CH_2-61 and $\delta = 4.61$ for CH_2-64). At 213 K two AB systems are observed ($\delta_B = 4.82$, $\delta_A = 4.74$, $J_{AB} = 14.7$ Hz for CH_2-61 and $\delta_B = 4.65$, $\delta_A = 4.6$, $J_{AB} = 13.9$ Hz for CH_2-64), and these quartets coalesce at 241 and 245 K, respectively.

Similarly, compound **8** displays at 293 K two sharp singlets ($\delta = 4.89$ for CH_2-61 and $\delta = 4.84$ for CH_2-64). At 213 K two AB spin systems are observed ($\delta_B = 4.90$, $\delta_A = 4.73$, $J_{AB} = 15.4$ Hz for CH_2-61; and $\delta_B = 4.90$, $\delta_A = 4.61$, $J_{AB} = 15.4$ Hz for CH_2-64), and the coalescence is produced at 223 and 231 K, respectively.

It is remarkable that T_c and $\Delta G^{\ddagger}$ values in **15a** and **15b**, which possess a six-membered pyrazine ring, are similar to those described for carbocyclic compounds,[19a] while in compounds **7** and **8** with a five-membered thiophene ring, T_c values decrease 80 and 100 deg and $\Delta G^{\ddagger}$ values decrease 15 and 20 kJ·mol^{-1}, respectively (Table 3).

In order to gain information about the origin of these conformational differences, the molecular geometries of adducts **7** and **15a** were optimized at the semiempirical PM3 level. The most relevant bond distances and bond angles are illustrated in Figure 3.

Both adducts show clearly a boat conformation in the cyclohexene defined by C(1)−C(6)−C(64)−C(63)−C(62)−C(61). The calculated bond lengths C(1)−C(6) are 1.59 Å in **7** and 1.58 Å in **15a**, slightly shorter than 1.62 Å, determined by X-ray diffraction for 63,66-dimethyl-64,65-diphenyl-1,9-(methano[1,2]benzenomethano)fullerene-[60] by Rubin *et al.*[19a] As expected, the outer angles to the heterocyclic ring which form part of the boat are larger for the thiophene (120.4° and 120.9°) than for the pyrazine ring, which shows a value of 116.6°. Interestingly, calculations indicate that the boat is more planar in **7** than in **15a**; the torsional angle defined by C(1)−C(61)−C(62)−S(65) is 148.1° and for C(6)−C(64)−C(63)−C(67) is 149.3° in **7**, while that defined by C(1)−C(61)−C(62)−N(65) in **15a** resulted to be 131.5°, closer to the value (135°) found by Rubin for the above carbocyclic system.[19a]

The high barrier inversion of these compounds (**15a**,**b**) could be accounted for by the high torsional and angular constraints of the structures due to the rigidity of the C_{60} core.[19,21] Because the transition state for the boat-to-boat inversion should be at least partially planar, the observed lower barrier of inversion in the thiophene-containing adducts can be related to the higher planarity of the boat and, consequently, a major proximity to the transition state for the inversion. The intermediate values for $\Delta G^{\ddagger}$ (61.0 kJ·mol^{-1}) and planarity (135°) found by Rubin fit quite well with this suggestion.

In order to confirm the influence of the heteroatoms and electronic factors to the observed $\Delta G^{\ddagger}$ differences, work is in progress on the preparation of some new derivatives derived from six- and five-membered heterocyclic *o*-quinodimethanes.

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Table 4. CV Data of Carbo and Heterocyclic Cycloadducts[a]

compd	E^1_{red}[b]	E^2_{red}[b]	E^3_{red}[b]	E^4_{red}[b]	E_{red} (organic addend)
C_{60}	−0.60	−1.00	−1.52	−2.04	
3	−0.71	−1.14	−1.69	−	
7	−0.66	−1.17	−1.89	−	
8	−0.70	−1.16	−2.25[c]	−	
15a	−0.60	−1.00	−1.56[d]	−2.10	−1.94
15b	−0.64	−1.04	−1.56	−	−1.31; −1.74
15c	-0.57	−0.97[e]	−1.64	−	-1.06[e]

[a] All potentials in V *vs* SCE; toluene/MeCN (5:1); 0.1 M Bu_4NClO_4; scan rate: 0.2 V s^{-1}. [b] Reduction potentials of the C_{60} moiety. [c] Very broad wave. [d] The intensity of the wave suggest a two electron process. [e] These values could be interchanged.

The electrochemical properties of the novel pyrazine-containing cycloadducts (**15a**−**c**) were measured by cyclic voltammetry at room temperature using toluene/acetonitrile (5:1) as solvent, and the data are shown in Table 4 together with the thiophene-substituted analogues (**7**, **8**). The carbocyclic analogue **3** and [60]fullerene are also included for comparison purposes.

From the reduction potential values (Table 4) it is clear that substitution on the C_{60} cage does not alter significatively the acceptor properties of the parent C_{60}. Most of the studied cycloadducts show four one-electron quasireversible reduction waves corresponding to the reduction steps of the fullerene moiety. Compounds **15** show additional waves corresponding to the reduction of the substituted pyrazine fragments. It has been previously established that substitution on the C_{60} cage results in a raising of the LUMO energy of the organofullerene as a consequence of the saturation of a double bond.[22] In agreement with this observation, the first reduction potentials are slightly shifted to more negative values, related to [60]fullerene. Only cycloadduct **15c** showed a slightly more positive value than the parent C_{60} measured under the same experimental conditions. In order to ascertain these CV data, theoretical calculations (PM3) were carried out on compound **15c**. The LUMO energy level of **15c** (−3.03 eV) lies at a slightly lower energy than that found for [60]fullerene (−2.89 eV), thus supporting the experimental electrochemical observations. Although the difference between the reduction potentials of **15c** and C_{60} are not very significant, this experimental finding could indicate the electronic interaction between the acceptor pyrazine moiety bearing two cyano groups and the [60]fullerene core.

Summary and Conclusions

In summary, we have carried out the synthesis of several cycloadducts of [60]fullerene and six-membered heteroaromatic *o*-quinodimethanes under both thermal and microwave irradiation, in addition to other cycloadducts prepared from five-membered sulfur-containing *o*-quinodimethanes by microwave irradiation in comparison with the previously reported thermal conditions. Variable-temperature NMR experiments reveal that these cycloadducts present a flipping cyclohexene ring with activation free energies depending upon the nature of the heterocyclic system covalently attached to the C_{60} cage. This is the first case in which the coalescence temperature and $\Delta G^{\ddagger}$ values for C_{60}-based cycloadducts bearing five- or six-membered heterocycles have been comparatively studied in reference to the six-membered carbocyclic analogue. Interestingly, the activation energies found for the six-membered pyrazine adducts (**15a,b**) were very close to that found for the carbocyclic compound (**3**), and striking lower values were obtained for the five-membered thiophene adducts, which showed two different coalescence temperatures for the two different methylene units present in compounds **7** and **8**.

The molecular geometry was optimized for compounds **7** and **15a** by semiempirical calculations (PM3), showing a significative more planar boat for the five-membered heterocycle containing adduct (**7**). The electronic structure for the heterocyclic *o*-quinodimethanes indicate that the cycloaddition is controlled by the HOMO of these dienes, all the cycloadditions being energetically favored.

Finally, the redox properties of the prepared cycloadducts were studied by cyclic voltammetry and show cathodically shifting reduction potential values in comparison with C_{60}. Only compound **15c** bearing two strong electron-withdrawing cyano groups showed a different electrochemical behavior exhibiting a LUMO energy level lower than the parent [60]fullerene.

Work is in progress directed to the preparation of other five- and six-membered heterocyclic systems in order to study the effect that the presence of other heteroatoms has on the geometrical and electronic properties of the obtained organofullerenes.

Experimental Section

Cycloaddition Reactions by Classical Heating. General Procedure. To a refluxing solution of [60]fullerene (0.125 mg, 0.17 mmol), sodium iodide (0.104 mg, 0.69 mmol), and 18-crown-6 (138 mg, 0.52 mmol) in ODCB (25 mL) was added the respective pyrazine derivative (0.19 mmol). The resulting brown reaction mixture was refluxed for a variable period of time (24 h for **15a** and **15b** and 5 h for **15c**). The solvent was removed under vacuum, and the residue was chromatographed on silica gel using cyclohexane/$CHCl_3$ as eluent. Further purification was accomplished by washing the obtained solid three times with methanol.

Adduct 15a: 13% (22% based on consumed C_{60}); FTIR (KBr, cm^{-1}) 1492, 1453, 1033, 758, 747, 526; ^1H NMR ($CDCl_3/CS_2$) δ 4.92 (br d, J = 12.5 Hz, 2H), 5.23 (br d, J = 12.5 Hz, 2H), 7.88 (dd, J = 3.4 and 6.3 Hz, 2H), 8.27 (dd, J = 3.4 and 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3/CS_2$) δ 47.46, 64.53, 127.30, 129.35, 129.56, 130.27, 132.64, 135.21, 140.14, 141.55, 141.78, 141.90, 142.42, 142.70, 144.45, 145.28, 145.52, 146.09, 146.31, 147.51, 153.05, 155.17; MS *m/z* 876 (M^+), 720 (C_{60}); UV−vis ($CHCl_3$) λ_{max} (nm) 254, 282, 326, 434, 706.

Adduct 15b: 5% (14% based on consumed C_{60}); FTIR (KBr, cm^{-1}) 2954, 2921, 2842, 1466, 1433, 1387, 1262, 1117, 900, 769, 578, 538; ^1H NMR ($CDCl_3/CS_2$) δ 4.96 (d, J = 13.9 Hz, 2H), 6.35 (d, J = 13.9 Hz, 2H), 7.67 (dd, J = 3.2 and 6.6 Hz, 2H), 8.22 (dd, J = 3.2 and 6.6 Hz, 2H), 8.89 (s, 2H); MS *m/z* 927 (M^+), 720 (C_{60}); UV−vis ($CHCl_3$) λ_{max} (nm) 272, 432.

Adduct 15c: 16% (43% based on consumed C_{60}); FTIR (KBr, cm^{-1}) 2963, 2920, 1377, 1261, 1096, 1020, 800, 767, 526; ^1H NMR ($CDCl_3/CS_2$) δ 4.98 (bs, 4 H); ^{13}C NMR ($CDCl_3/CS_2$) δ 46.82, 64.02, 112.85, 132.88, 135.15, 140.43, 141.78, 142.09, 142.73, 143.21, 144.30, 144.58, 145.56, 145.76, 146.61, 147.80, 153.70, 157.51; MS *m/z* 876 (M^+), 720 (C_{60}); UV−vis ($CHCl_3$) λ_{max} (nm) 342, 432, 692.

Cycloaddition Reactions by Microwave Irradiation: Reaction of C_{60} with Methyl 2,3-Bis(chloromethyl)thiophene-5-carboxylate. Method A. A solution of C_{60} (40 mg, 0.055 mmol), methyl 2,3-bis(chloromethyl)thiophene-5-carboxylate (19 mg, 0.079 mmol), and tetrabutylammonium bromide (TBAB, 224 mg, 0.696 mmol) in toluene (30 mL) was

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irradiated at 60 W for 45 min. The resulting brown reaction mixture was washed with water, dried, and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column with hexane/toluene (5:2) as the eluent, recovering 12 mg of unreacted C_{60} and 10 mg of **7** (16%, 28% based on consumed C_{60}). Further purification of the solids was accomplished by washing three times with methanol. The spectroscopical data of adduct **7** thus obtained agree with those previously reported.[7] When the reaction was carried out in ODCB, an 11% (17% based on consumed C_{60}) yield was obtained.

Method B. A solution of C_{60} (50 mg, 0.069 mmol), methyl 2,3-bis(chloromethyl)thiophene-5-carboxylate (19 mg, 0.079 mmol), KI (86 mg, 0.558 mmol), and 18-crown-6 (61 mg, 0.242 mmol) was irradiated at 105 W for 75 min. The resulting brown solution was washed with water, dried, and evaporated to dryness. The solid residue was purified by column chromatography on silica gel with hexane/toluene, recovering 12 mg of unreacted C_{60} and 10 mg of adduct **7** (16%, 21% based on consumed C_{60}).

Reaction of C_{60} with 2,3-Bis(bromomethyl)benzo[*b*]thiophene. A solution of C_{60} (50 mg, 0.069 mmol), 2,3-bis(bromomethyl)benzo[*b*]thiophene (19 mg, 0.079 mmol), NaI (86 mg, 0.558 mmol), and 18-crown-6 (61 mg, 0.242 mmol) in toluene (30 mL) was irradiated at 70 W for 70 min. The resulting brown solution was washed with water, dried, and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column with hexane/toluene (7:2) as eluent, recovering 8 mg of unreacted C_{60} and 14 mg of **8** (23%, 28% based on consumed C_{60}). Further purification of the solids was accomplished by washing three times with methanol. The spectroscopical data of adduct **8** thus obtained agree with those previously reported.[7]

Reaction of C_{60} with 2,3-Bis(bromomethyl)quinoxaline. A solution of C_{60} (50 mg, 0.069 mmol), 2,3-bis(bromomethyl)quinoxaline (44 mg, 0.139 mmol), and TBAB (224 mg, 0.696 mmol) in ODCB (30 mL) was irradiated at 60 W for 30 min. The resulting brown solution was washed with water, dried, and evaporated to dryness. The solid residue was chromatographed on silica gel with hexane/toluene, recovering 14.5 mg of C_{60} and 16 mg of **15a** (26%, 37% based on consumed C_{60}). Further purification was accomplished by washing the obtained solid three times with methanol.

Reaction of C_{60} with 2,3-Bis(bromomethyl)benzo[*g*]quinoxaline. A solution of C_{60} (50 mg, 0.069 mmol), 2,3-bis(bromomethyl)benzo[*g*]quinoxaline (51 mg, 0.139 mmol), and TBAB (224 mg, 0.696 mmol) in ODCB (30 mL) was irradiated at 60 W for 30 min. The resulting brown reaction mixture was washed with water, dried, and evaporated to dryness under reduced pressure. The solid obtained was purified by column chromatography on silica gel with toluene/$CHCl_3$ as eluent, recovering 10 mg of unreacted C_{60} and 14 mg of adduct **15b** (22%, 52% based on consumed C_{60}). Further purification was accomplished by washing the obtained solid three times with methanol.

Reaction of C_{60} with 2,3-Bis(bromomethyl)-5,6-dicyanopyrazine. A solution of C_{60} (50 mg, 0.069 mmol), 2,3-bis(bromomethyl)-5,6-dicyanopyrazine (24 mg, 0.077 mmol), and TBAB (124 mg, 0.385 mmol) in toluene (30 mL) was irradiated at 60 W for 20 min. The resulting brown solution was washed with water, dried, and evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column with hexane/toluene (1:1) and hexane/toluene (1:5) as eluent, recovering 40 mg of unreacted C_{60} and 5 mg of **15c** (9%, 42% based on consumed C_{60}). Further purification of the solid was accomplished by washing three times with methanol.

Acknowledgment. Financial support from Spanish DGICYT (PB94−0742 and PB95−0428-CO2) is gratefully acknowledged. We are indebted to Drs. Javier Garín and Jesús Orduna for the FAB-MS measurements.

JO9701344