Reaction of C_{60} with Sultines: Synthesis, Electrochemistry, and Theoretical Calculations of Organofullerene Acceptors

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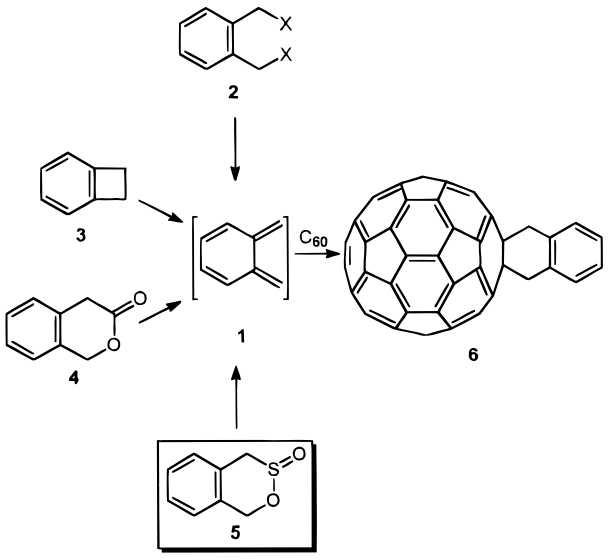
The [4 + 2] cycloaddition reaction of *o*-quinodimethanes, generated *in situ* from 4,5-benzo-3,6-dihydro-1,2-oxathiin 2-oxides (**10a,b**, **13**, and **19**) (sultines), to [60]fullerene is described. Sultines are readily accesible from the commercially available rongalite and smoothly generate o-quinodimethanes, by extrusion of sulfur dioxide, which are efficiently trapped by the active dienophile C_{60}. The cycloadducts formed (**21a**−**d**) were further oxidized to the respective *p*-benzoquinone-containing fullerenes **23a**−**c**. The temperature dependent ^{1}H NMR spectra show a dynamic process of the methylene protons. The activation free energy determined for the boat-to-boat inversion (11.3−11.6 kcal/mol) is remarkably lower than that obtained for other related carbocyclic or heterocyclic analogues. Semiempirical PM3 calculations show that the geometrical features and not the electronic properties of the organic addend in **23** are responsible for the low activation energy barriers. A linear correlation is found between the activation energy barriers and the length of the C62−C63 bond. The electrochemical properties of **23a**−**c** have been rationalized on the basis of DFT-B3P86/3-21G calculations. The attachment of the first electron in the reduction process takes place in either the C_{60} cage or the organic addend depending upon the nature of the substituents on the *p*-benzoquinone ring, which controls the relative energy of the LUMO of the *p*-benzoquinone moiety. A full agreement between the theoretical predictions and the electrochemical measurements is found.

Introduction

The chemical reactivity of [60]fullerene is characterized by the absence of hydrogens in its structure. Addition reactions instead of substitution reactions are therefore typically undergone by the C_{60} molecule to form exohedrally functionalized derivatives.[1] Among the derivatization methods available, cycloaddition reactions have played a very important role, the Diels−Alder reaction being particularly successful.[2] Some of the resulting cycloadducts are thermally unstable because of their fast cycloreversion to their components. In contrast, adducts obtained from *o*-quinodimethanes as dienes are thermally stable due to the additional stabilization provided by the aromatic system.[3] The regioselectivity of multiple 1,2-additions to [60]fullerene is currently a very active research field with interesting symmetrical and stereochemical implications.[4]

Recent advances in the generation of *o*-quinodimethanes have made it possible to obtain this highly reactive intermediate under mild conditions and with control of the stereochemistry of the cycloaddition reactions with dienophiles.[5] As depicted in Scheme 1, different synthetic procedures have been used for the *in situ* generation of *o*-quinodimethane for the subsequent [4 + 2] cycloaddition to [60]fullerene. Although these reactions proceed reasonably well and the [60]fullerene-based cycloadducts **6** are formed, the reported procedures to

Scheme 1



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

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generate *o*-quinodimethane (**1**) present different drawbacks. The most widely used method from α,α′-dihalo-*o*-xylenes **2** requires the presence of an ion such as iodide to induce the 1,4-elimination and also a phase transfer catalyst.[3,5] Thermolysis of benzocyclobutenes **3** is carried out in high-boiling-point solvents to promote the ring opening[6] even when alkoxy substituents, which produce a lowering of the activation energy, are present.[7] The same occurs with isochromanone derivatives **4**, which require high temperatures for the extrusion of CO_2.[8] In contrast to the above procedures, generation of *o*-quinodimethanes from 4,5-benzo-3,6-dihydro-1,2-oxathiin 2-oxide (**5**) (sultine)[9] takes place smoothly around 80 °C by extrusion of sulfur dioxide without production of any organic or inorganic byproducts. Although preparation of sultines initially involved a multistep, time-consuming procedure,[10] they can nowadays be easily generated in a one-step procedure from α,α′-dibromo-*o*-xylenes and sodium hydroxymethanesulfinate ("rongalite") as stable compounds in high yields.[11]

In a previous communication we reported the facile formation of [60]fullerene adducts from sultines *via* a Diels−Alder reaction as an alternative procedure for the functionalization of C_{60} under mild conditions.[12] Here, we describe the reaction of various substituted sultines with [60]fullerene to form the respective cycloadducts, thus proving the suitability of the method, followed by the transformation of the substituted 1,4-dialkoxybenzenes into the corresponding *p*-benzoquinone moiety. In contrast to the wide variety of C_{60}-based donor−*σ*-acceptor systems that have recently been reported in the search for *inter*- or *intra*molecular electron-transfer processes,[13] the number of organofullerenes in which an acceptor unit is covalently attached to the C_{60} cage is very small. To the best of our knowledge, only a few examples have been reported in which the presence of electronegative atoms[14] or strong electron-withdrawing groups[15] linked to the C_{60} framework lead to more electronegative organofullerenes than the parent [60]fullerene. "Periconjugation" has also been used to prepare methanofullerenes exhibiting better accepting properties than those of C_{60}.[16] We have very recently reported the synthesis of the first C_{60}-based electron acceptors with attached tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinonediimine (DCNQI) moieties as molecules that can accept up to eight electrons in solution.[17]

Recently, a nice study including X-ray analysis and reduction to the mono- and dianion species on the synthesis and characterization of benzoquinone-linked [60]fullerene has been reported by Iyoda *et al.*[18] In that work, the benzoquinone-containing cycloadducts were obtained from the appropriately substituted benzocyclobutenes followed by oxidation of the cycloadducts. In this paper, we present an alternative and milder synthetic procedure from readily accessible sultines for the preparation of novel [60]fullerene−*p*-benzoquinone systems. The electrochemical properties of the obtained cycloadducts were determined by cyclic voltammetry in solution. Molecular orbital calculations were also performed in order to gain information on the geometrical features and to rationalize the observed electrochemical behavior.

Results and Discussion

The synthesis of the starting sultines **10a,b**, **13**, and **19** was carried out from the respective α,α′-dihalo-*o*-xylenes in one step by reaction with sodium hydroxymethanesulfinate ("rongalite") in *N*,*N*-dimethylformamide (DMF) in the absence of water and with addition of a catalytic amount of tetrabutylammonium bromide (TBAB) at 0 °C. Under these conditions,[11] polymerization of the *o*-quinodimethane is avoided and the corresponding sultines are obtained in good yields (49−80%). This procedure has recently been used for the preparation of furan-, thiophene-, and pyrrole-fused sultines which have been successfully applied in Diels−Alder reactions.[19]

The α,α′-dibromo-*o*-xylenes **9**, **12**, and **18** were in turn obtained in a multistep synthetic procedure by following the methods previously reported in the literature[20] as depicted in Scheme 2. 2,3-Dimethyl-1,4-hydroquinone (**7**) was used as the starting material for the preparation of sultines **10** and **13**, and the intermediate benzo analogue **16**, obtained from 2,3-dimethylnaphthalene (**14**) by oxidation with chromium trioxide and subsequent reduction, was used as precursor for sultine **19**. α,α′-Dibromo-*o*-xylene (**18**) was prepared in high yield from 2,3-dimethyl-1,4-dimethoxynaphthalene (**17**)[21] by following the same bromination procedure (see Experimental Section).

10a,b, **13**, and **19** react with [60]fullerene in refluxing toluene by extrusion of SO_2 and *in situ* generation of the respective substituted *o*-quinodimethanes which are readily trapped by [60]fullerene acting as the dienophile. *o*-Quinodimethanes **20b** and **20c** had already been de-

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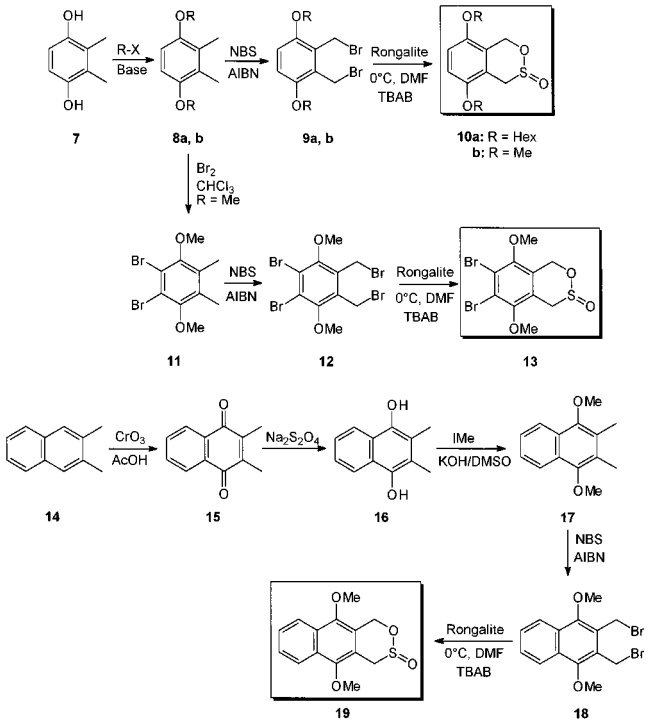
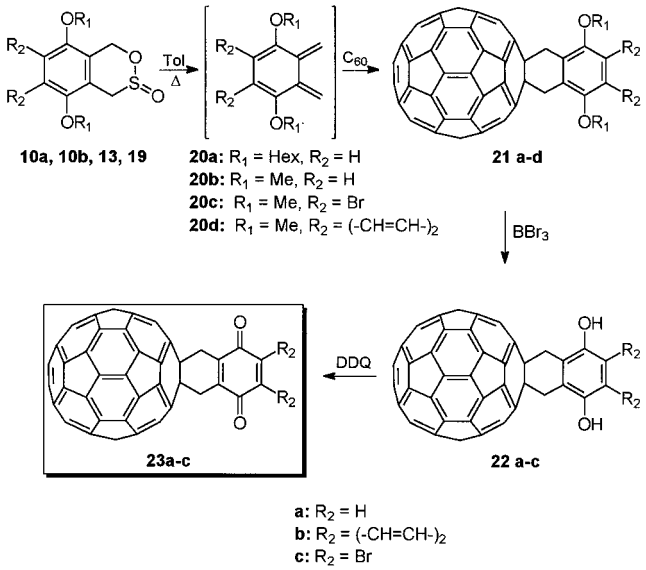
Scheme 2



Scheme 3



scribed by metallic nickel assisted room-temperature generation,[20] and the *o*-xylylene intermediate **20d** is reported now for the first time. The reaction, which can be also carried out in benzene as solvent,[12] leads to the respective 1,2-dihydrofullerene cycloadducts **21a**−**d** in moderate yields (22−45%) [44−58% based on recovered C_{60}]. Formation of a regioisomeric mixture of bisadducts was only detected in the preparation of monoadduct **21c** due to the longer reaction time required for its synthesis. The experimental conditions used in these thermal [4 + 2] cycloadditions are milder than those recently reported for cycloadduct **21b** from 3,6-dimethoxybenzocyclobutene, which requires heating in *o*-dichlorobenzene at 220 °C for 24 h,[18] the yields obtained being similar in both procedures.

The prepared cycloadducts (**21a**−**d**) can be easily transformed into the corresponding C_{60}-based *p*-benzoquinone derivatives by removing the alkyl groups using boron tribromide. The expected hydroquinone **22** was obtained together with the totally oxidized *p*-benzoquinone **23** in compounds **23a** and **23c**. The obtained mixture (**22a** and **23a**) was separated by flash chromatography in 25% and 51% yields, respectively. The bromine containing mixture (**22c** and **23c**) was directly submitted to further oxidation with dichlorodicyano-*p*-benzoquinone (DDQ) to afford **23c** in very high yield. Only the cycloadduct **23b** was directly obtained from **21b** by treatment with BBr_3 in 84% yield without isolation of the intermediate hydroquinone **22b** (see Scheme 3).

The 1,2-dihydrofullerenes **21a**−**d** show spectroscopic data in agreement with the proposed structures. These kinds of cycloadducts have been thoroughly studied for other substituted derivatives,[22] including structural[8] and conformational equilibrium[7a] aspects. On the contrary, *p*-benzoquinone-containing organofullerenes have only recently been introduced[18] and show the typical weak absorption band of dihydrofullerenes around 430 nm in the UV−vis spectra. The ^{13}C NMR spectrum of the more soluble cycloadduct **23b** shows the presence of 23 signals of which 21 correspond to sp^2 carbons, indicating that the molecule has an average C_{2v} symmetry resulting from the fast flipping motion of the cyclohexene ring connecting the C_{60} cage to the organic addend. In addition to the carbonyl carbon, which appears at 181.7 ppm, the signal at δ = 37.0 (CH_2) and the peak at δ = 64.8, characteristic of the quaternary sp^3-hybridized carbons to which the substituent is attached, were also observed.

The ^1H NMR spectra show the methylene protons as a broad singlet at δ ~4.6 at room temperature. The singlet becomes sharp at higher temperatures indicating a dynamic process, which should be attributed to the boat-to-boat interconversion of the cyclohexane ring already reported for related organofullerenes.[6,7,23,24] The activation free energy for the boat-to-boat inversion was determined by DNMR experiments for compounds **23**.

The ^1H NMR spectra of **23b** and **23c** (see Figure 1) show sharp AB systems at 223 K (**23b**: δ_B = 5.80, δ_A = 4.24, J_{AB} = 14.15 Hz) and 213 K (**23c**: δ_B = 4.98, δ_A = 4.24, J_{AB} = 14.65 Hz), which coalesce at 252 and 255 K, respectively. The activation energy, $\Delta G^{\neq}$, for the ring inversion is 11.6 ± 0.1 kcal/mol for **23b** and 11.5 ± 0.1 kcal/mol for **23c**. These experimental values are very close to those obtained for the parent **23a** ($\Delta G^{\neq}$ = 11.3 ± 0.1 kcal/mol) and confirm the remarkable lower activation energy values obtained for the *p*-benzoquinone-containing fullerenes **23** compared to those reported for other carbocyclic (14.6−16.6 kcal/mol)[6,7,23] or heterocyclic (15.4−15.8 kcal/mol)[24] analogues.

In order to rationalize the low activation energies found for the cyclohexene inversion in compounds **23**, we optimized the molecular structure of the parent cycloadduct **23a** and of its closely related analogue **6**, where the *p*-benzoquinone unit is substituted by an unsubstituted benzene ring, at the semiempirical PM3 level.[25] Figure 2 displays the optimized structure of **23a** together with

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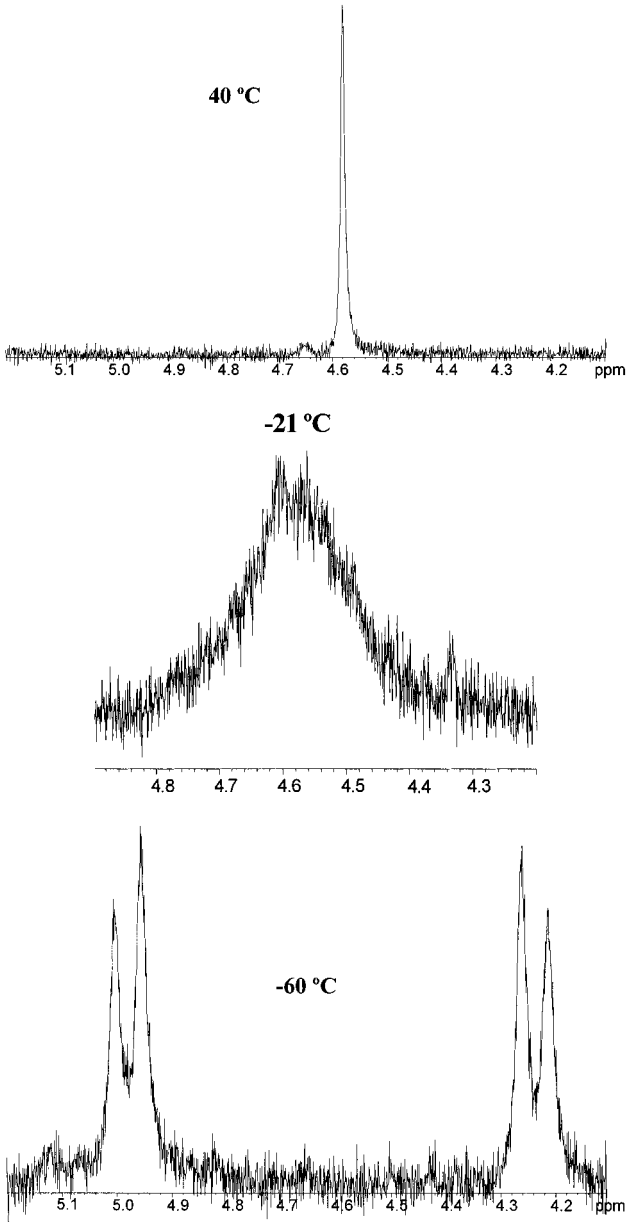

Figure 1. Temperature-dependent ^{1}H NMR spectra of compound **23c** in $CDCl_3$ at 40 °C (top), −21 °C (center), and −60 °C (bottom).

the bond lengths and bond angles obtained for the organic addend of **23a** and **6**.

Both for **23a** and for **6**, the PM3 method predicts a C_s geometry with a symmetry plane bisecting the C1−C2 bond and where the cyclohexene ring adopts a boat conformation as the minimum energy structure. The C1−C2 bond, where the 6/6 junction with the organic addend takes place, presents similar values for **23a** (1.583 Å) and **6** (1.586 Å). These values are very close to that recently found by X-ray analysis for **23a** [1.593(2) Å][18b] and suggest that the value of 1.62(4) Å reported for a derivative of **6** is too large.[6] The remaining bond lengths and bond angles are in good agreement with those derived from X-ray analysis,[18b] thus confirming the reliability of the PM3-optimized structure. The angle of folding of the cyclohexene unit along the C61−C64 axis is calculated to be slightly different for **23a** (132.8°) and **6** (131.9°). These values compare well with the X-ray value measured for **23a** (128.2°) in the crystal,[18b] where the packing forces determine the higher folding in order to achieve a more compact packing.

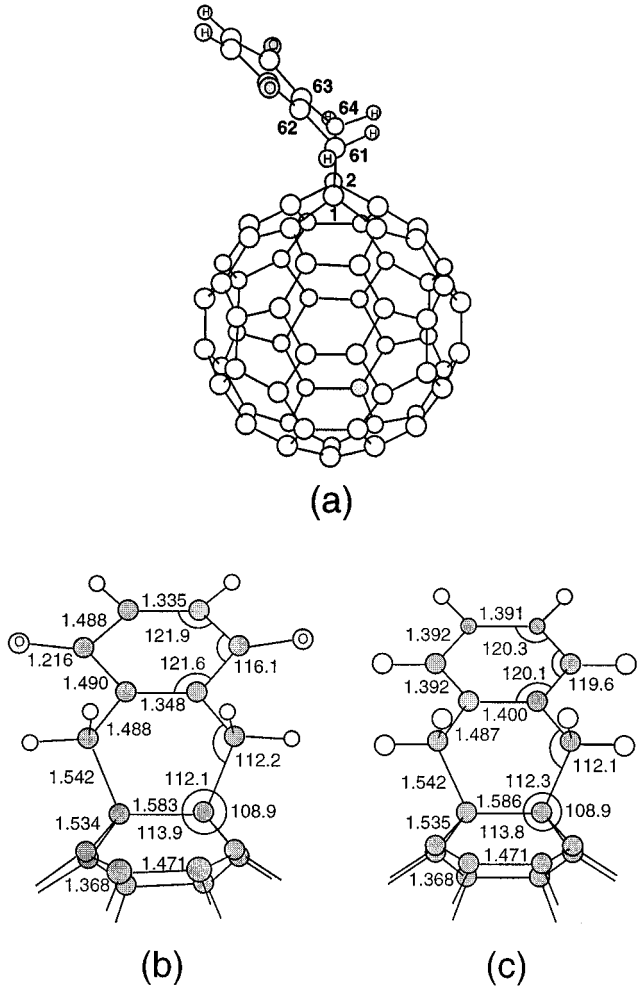

Figure 2. Detail of the PM3-optimized molecular structures of **23a** and **6**. (a) Minimun energy C_s conformation of **23a** and cyclohexene atom numbering. (b) Geometry of the organic addend for **23a**. (c) Geometry of the organic addend for **6**. Bond lengths are in angstroms and bond angles in degrees.

The most remarkable geometrical difference between **23a** and **6** comes from the length of the C62−C63 bond (cf. Figures 2b and 2c). While for **6**, the benzene ring is fully aromatic and the C62−C63 bond has a length of 1.400 Å, the benzoquinone moiety in **23a** presents a large single−double carbon−carbon bond length alternancy, and the C62−C63 bond has a length of 1.348 Å. The shortening of the C62−C63 bond widens the C61−C62−C63 and C62−C63−C64 angles and determines the slightly smaller folding of the cyclohexene structure in **23a**. These structural differences although small are the reason for the lower inversion barriers found for **23**.

To support this idea, the boat-to-boat inversion barrier through the C_{2v} structure resulting from the planarization of the cyclohexene ring was calculated. For both **23a** and **6**, the C_{2v} structure was optimized and the resulting stationary points were characterized at the PM3 level. In both cases, it has a unique imaginary frequency whose associated normal-coordinate vector points to the boat-cyclohexene C_s minima, thus identifying the C_{2v} structure as a true transition state for the boat-to-boat inversion process. The C_{2v} transition state is calculated to lie 8.2 kcal/mol above the C_s minima for **6** and 6.7 kcal/mol above for **23a**. These energies reproduce the larger activation energy obtained from NMR measurements for **6** (15.2 kcal/mol)[23b] than for **23a** (11.3 ± 0.1 kcal/mol), although they underestimate the experimental values.

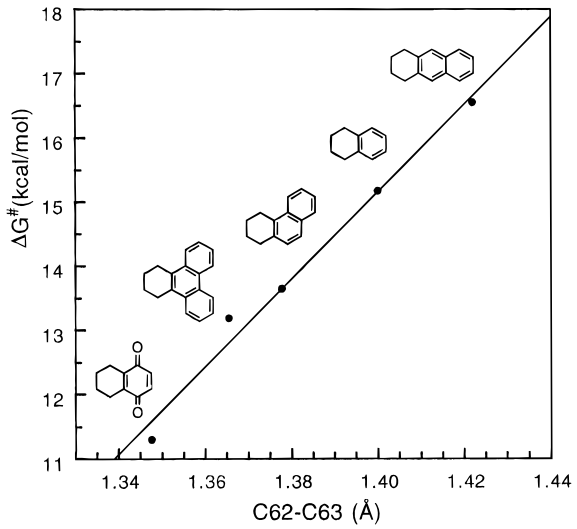

Figure 3. Linear correlation between the activation energies, $\Delta G^{\neq}$, measured experimentally for C_{60}-*o*-quinodimethane adducts and the PM3-optimized C62−C63 bond lengths calculated for the respective compounds. $\Delta G^{\neq}$ values are taken from ref 23b. The structures of the addends are sketched.

This is a well-known shortcoming of the PM3 method which usually leads to too low rotational and inversion barriers.[26] To overcome this shortcoming, the PM3-optimized C_s and C_{2v} structures of **23a** and **6** were recalculated at the density functional theory (DFT) level[27] using the hybrid gradient-corrected B3P86 density functional[28] and the 3-21G basis set.[29] The energy differences between C_s and C_{2v} structures calculated at the B3P86/3-21G level are 17.8 kcal/mol for **6** and 13.9 kcal/mol for **23a**. These values confirm the PM3 predictions and are in better accord with the NMR estimates.

The theoretical results thus show that the structural modifications associated with the aromatic or quinoid character of the organic rest are the factors that determine the height of the boat-to-boat inversion barrier. A direct correlation is in fact found between the length of the C62−C63 bond and the height of the barrier: as the bond length increases the barrier also increases. This correlation is inferred by comparing the activation energies estimated experimentally for **23a** and for the different carbocyclic C_{60}−*o*-quinodimethane adducts reported in ref 23b with the length of the respective C62−C63 bond calculated at the PM3 level. As shown in Figure 3, a nearly perfect linear correlation is found between both magnitudes.

Table 1. Reduction Potentials of the Novel Cycloadducts 23a−c[a]

compd	$E^{quinone}_{red}$	E^{1}_{red}	E^{2}_{red}	E^{3}_{red}	E^{4}_{red}
C_{60}		−0.60	−1.00	−1.52	−2.04
23a	−0.51	−0.68	−1.17	−1.74	
23b	−0.77 −1.32	−0.63	−1.11	−1.76	−1.94
23c	−0.21	−0.64	−1.07	−1.68	
p-benzoquinone	−0.47[b]				

[a] All potentials in V *vs* SCE; GCE as working electrode; 0.1 mmol/dm^3 $NBu_4^+ClO_4^-$; Tol:MeCN (5:1); 200 mV/s. [b] Measured in CH_2Cl_2.

The electrochemical properties of compounds **23a−c** were studied by cyclic voltammetry (CV) at room temperature. The reduction potentials estimated by the position of the reduction peaks are given in Table 1 together with those measured for C_{60} and *p*-benzoquinone for comparison purposes.

Cycloadducts **23a−c** show three or four reduction waves at potential values similar to those found for the parent C_{60} under the same experimental conditions. These waves correspond to the reduction of the C_{60} moiety to form the respective anions and are slightly shifted to more negative potentials due to the saturation of a double bond in the C_{60} cage.[30] In addition, another reduction wave is observed at potential values very close to the first reduction potential of the C_{60} moiety. For **23a**, this wave appears at almost the same potential as that for *p*-benzoquinone (see Table 1) and has been assigned to the reduction of the *p*-benzoquinone fragment to form the semiquinone radical.[18] Substitution on the *p*-benzoquinone moiety has a striking influence on the redox behavior. The presence of two bromine atoms in **23c** leads to a strong shift of the first reduction potential to more positive values as a consequence of the electronegative character of the substituents. In contrast, the presence of a benzene ring fused to the *p*-benzoquinone moiety in **23b** cathodically shifts the first reduction potential of the quinone moiety which now appears at more negative values than the first reduction potential of the C_{60} core. An additional wave is observed at −1.32 V for **23b** which can be reasonably assigned to the second reduction wave of the organic addend.

In order to rationalize the electrochemical findings, we calculated the electronic structure of the cycloadducts **23a−c** at the B3P86/3-21G level. Figure 4 sketches the energetic ordering and orbital assignment of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) obtained for **23a−c** and for the tetracyano and the dicyano analogues of **23a** and **23c** that were calculated for comparison purposes.

The most immediate effect of substitution on the C_{60} cage is that the 5-fold degenerate HOMO of C_{60}, calculated at −7.32 eV, splits into five MOs which show no contribution from the addend. The 3-fold LUMO of C_{60}, calculated at −4.34 eV, split into three MOs which have no contribution from the addend. A new MO, localized on the quinone moiety, appears close to the LUMOs of the C_{60} moiety. For **23a**, this orbital lies at −4.29 eV slightly below the LUMO of the C_{60} moiety (−4.25 eV), thus explaining the attachment of the first electron to the *p*-benzoquinone ring observed by CV. The energy difference between the LUMOs of the C_{60} and the quinone fragments increases when two bromine atoms are linked

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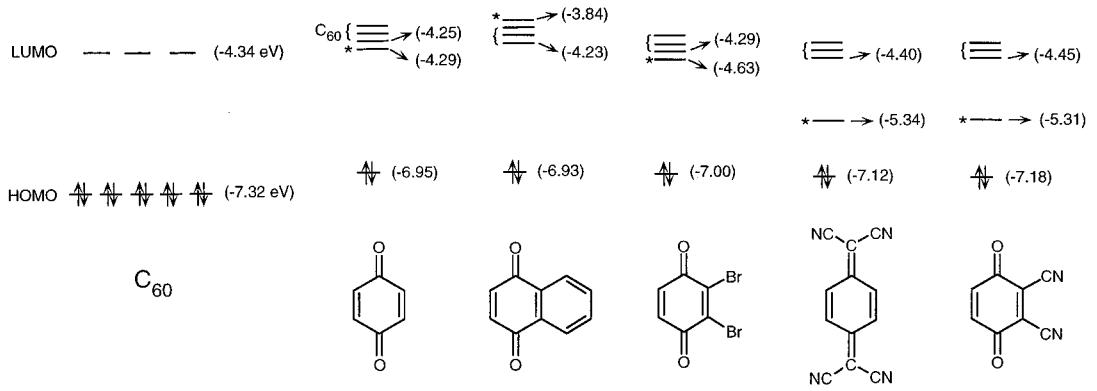

Figure 4. B3P86/3-21G molecular orbital distribution calculated for C_{60} and compounds **23**. The chemical structure of the *p*-benzoquinone-type addend is indicated below. The energy of the orbitals (in eV) are given within parentheses. The three LUMOs of C_{60} are enclosed by a brace; the LUMO localized on the *p*-benzoquinone moiety is denoted by an asterisk.

to the *p*-benzoquinone moiety in **23c** due to the stabilization of the LUMO of this moiety which now lies at −4.63 eV. The effect is much more pronounced when the carbonyl groups of **23a** are substituted by $C(CN)_2$ groups or the bromine atoms of **23c** are replaced by cyano groups. In both cases, the LUMO of the addend lies at about −5.3 eV, i.e., almost 1 eV below the LUMO of C_{60} which is also slightly stabilized with respect to C_{60}. Both the C_{60} cage and especially the organic addend in these compounds are thus expected to behave as excellent electron acceptors. The almost identical orbital energies obtained for the LUMOs suggest that similar reduction potentials would be obtained for both compounds.

The presence of a benzene ring fused to the quinone unit in **23b** produces a destabilization of the LUMO of the organic addend (−3.84 eV), which now lies above those of the C_{60} core. This result explains the electrochemical finding that, for **23b** and in contrast with **23a** and **23c**, the C_{60} cage is first reduced due to the cathodic shift of the first reduction potential of the naphthoquinone moiety in **23b**. The destabilization of the LUMO of benzoquinone in passing to naphthoquinone has been previously shown to be due to the antibonding interaction of the fused benzene ring with the quinone ring.[31]

Summary and Conclusions

In summary, the synthesis of novel electron acceptor organofullerenes has been carried out under very mild conditions from readily accesible sultines by using the commercially available rongalite. This quick functionalization procedure involves the smooth generation of the elusive *o*-quinodimethane and has been proved to be of a general scope, being particularly useful to prepare C_{60} adducts which decompose under high temperatures.

Semiempirical PM3 calculations show that the geometrical features and not the electronic properties of the organic addend are responsible for the lower activation energy barriers found for the boat-to-boat cyclohexene ring inversion in **23a**−**c** in comparison with benzene-fused cycloadducts of type **6**. A linear correlation is found between the activation energy barriers and the length of the C62−C63 bond.

The electrochemical properties of **23a**−**c** have been rationalized on the basis of DFT-B3P86/3-21G calculations. The nature of the substituents on the *p*-benzoquinone ring allows one to address the attachment of the first electron in the reduction process either to the C_{60} cage or to the organic addend, by controlling the relative energy of the LUMO of the organic addend with respect to the LUMO of the C_{60} cage. The theoretical predictions are in full agreement with the electrochemical behavior found for compounds **23a**−**c**.

These *p*-benzoquinone-containing C_{60}-based cycloadducts are interesting precursors for the preparation of stronger organofullerene acceptors derived from tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinonediimine (DCNQI), which are usually prepared from the respective quinones.[32] Furthermore, the regioselective 1,2-addition of a donor fragment to the C_{60} core would allow formation of triads of multichromophoric systems with a gradient of redox centers ($D\text{-}A_1\text{-}A_2$) with spatially well-defined structures.[33] Work is in progress for the preparation of such systems.

Experimental Section

2,3-Bis(bromomethyl)-1,4-dimethoxybenzene,[20] 5,6-dibromo-2,3-bis(bromomethyl)-1,4-dimethoxybenzene,[20] and 1,4-dimethoxy-2,3-dimethylnaphthalene[21] were prepared according to previously reported procedures.

2,3-Bis(Bromomethyl)-1,4-dimethoxynaphthalene (18). To a refluxing solution of 2,3-dimethyl-1,4-dimethoxynaphthalene (6 g, 0.028 mol) in 50 mL of carbon tetrachloride, under an argon atmosphere was added *N*-bromosuccinimide (10 g, 0.056 mol) in portions. A small amount of, α,α′-azobis(isobutyronitrile) (AIBN) was added before each NBS addition. After all the NBS was added (about 2 h), the succinimide was filtered off and the solvent was evaporated. The crude product was chromatographed on silica gel with hexane. **18**: 97%; mp 118 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (dd, J = 3.7 and 6.6 Hz, 2H), 7.58 (dd, J = 3.7 and 6.6 Hz, 2H), 5.02 (s, 4H), 4.08 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 152.11, 128.92, 127.43, 125.77, 123.11, 62.58, 24.60; IR (KBr): 3000, 2940, 2840, 1710, 1590, 1500, 1450, 1410, 1355, 1280, 1210, 1100, 1040, 960 cm^{-1}. Anal. Calcd for $C_{14}H_{14}O_2Br_2$: C, 44.92; H, 3.74. Found: C, 45.21; H, 3.85.

Synthesis of Sultines. General Procedure. To a solution of the corresponding bis(bromomethyl) derivative (1 equiv) in DMF at 0 °C were added sodium hydroxymethanesulfinate (rongalite, 3 equiv for sultines **10a** and **19**; 4 equiv for **10b** and **13**) and tetrabutylammonium bromide (TBAB, 0.3 equiv for sultines **10a** and **19**; 0.4 equiv for **10b** and **13**) under argon. After 24 h, water was added and the mixture was extracted

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(two times) with ether and methylene chloride. The organic extracts were dried over $MgSO_4$, and the solvent was evaporated to dryness. The solid residue was purified by column chromatography on silica gel, using hexane/ethyl acetate as the eluent.

4,5-(1,4-Bis(hexyloxy)benzo)-3,6-dihydro-1,2-oxathiin 2-oxide (10a): 0.67 g (50%); mp 36 °C; ^{1}H NMR ($CDCl_3$) δ 6.69 (s, 2H), 5.18 (d, J = 15.4 Hz, 1H), 5.10 (d, J = 15.4 Hz, 1H), 4.07 (d, J = 17.3 Hz, 1H), 3.87 (t, 4H), 3.59 (d, J = 17.3 Hz, 1H), 1.74 (m, 4H), 1.42 (m, 4H), 1.33 (m, 8H), 0.91 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 150.54, 148.44, 121.81, 114.49, 110.10, 109.92, 68.57, 68.48, 56.67, 48.17, 31.53, 29.21, 25.79, 22.75, 14.02; IR (KBr) 2940, 2870, 1610, 1490, 1470, 1270, 1130, 1090, 810 cm^{-1}; MS m/z 368 (M^+, 1), 304 ($M^+ - SO_2$, 30), 220 (13), 177 (4), 136 (100), 108 (13), 79 (11), 64 (23), 57 (11), 55 (26). Anal. Calcd for $C_{20}H_{32}SO_4$: C, 65.20; H, 8.70. Found: C, 65.06; H, 8.58.

4,5-(1,4-Dimethoxybenzo)-3,6-dihydro-1,2-oxathiin 2-oxide (10b): 2.02 g (80%); mp 113−116 °C; ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 2H), 5.16 (d, J = 15.4 Hz, 1H), 5.10 (d, J = 15.4 Hz, 1H), 4.15 (d, J = 16.2 Hz, 1H), 3.78 (s, 6H), 3.62 (d, J = 16.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 151.15, 149.07, 121.75, 114.42, 109.09, 108.93, 56.60, 55.76, 55.68, 48.05; IR (KBr) 3000, 2900, 2880, 1610, 1500, 1475, 1270, 1130, 1100, 810 cm^{-1}; MS m/z 228 (M^+, 3), 164 ($M^+ - SO_2$, 100), 149 (63), 121 (32), 91 (51), 78 (20), 77 (41), 64 (47), 51 (25). Anal. Calcd for $C_{10}H_{12}SO_4$: C, 52.60; H, 5.30. Found: C, 52.34, H, 5.41.

4,5-(2,3-Dibromo-1,4-dimethoxybenzo)-3,6-dihydro-1,2-oxathiin 2-oxide (13): 0.44 g (70%); mp 136−138 °C; ^{1}H NMR ($CDCl_3$) δ 3.62 (d, J = 15.9 Hz, 1H), 3.81 (s, 3H), 3.84 (s, 3H), 4.21 (d, J = 15.9 Hz, 1H), 5.14 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 49.49, 56.90, 61.27, 61.15, 120.35, 120.65, 120.88, 127.17, 150.66, 153.10; IR (KBr) 2900, 1440, 1370, 1100, 1050, 985, 795 cm^{-1}; MS m/z 386 (M^+, 1) 322 ($M^+ - SO_2$, 100), 307 (57), 305 (29), 185 (12), 183 (12), 133 (11), 131 (12), 89 (16), 75 (17), 64 (21). Anal. Calcd for $C_{10}H_{10}Br_2O_4S$: C, 31.09; H, 2.59. Found: C, 31.38; H, 2.57.

4,5-(1,4-Dimethoxynaphtho)-3,6-dihydro-1,2-oxathiin 2-oxide (19): 0.26 g (49%); 125 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (dd, 2H), 7.58 (dd, 2H), 5.43 (d, J = 13.8 Hz, 1H), 5.32 (d, J = 13.8 Hz, 1H), 4.73 (d, J = 15.6 Hz, 1H), 3.94 (s, 6H), 3.67 (d, J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 150.81, 148.71, 128.17, 127.76, 126.86, 126.80, 122.64, 122.51, 122.40, 115.55, 63.01, 62.67, 57.93, 51.30; IR (KBr) 2940, 2840, 1600, 1500, 1450, 1440, 1360, 1280, 1120, 1070 cm^{-1}; MS m/z 278 (M^+, 6), 214 ($M^+ - SO_2$, 100), 199 (66), 171 (22), 141 (28), 128 (30), 115 (32), 76 (14). Anal. Calcd for $C_{14}H_{14}SO_4$: C, 60.43; H, 5.03. Found: C, 60.14; H, 5.02.

Cycloaddition Reactions of Sultines (10a,b, 13 and 19) with C_{60}. General Procedure. To a refluxing solution of C_{60} (0.150 g, 0.21 mmol) in toluene (100 mL), under argon, was added the corresponding sultine (0.21 mmol). The resulting brown reaction mixture was refluxed for a variable period of time (24 h for **10a,b** and **19** and 6 h for **13**). The solid obtained by evaporation to dryness was purified on a silica gel column using cyclohexane/toluene as eluent. Further purification of the products was accomplished by washing the obtained solid three times with methanol.

Cycloadduct of 4,5-(1,4-Bis(hexyloxy)benzo)-3,6-dihydro-1,2-oxathiin 2-Oxide with C_{60}. 21a: 45%. (55% based on consumed C_{60}); ^{1}H NMR ($CDCl_3$) δ 7.03 (2H), 4.91 (bs, 2H), 4.43 (bs, 2H), 4.08 (t, 4H), 1.8 (quint., 4H), 1.43 (quint., 4H), 1.27 (m, 8H), 0.83 (t, 6H); ^{13}C NMR ($CDCl_3$) δ 157.11, 150.38, 147.62, 146.39, 146.18, 145.76, 145.66, 145.38, 145.29, 144.66, 143.04, 142.49, 142.22, 142.02, 141.54, 135.56, 135.40, 128.23, 111.86, 69.62, 65.71, 37.49, 31.42, 29.32, 25.70, 22.51, 13.94; FTIR 2921, 2850, 1462, 1427, 1261, 1112, 1084, 790, 765, 526 (cm^{-1}); MS m/z 1024 (M^+), 720; UV−vis ($CDCl_3$) λ_{max} (nm) 254, 282, 326, 434, 706.

Cycloadduct of 4,5-(1,4-Dimethoxybenzo)-3,6-dihydro-1,2-oxathiin 2-Oxide with C_{60}. 21b: 47% (54% based on consumed C_{60}).

Cycloadduct of 4,5-(2,3-Dibromo-1,4-dimethoxybenzo)-3,6-dihydro-1,2-oxathiin 2-Oxide with C_{60}. 21c: 32% (44% based on consumed C_{60}); ^{1}H NMR ($CDCl_3/CS_2$) δ 3.90 (s, 6H), 4.45 (bd, 2H), 4.85 (bd, 2H); FTIR (KBr) 2924, 1513, 1428, 1454, 1389, 1184, 1043, 992, 527 cm^{-1}; UV−vis λ_{max} (nm) 252, 278, 328, 434, 702.

Cycloadduct of 4,5-(1,4-Dimethoxynaphtho)-3,6-dihydro-1,2-oxathiin 2-Oxide with C_{60}. 21d: 22% (58% based on consumed C_{60}); ^{1}H NMR ($CDCl_3/CS_2$) δ 8.26 (dd, J = 6.4 and 3.3 Hz, 2H), 7.64 (dd, J = 6.4 and 3.3 Hz, 2H), 5.06 (d, J = 14.0 Hz, 2H), 4.69 (d, J = 14.0 Hz, 2H), 4.06 (s, 6H); FTIR (KBr) 2918, 2849, 1354, 1261, 1091, 1046, 1023, 800, 668, 526 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) 256, 280, 306, 324, 432, 702.

Reaction of Adduct 21b with BBr_3. To a solution of **21b** (83 mg, 0.094 mmol) in anhydrous benzene (50 mL) under argon was added an excess of BBr_3 (0.47 mmol, 0.47 mL of a 1 M solution of BBr_3 in CH_2Cl_2). After 21 h, the reaction mixture was washed with water and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The solid residue thus obtained was purified by flash chromatography over silica gel, using cyclohexane/toluene as eluent, giving 41 mg of **22a** (51%) and 20 mg of **23a** (25%).

Reaction of Adduct 21d with BBr_3. To a solution of **21d** (60 mg, 0.064 mmol) in anhydrous *o*-dichlorobenzene (100 mL) was added an excess of BBr_3 (1.6 mmol, 1.6 mL of a 1 M solution of BBr_3 in CH_2Cl_2) under an argon atmosphere. After 7 d of stirring at room temperature, the mixture was washed with water and dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting solid residue was purified by flash chomatography over silica gel using toluene as the eluent. Further purification was accomplished by washing the solid three times with methanol, giving 49 mg (84%) of **23b:** ^{1}H NMR ($CDCl_3/CS_2$) δ 4.65 (bs, 4H), 7.87 (dd, J = 5.7 and 3.3 Hz, 2H), 8.31 (dd, J = 5.7 and 3.3 Hz, 2H); ^{13}C NMR ($CDCl_3/CS_2$) δ 37.03, 64.83, 126.70, 127.06, 132.22, 133.69, 134.02, 135.27, 140.15, 141.56, 141.96, 142.50, 142.97, 144.50, 144.97, 145.36, 145.50, 145.58, 146.16, 146.42, 147.57, 155.36, 181.70; FTIR (KBr) 1665, 1626, 1592, 1511, 1428, 1330, 1278, 718, 527 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) 255, 284, 312, 324, 432, 700.

Reaction of Adduct 21c with BBr_3. To a solution of **21c** (119 mg, 0.11 mmol) in toluene anhydrous (50 mL) was added an excess of BBr_3 (4.56 mmol, 4.56 mL of a 1 M solution of BBr_3 in CH_2Cl_2) under an argon atmosphere. After 7 d of reaction, the mixture was washed with water and dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The solid residue was purified by flash chromatography over silica gel, using cyclohexane/toluene as the eluent. The solid product thus obtained (115 mg) consisted of a mixture of hydroquinone **22c** and quinone **23c** which was oxidized without previous separation. Thus, a solution of 115 mg of the solid previously obtained and an excess of DDQ (257 mg, 1.13 mmol) in 50 mL of toluene was stirred for 5 d. The solvent was removed under reduced pressure, and the residue was chromatographed over silica gel using cyclohexane/toluene as the eluent, giving 112 mg (97% of overall yield) of quinone **23c:** ^{1}H NMR ($CDCl_3/CS_2$) δ 4.61 (bs, 4H); FTIR (KBr): 527, 719, 1143, 1263, 1429, 1552, 1670, 2920 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (nm) 252, 286, 356, 434, 698.

Reaction of Hydroquinone 22a with DDQ. To a solution of **22a** (111 mg, 0.13 mmol) in benzene (50 mL), was added an excess of DDQ (1.3 mmol). After 24 h of stirring at room temperature, the solvent was removed under reduced pressure, and the solid residue was purified by flash chromatography using silica gel and cyclohexane/toluene as the eluent, recovering 40 mg of unreacted **22a** and obtaining 60 mg (54%) of quinone **23a**.

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