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Isomers of the Dimeric Fullerene $C_{120}O_2$

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Two products, **A** and **B**, with the formula $C_{120}O_2$ have been characterized by HPLC, MALDI-TOF MS, FT-Raman, and ^{13}C NMR spectroscopy. $C_{120}O_2$(**A**) was found as a byproduct accompanying $C_{120}O$ in the solid-phase reaction at 200 °C of mixtures containing approximately a 4:1 ratio of C_{60} to $C_{60}O$ and traces of $C_{60}O_2$. Raman spectra indicated that **A** has a furanoid bridge (analogous to $C_{120}O$) linking a C_{60} fullerene cage with a $C_{60}O$ cage containing an epoxy group. ^{13}C NMR confirmed this and showed that the isolated product **A** consists of two closely related isomers with C_1 symmetry in a 4:1 ratio. $C_{120}O_2$(**A**) can be formed by the [3 + 2] cycloaddition of $C_{60}O$ to a second $C_{60}O$ or possibly by the addition of $C_{60}O_2$ to C_{60}. The 16 possible regioisomers of **A** were modeled by semiempirical methods, and isomers with the epoxy group located in the cis-1, e, or trans positions relative to the furanoid bridge have lower energies compared with those of cis-2 or -3 forms. The NMR and modeling data provide strong evidence that the two isomers of **A** represent the two possible cis-1 configurations. The other isomers (but not cis-1 forms) can react further with C_{60} to form trimeric $C_{180}O_2$ compounds, which were also observed. Thermolysis of solid $C_{120}O$ at temperatures above 300 °C yielded $C_{120}O_2$(**B**) and other products but no **A**. $C_{120}O_2$(**B**) consists of a single isomer with C_{2v} symmetry in which the C_{60} cages are linked by two neighboring furanoid bridges in a cis-1 configuration. Modeling calculations indicate that this isomer has an energy that is significantly lower than that of other possible double-bridged isomers and ca. 50 kcal/mol below the energy of the **A** isomers.

Introduction

During our search for a method of preparing C_{119},[1] we have studied the thermal transformations in the $C_{60}/C_{60}O/C_{60}O_2$ system and have shown that moderate heating (200 °C) of a dilute mixture of $C_{60}O$ in C_{60} (typically in a 1:4 ratio with ca. 2% $C_{60}O_2$ as an impurity) results in complete disappearance of C_{60} oxides with the formation of $C_{120}O$ as the main product.[2] Smith et al.[3] have reported that $C_{120}O$ also forms in boiling *o*-dichlorobenzene, but we performed the $C_{60}/C_{60}O$ reaction exclusively in the solid state and studied the soluble product mixture. $C_{120}O$ is a dimeric C_{60} oxide with a five-membered furanoid ring forming a symmetrical bridge between [6,6] ring junctions in the two fullerene cages.[2,3] Presumably, the mechanism of formation involves the [3 + 2] cycloaddition of the 1,2-epoxy[60]fullerene across a [6,6] double bond in C_{60}.[2] More recently, Balch et al.[4] have used the same solid-phase reaction to produce $C_{120}O$ for electrochemical studies.

With HPLC and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS we found that minor byproducts of the thermolysis reaction are $C_{120}O_2$ (denoted here as product **A**) and $C_{180}O_2$; isomers of the latter were isolated as three HPLC fractions.[5] We also investigated the thermolysis of the product mixture generated as described above and of ca. 95% pure $C_{120}O$ powder samples at 300−600 °C.[5] The following transformations were detected, in order of increasing probability at higher temperatures: (i) decay of $C_{120}O$ back to C_{60} and the disappearance of $C_{120}O_2$(**A**), which was unstable at higher temperatures;[6] (ii) formation of a different $C_{120}O_2$, hereafter denoted as **B**[7] and other oligomeric oxides of the formula $(C_{60})_nO_m$ ($n = 2-5$; $m = 2-9$); (iii) the formation of species with modified cage structure (e.g., $C_{179}O_2$, $C_{178}O_3$, C_{119}).[1,5]

$C_{120}O_2$(**B**) differed from $C_{120}O_2$(**A**) in both its HPLC behavior and fragmentation pattern in MALDI-TOF mass spectra, and **B** has been established by ^{13}C NMR and IR spectroscopy to consist of two C_{60} cages bridged via *two* neighboring furanoid rings.[7] Analogous to $C_{120}O$, these bridges are attached at the sites of neighboring [6,6] fullerene double bonds in each cage (with cis-1 regiochemistry according to the scheme of Hirsch et al.[8−10]) and exhibit a "head-to-head" or syn configuration with respect to the oxygen atoms, while the "tails" of the furanoid rings form an additional four-membered ring linking [5,6] junctions in each of the two cages. In this communication we report on further spectroscopic and molecular modeling studies of the isomers of $C_{120}O_2$, with emphasis on the characterization of $C_{120}O_2$(**A**). During the preparation of this report, a modeling study by Fowler et al.[11] appeared, which investigated a family of dimeric structures of the **B** type. Our results are in agreement with theirs, with the NMR-derived structure of **B** being lowest in energy.

Experimental Section

Materials and Reactions. A mixture of C_{60} and $C_{60}O$ with traces of $C_{60}O_2$ as an impurity was produced by controlled ozonolysis of commercial C_{60} (Hoechst Gold grade) at a

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concentration of ca. 2 mg/mL in *o*-dichlorobenzene (OCDB). After filtration and evaporation of the solvent a solid mixture containing typically 79% C_{60}, 19% $C_{60}O$, and 2% $C_{60}O_2$ by weight was obtained and used as starting material for subsequent reactions. The bis(epoxide) $C_{60}O_2$, present as an impurity, was not characterized further by us but has been studied by Balch et al.[12] It is formed as a mixture of regioisomers during ozonolysis of C_{60} or by chemical oxidation with *m*-chloroperoxybenzoic acid. Our solid starting material was heated under argon at 200 °C for 1 h, as previously described,[2,5] to give a product mixture containing $C_{120}O$, $C_{120}O_2$(**A**), $C_{180}O_2$, and unreacted C_{60}.[5] The product was dissolved in ODCB to a concentration of ca. 1 mg/mL with less than 3% remaining as an insoluble residue. The $C_{120}O_2$(**A**) fraction (ca. 10 wt % relative to the amount of $C_{120}O$ obtained) was isolated by three-stage HPLC (Cosmosil Buckyprep column, 250 mm × 20 mm, elution with toluene at 18 mL/min). Retention times were 7.8 min for C_{60}, 15.0 min for $C_{120}O$, 16.2 min for $C_{120}O_2$(**A**), and ca. 25 min for $C_{180}O_2$ (three overlapping bands). For ^{13}C NMR studies a sample was prepared from starting materials enriched to 7% in ^{13}C.[7]

$C_{120}O_2$(**B**) was produced, as described previously,[7] by the solid-phase thermolysis of $C_{120}O$ under argon at 400 °C for 1 h and isolated from other soluble products by HPLC (see above) with a retention time of 17.5 min.

Spectroscopy. MALDI-TOF mass spectrometry with 9-nitroanthracene as a matrix was performed with a Bruker Biflex instrument, and FT-Raman spectra were obtained from solid samples with a Bruker FRA 106 spectrometer.

^{13}C NMR at 125.76 MHz (11.7 T) was carried out at 30 °C with a Bruker AM-500 FT-NMR spectrometer using a gated-decoupling spin−echo technique for dealing with extreme dynamic range problems associated with the solvent, as described in detail previously.[1] The 5 mm NMR sample tube contained 1.7 mg of $C_{120}O_2$(**A**) (7% ^{13}C) dissolved in 0.24 mL of ODCB (not deuterated) containing 17.5 mM $Cr(acac)_3$ as paramagnetic relaxation agent. A 2 mm capillary containing acetone-d_6 provided a deuterium lock signal. At this concentration of $Cr(acac)_3$ the T_1 relaxation time of C_{60} was determined to be 1.7 s. The repetition time used with a 90° excitation pulse was 2.5 s so that ^{13}C signal integrals for all sp^2 carbons are expected be at least 80% of their theoretical values. Data acquisition was performed for a total of 64 h. A control spectrum of a small amount of C_{60} in the same solvent was acquired for 32 h in order to identify unavoidable artifact signals.[1] Spectra were processed with various window functions (Lorentz−Gauss line shape transformation for resolution enhancement), and integration of each spectrum resulted in consistent results for the number of sp^2 and sp^3 carbons. Chemical shifts were calibrated relative to C_{60} shift at 142.827 ppm, as determined in separate experiments (TMS shift at 0 ppm, C−Cl carbon shift of the solvent at 132.526 ppm).

Modeling. Molecular modeling was performed on a 200 MHz Pentium PC using the MM2+SCF force field of Chem3D (version 3.2, CambridgeSoft Corp., Cambridge, MA) and the semiempirical methods AM1 and PM3 (requiring 64 MB RAM) with the parametrization supplied by HyperChem (version 3, Hypercube, Inc. and Autodesk). Structures were optimized in HyperChem using the restricted Hartree−Fock method without configuration interaction. Energy minimization via the Polak−Ribiere conjugate-gradient method was terminated at an rms gradient of <0.10 kcal mol^{-1} Å^{-1} for all **A** isomers and <0.15 for the important **B** isomers. This required 3−6 days of calculations per isomer. With MM2 a so-called steric energy is calculated, whereas AM1 and PM3 report the heat (enthalpy) of formation (total energy minus atomic heats of formation) but on different scales. We have also made use of the so-called Mulliken atomic charges computed by HyperChem as the core charge (nuclear charge minus inner-shell electrons) minus the sum of the atomic orbital electron populations.

Predictions of ^{13}C NMR chemical shifts for partial structures modeling the fullerene oxides of interest were performed using SpecTool software (version 2.1, Chemical Concepts, Weinheim, FRG). Since the program cannot handle complete fullerene molecules, the following model structures were used: (a) tetrahydrofuran with eight phenyl substituents, (b) a furan ring fused on each side with two hexadiene rings or the central ring of two phenanthrene systems, (c) two phenanthrenes fused at the central rings together with an epoxide ring (oxiran), and (d) extensions of these, involving additional five- or six-membered rings. SpecTool was then used to estimate a priori the chemical shifts for these model structures. As an alternative strategy, individual position-dependent shift increments for various substituents were also extracted from SpecTool or from Pretsch et al.[13] and used to calculate composite shift increments for estimating the effect of replacing a fullerene double bond with an epoxy group or the furanoid bridge moiety. These increments were then used to predict chemical shifts for the **A** isomers starting from the known shifts for $C_{60}O$ and $C_{120}O$.

Results

The solid-phase thermolysis of a $C_{60}/C_{60}O/C_{60}O_2$ mixture (see Experimental Section) resulted in the following product mixture (typical wt %): 60% C_{60}, 30% $C_{120}O$, 3% $C_{120}O_2$(**A**) (one HPLC fraction), and 7% $C_{180}O_2$ (in three HPLC fractions).

The MALDI-TOF mass spectrum of $C_{120}O_2$(**A**) (Figure 1a) displays a molecular ion peak at 1473.6 amu for $C_{120}O_2$ (calculated: 1473.32 amu) and intensive peaks at 720.5, 736.7, and 752.7 amu for the fragment ions C_{60}, $C_{60}O$, and $C_{60}O_2$, respectively. The mass spectrum of $C_{120}O$ (Figure 1b) also shows C_{60} and $C_{60}O$ as major fragment ions. In contrast, the MALDI-TOF mass spectrum of $C_{120}O_2$(**B**) (Figure 1c) shows only very small fragment peaks at 720.2 (C_{60}) and 736.6 ($C_{60}O$) amu in addition to the intense molecular ion peak at 1473.3 amu. A weak signal at 1489.8 amu ($C_{120}O_3$) suggests that some oxidation by the matrix may occur under MALDI conditions.

Figure 2 presents FT-Raman spectra of $C_{120}O$ and both $C_{120}O_2$ products (**A** and **B**) in comparison with a reference spectrum of C_{60} (discussed in ref 14, for example). The region 100−600 cm^{-1} shown in Figure 2a includes the [60]fullerene $H_g(1)$ squashing mode (272 cm^{-1}) and the $A_g(1)$ breathing mode (496 cm^{-1}), while the $A_g(2)$ pentagonal pinch mode (1468 cm^{-1}) appears in the expansion of Figure 2b. The spectra of $C_{120}O$ and the $C_{120}O_2$ species exhibit signals near the positions of major C_{60} peaks but with additional splitting and shifts as a result of the reduced symmetry. All of the investigated dimeric compounds showed new lines at low frequencies (100−200 cm^{-1}), which are not present in the spectra of C_{60} or $C_{60}O$. These originate from (rotational) twisting and (translational) vibration modes of the two cages with respect to each other and yield information on the nature of the bridge connecting the two fullerene cages.

The ^{13}C NMR spectrum of $C_{120}O_2$(**A**) in *o*-dichlorobenzene, when processed for high resolution (Figure 3), exhibited in the range 155−135 ppm 94 resolved sp^2 carbon resonances, integrating to 114 carbons, and in the range 100−77 ppm 6 sp^3 carbon resonances of equal but lower intensity, consistent with a molecule of C_1 symmetry. The sp^3/sp^2 intensity ratio was

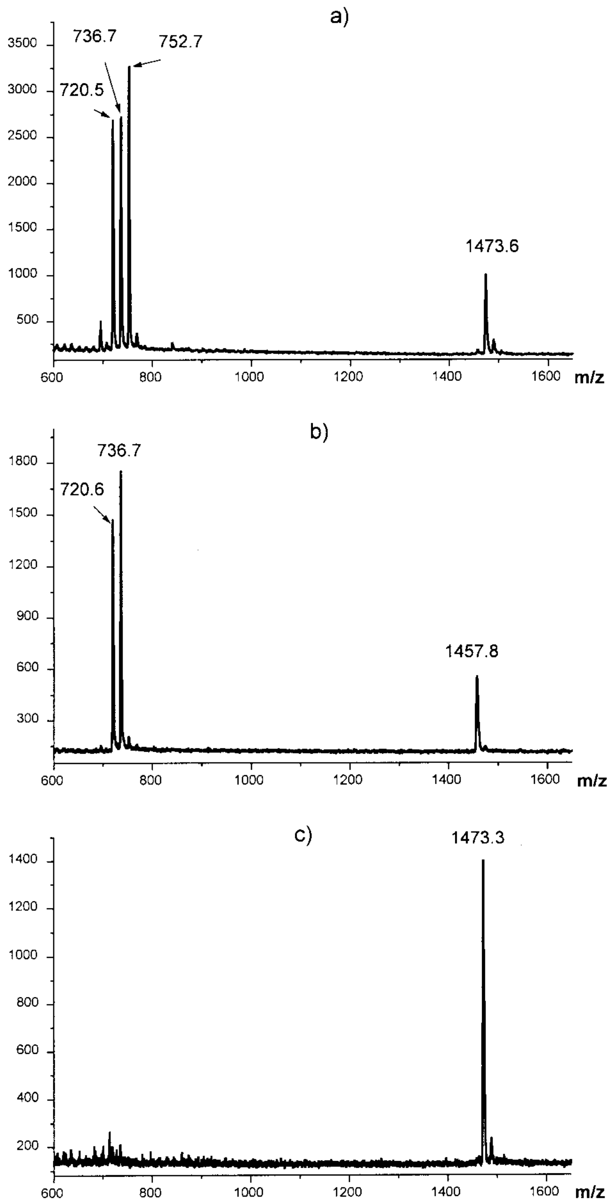


Figure 1. MALDI-TOF mass spectra of (a) $C_{120}O_2$(**A**), (b) $C_{120}O$, (c) $C_{120}O_2$(**B**). Matrix is 9-nitroanthracene, and spectra were taken in negative-ion mode.

0.7, indicating that sp^3 carbons have longer T_1 relaxation times. When processed for enhanced sensitivity (Figure 4), the spectrum revealed many additional weak resonances or shoulders on the major resonances, indicating that a second isomer was present. Detailed integration analysis indicated that the minor isomer represented ca. 20% of the material. Only when this was taken into account could a reliable signal integration and carbon count for the major isomer in the complex sp^2 carbon region be achieved. Table 1 presents the complete list of resonances detected for the major isomer and a partial list of assignable or suspected resonances for the minor isomer.

The sp^2 region of the NMR spectrum (Figure 3) features a central part (147−141 ppm) that contains the majority of densely packed resonances while a smaller number of resonances appeared well-separated on either side (155−147 and 141−135 ppm). This pattern is typical of substituted fullerenes or fullerence dimers such as $C_{120}O$, and we have tentatively assigned the most widely separated resonances (labeled 1−7 in Figures 3 and 4) to the [6,6] double bonds immediately adjacent to the furanoid bridge in $C_{120}O_2$(**A**) (see Discussion). Signals from the minor isomer of **A** can be most easily recognized in these sp^2 regions as well as in the sp^3 region (Figure 4) but are also scattered throughout the central sp^2 region. The low signal-to-noise ratio of the spectrum did not allow us to obtain a complete list of chemical shifts or a precise carbon count for the minor isomer. In particular, in the sp^3 signal region (110−70 ppm) six additional weak signals (* in Figure 4C) and two possible shoulders (on peaks 4 and 5) were detected when the spectrum was processed with sensitivity enhancement (see Table 1). However, these signals were at the limit of detectability, and their amplitudes were equal to or less than the amplitudes of several identified artifact signals, which were also oberved in the control spectrum. Thus, two of these eight possible signals are probably artifacts, and we cannot unequivocally assign six sp^3 chemical shifts to the minor isomer at this time. However, wherever minor isomer peaks were observed or implied by integration, a 4:1 ratio of major to minor peaks was uniformly found. The minor resonances did not have chemical shifts that matched any of those documented for other fullerene oxides. Thus, we conclude that the major and minor isomers have very similar structures and that both possess C_1 symmetry.

Discussion

If we assume a random distribution of molecules in the solid-phase reaction mixture (see Experimental Section), then, on the basis of simple rules of combinatorial probability, the relative yields of bimolecular reactions should be $C_B p_X p_Y$, where p_X and p_Y are the fractional populations for reactants X and Y and the binomial coefficient $C_B = 1$ (when X = Y) or 2 (X ≠ Y). Therefore, the predicted yields are (in mol %, nearly equal to wt % when the additional mass from oxygen atoms is ignored) 62.4% unreacted pairs of C_{60}, 30% $C_{120}O$ from $C_{60} + C_{60}O$, 3.6% $C_{120}O_2$ from $C_{60}O + C_{60}O$, and 3.2% $C_{120}O_2$ from $C_{60}O_2 + C_{60}$. Thus, a total yield of up to 6.8% $C_{120}O_2$ would be expected (22.7% relative to $C_{120}O$). Experimentally, we observed only about 3% $C_{120}O_2$(**A**) (10% relative to $C_{120}O$). This would be the result if for some reason only one of the two reactions described above occurred. A more likely explanation can be found if we invoke the following trimolecular reactions: $2C_{60}O + C_{60} \rightarrow C_{180}O_2$ (maximum probability of 8.6%) and $C_{60}O_2 + 2C_{60} \rightarrow C_{180}O_2$ (maximum probability of 3.7%). For example, if 56% of the maximum possible yield of $C_{120}O_2$ reacts further to form trimeric species, then the predicted yields are 3% $C_{120}O_2$(**A**) and 6.9% $C_{180}O_2$, in good agreement with our observations. Furthermore, the predicted yield of $3C_{60}O \rightarrow C_{180}O_3$ is only 0.7%; this species was not detected in these experiments.

Raman spectroscopy provides us with useful information for distinguishing the various dimeric fullerene oxides. We see in Figure 2 that the spectra of $C_{120}O$ and $C_{120}O_2$(**A**) are remarkably similar in the range 100−600 cm^{-1} while the spectrum of $C_{120}O_2$(**B**) differs significantly with low-frequency bands at 121 and 161 cm^{-1} (peaks η and κ in Figure 2a) instead of 100 cm^{-1} (peak ϵ in Figure 2a). The pentagonal pinch mode has the same frequency of 1463.6 cm^{-1} for $C_{120}O$ and $C_{120}O_2$(**A**) but is shifted to ca. 1465 cm^{-1} for $C_{120}O_2$(**B**). This evidence implies that $C_{120}O$ and $C_{120}O_2$(**A**) have very similar structures; i.e., each possesses a furanoid bridge between fullerene cages while **A** also contains an epoxy group, as in $C_{60}O$. On the other hand, $C_{120}O_2$(**B**) must differ significantly with a stiffer bridging structure, i.e., the two furanoid bridges proposed on the basis of NMR data.[7] This interpretation is consistent with the MS

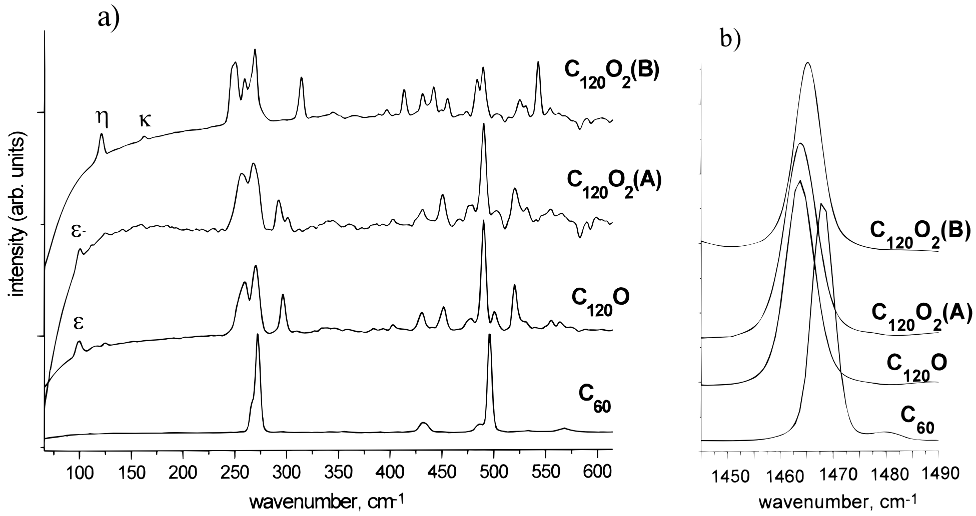


Figure 2. FT-Raman spectra (Nd:YAG laser, excitation at 1064 nm) of solid C_{60}, $C_{120}O$, $C_{120}O_2$(**A**), and $C_{120}O_2$(**B**) acquired at a resolution of 2 cm^{-1}. Low-frequency bands that characterize the bridging structure between fullerene cages are labeled with the letters ϵ, η, and κ.

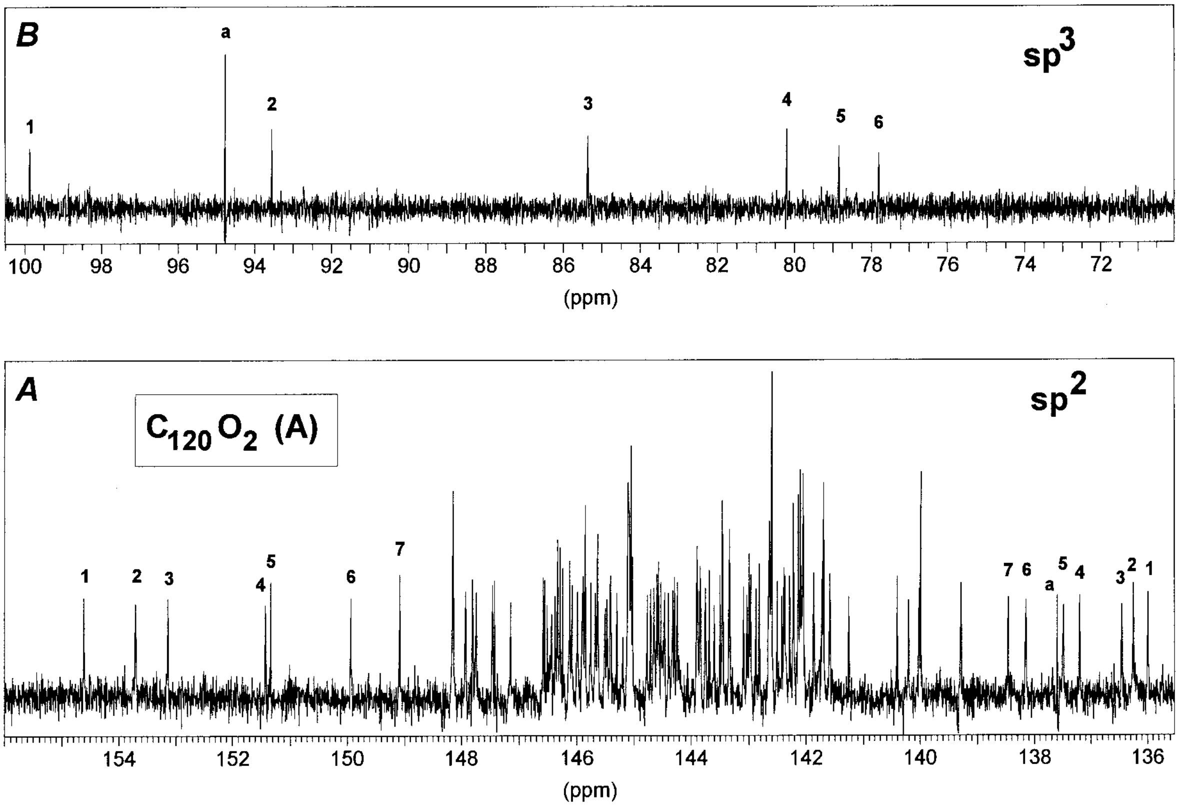


Figure 3. ^{13}C NMR spectrum (125.76 MHz) of 1.7 mg $C_{120}O_2$(**A**) enriched to 7% ^{13}C (solvent: *o*-dichlorobenzene, 30 °C, 64 h acquisition). The data have been processed for high resolution at the expense of signal-to-noise ratio using a Lorentz−Gauss window function with parameters LB = −3 Hz, GB = 0.26 (Bruker software). Only signals from the major isomer are clearly observed, and the chemical shifts of the resolved peaks are given in Table 1. Artifact signals that were also detected in a control spectrum are labeled "a". In part A the sp^2 signals with the largest shifts away from the "center of mass" are assigned pairwise to the cis-1 double bonds and are labeled 1−7 from "outside" to "inside". In part B the six sp^3 carbons are labeled 1−6.

results, which demonstrate that the bridging unit in the **B** isomer is significantly more stable than in **A**, which readily dissociates into two $C_{60}O$ or $C_{60} + C_{60}O_2$.

^{13}C NMR provides us with more definitive data. When the six observed sp^3 chemical shifts for the major **A** isomer (Table 1) are compared with the values found for the furanoid bridge in $C_{120}O$ ($\delta C-O-C = 99.0$ ppm and $\delta C-C = 78.9$ ppm)[3] and the epoxy group in $C_{60}O$ (90.18 ppm),[15] it is clear that a significant perturbation of the shifts and a lifting of the local 2-fold symmetry of these groups has occurred. One possible set of assignments is furanoid $\delta C-O-C = 99.88$ and 93.55 ppm (signals 1 and 2 in Figure 3B), furanoid $\delta C-C = 78.84$ and 77.80 ppm (signals 5 and 6), epoxy shift = 85.36 and 80.20 ppm (signals 3 and 4), with perturbations of up to 10 ppm for carbons bound to oxygen. Other assignments would imply even larger perturbations. In any event, such shift effects are consistent with α- and β-substituent effects but are less likely to occur through γ or δ effects.[13] This implies that the epoxy group in **A** is at most two bonds removed from the furanoid C−O−C bridge.

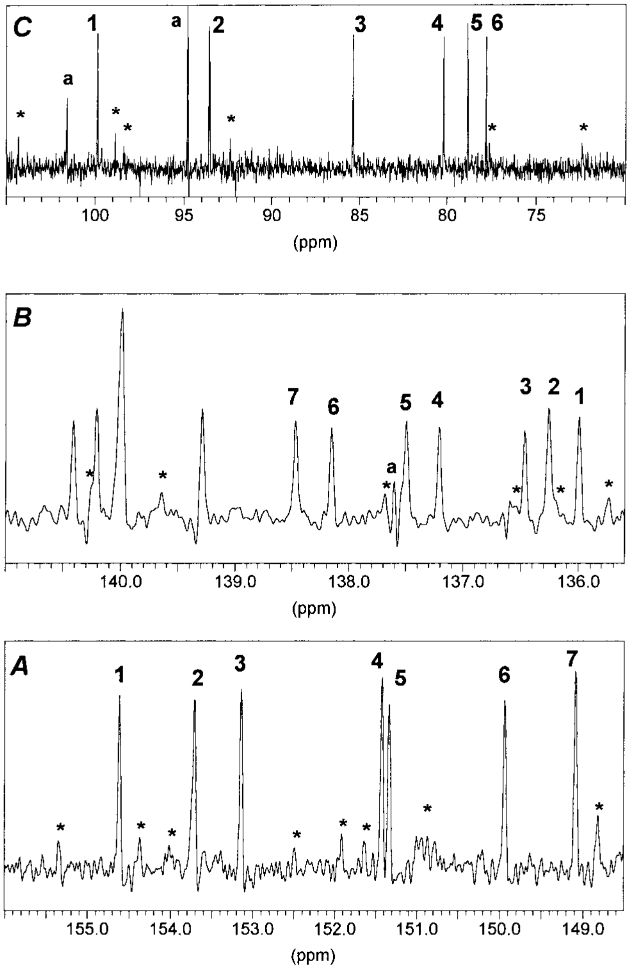


Figure 4. ^{13}C NMR spectrum of $C_{120}O_2$(**A**). The data of Figure 3 have been processed for improved signal-to-noise ratio at the expense of an increased Gaussian line width (LB = −3 Hz, GB = 0.05). Expanded regions for the extremely shifted sp^2 carbons (A, B) and for the sp^3 carbons (C) are shown, and peaks for the major isomer are labeled as in Figure 3. Additional weak signals and peak shoulders, marked with an asterix (*), are attributed to the minor isomer.

Thus, the spectroscopic data clearly establish that $C_{120}O_2$(**A**) is closely related to $C_{120}O$, i.e., is an epoxy derivative of this species. Such a structure can be considered, in mechanistic terms, to be the result of a [3 + 2] cycloaddition via the epoxy group of one $C_{60}O$ across a [6,6] bond of another $C_{60}O$ (dimerization, analogous to the formation of $C_{120}O$ from $C_{60}O$ and C_{60}). Alternatively, a cycloaddition of various isomeric forms of $C_{60}O_2$ (via one of the two epoxide groups) to C_{60} can occur with about equal probability for our reaction mixture. In either case, the expected result is an asymmetrical 2-fold adduct of C_{60} in a variety of isomeric forms.

Balch et al.[16] have observed that $C_{60}O$ and $C_{60}O_2$ slowly lose oxygen when exposed to PPh_3, indicating that this reaction might be useful as a chemical test for epoxide derivatives of fullerenes, but the general applicability of such a test has not been demonstrated. We have tried the PPh_3 reaction with $C_{120}O_2$(**A**) but observed no change in the HPLC profile. This negative result may be a result of the steric shielding of the epoxide group expected for the favored cis-1 isomers of $C_{120}O_2$(**A**) as discussed below.

TABLE 1: ^{13}C NMR Data for the Major and Minor Components of $C_{120}O_2$(A) in *o*-Dichlorobenzene[a]

major isomer						minor[b]
ppm	*I*	ppm	*I*	ppm	*I*	ppm
154.612	1	145.110	1	142.508	1	155.347
153.703	1	145.102	2	142.424	1	154.370
153.138	1	145.088	1	142.387	1	154.015
151.422	1	145.066	1	142.368	1	152.491
151.333	1	145.046	2	142.286	1	151.916
149.933	1	145.023	1	142.218	2	151.639
149.083	1	144.771	1	142.137	2	
148.149	3	144.708	1	142.098	2	148.818
147.928	1	144.647	1	142.052	2	
147.801	1	144.601	1	141.863	1	
147.741	1	144.569	1	141.715	1	
147.461	1	144.526	1	141.695	2	
147.428	1	144.467	1	141.583	1	
147.150	1	144.392	1	141.254	1	
146.584	1	144.321	1	140.406	1	
146.559	1	144.289	1	140.204	1	
146.514	1	144.240	1	140.012	1	
146.440	1	143.893	2	139.984	2	
146.378	1	143.841	1	139.286	1	
146.332	2	143.751	1	138.468	1	
146.287	1	143.681	1	138.152	1	139.644
146.241	1	143.598	1	137.492	1	138.400
146.121	1	143.502	1	137.206	1	137.682
146.081	1	143.461	2	136.461	1	136.540
145.986	1	143.340	2	136.252	1	136.200
145.899	1	143.093	1	135.993	1	135.737
145.888	1	143.035	1			
145.850	2	142.997	1	99.880	1	104.302
145.749	1	142.972	1	93.552	1	98.867
145.672	1	142.884	1	85.361	1	98.370
145.636	2	142.821	1	80.197	1	92.352
145.504	1	142.642	2	78.839	1	80.420
145.468	1	142.619	1	77.797	1	78.991
145.414	1	142.604	3			77.596
145.296	1					72.410

[a] Chemical shifts in ppm. *I* = signal integrals (integer values, ±20%).
[b] Only a partial list of minor peaks is given; some of these may be artifacts.

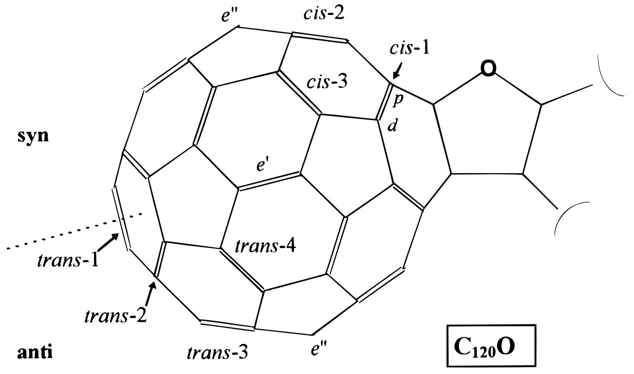
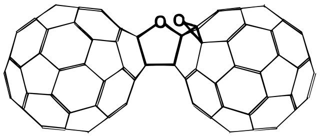
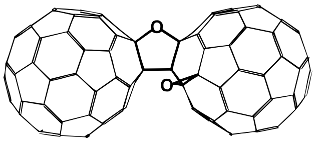


Figure 5. Labeling scheme for the [6,6] bonds in fullerenes as used to define the regioisomers of $C_{120}O_2$(**A**); syn and anti are defined relative to the furanoid oxygen bridge, and the labels p and d denote proximal and distal carbons in the cis-1 bond.

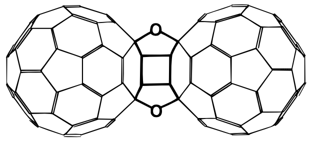
The regiochemistry of 2-fold additions to C_{60} has been studied in some detail.[8−10,17] The [3 + 2] cycloaddition of $C_{60}O$ across a [6,6] bond in a second $C_{60}O$ molecule can occur with two possible orientations of the oxygen in the resulting furanoid bridge relative to the remaining epoxy group, and the resulting isomers of $C_{120}O_2$(**A**) can be considered formally to be epoxides of $C_{120}O$. As shown in Figure 5 and according to the nomenclature of Hirsch,[8−10] relative to the furanoid bridge there are seven epoxy sites labeled cis-1, -2, -3, e″, and trans-2, -3, -4, which, in our case, occur in syn and anti configurations (syn refers to sites that are closer to the C−O−C part of the furanoid bridge than to the C−C part). The isomers e′ and trans-1 each exist in only one form. Thus, altogether there are 16 distin-



$C_{120}O_2$ (A) *cis*-1 *syn*



$C_{120}O_2$ (A) *cis*-1 *anti*



$C_{120}O_2$ (B)

Figure 6. Low-energy structures of $C_{120}O_2$(**A**) (cis-1 regioisomers) and $C_{120}O_2$(**B**) derived from semiempirical calculations (AM1). The furanoid and epoxide ring systems are highlighted.

guishable regioisomers of $C_{120}O_2$(**A**); these can also be formed by the reaction of the eight distinguishable isomers[12] of $C_{60}O_2$ with C_{60}. The three isomers trans-1, e″ syn, and e″ anti have C_s symmetry (not consistent with NMR), while e′ and the six pairs of cis and trans isomers have C_1 symmetry (consistent with NMR) and exist as enantiomeric pairs. Figure 6 presents the two cis-1 isomers of **A** in comparison with the established structure of **B**, which features two furanoid bridges in a cis-1 configuration.

According to the general rules established by Hirsch and co-workers,[10] it is expected that all isomers of **A** can be formed to some extent, but the cis-1, equatorial e′ and e″, and the trans-3 sites should be slightly preferred energetically. (Exception: cis-1 bis adducts of C_{60} will be sterically prohibited when *both* adducts are bulky.) We have examined the various $C_{120}O_2$ isomers of type **A** and **B** by molecular modeling techniques, and the energies of minimized structures are summarized in Table 2 and Figure 7. In agreement with the trends found by the Hirsch group,[10] we find with semiempirical calculations (AM1, PM3) that the [6,6] bond lengths in $C_{60}O$ show a systematic variation according to position, with cis-1 shortened by 0.8 pm and cis-2 and cis-3 lengthened by ca. 0.15 pm compared to C_{60}. For $C_{120}O_2$(**A**) the range of energies obtained is ca. 6 kcal/mol with cis-1 syn having the lowest energy. Other favorable isomers and their relative energies are cis-1 anti (2.7 kcal/mol), e′ (ca. 1.7 kcal/mol), e″, and various trans isomers (2−4 kcal/mol), while the cis-2 and -3 isomers are the least favored (ca. 4−6 kcal/mol).

We have also modeled the eight possible regioisomers of the bis(epoxide) $C_{60}O_2$. The pattern of energies is very similar to that shown in Figure 7 with cis-1 (the major product characterized by Balch et al.[12]) having the lowest energy (Table 2), cis-2 the highest (+4 kcal/mol), and the e and trans forms at intermediate energies (+2 kcal/mol).

We have also performed MM2 force field calculations, including SCF treatment of π orbitals. On the basis of steric energy, the cis-1 isomers of **A** are again preferred but in this case with anti at ca. 3.8 kcal/mol lower energy. This may reflect an overemphasis in the force field of the electrostatic repulsion between oxygens, which would be larger in the syn form. From a mechanistic viewpoint one might consider the individual atomic charges and their possible influence on a preferred syn or anti orientation of the cycloaddition reaction at the cis-1 bond. AM1 predicts for $C_{60}O$ that the Mulliken atomic charges on the proximal and distal sp^2 carbons of the cis-1 bond (i.e., at α and β positions relative to an epoxide sp^3 carbon) are −0.017 and 0.0057, respectively. This suggests that the oxygen of the forming furanoid bridge might show a weak preference for attacking the distal carbon to give the anti isomer.

In terms of a Boltzmann distribution (thermodynamic equilibrium) at 200 °C the energy differences calculated by PM3, for example, would translate into relative populations of 100 for cis-1 syn, 6 for cis-1 anti, 15 for e′, 10 for e″, a total of 44 for all trans isomers, and a total of 3 for cis-2 and -3 isomers. Thus, the cis-1 syn isomer would be about 56% of the population. At the other extreme, for a kinetically controlled reaction governed only by statistics (probably a more appropriate model for high-temperature reactions), the two cis-1 isomers would be expected to occur with a probability of only 2/29 or 7% each. In their investigations of bis adducts of C_{60}, Hirsch and co-workers found that usually all sterically allowed isomers could be isolated in significant amounts but with a product

TABLE 2: Molecular Modeling of Fullerene Oxides

		minimized energies (kcal/mol)		
		steric energy	heat of formation	
compound/isomer	symmetry	MM2+SCF	AM1	PM3
C_{60}		179.78	972.51	810.74
$C_{60}O$	D_{2h}	210.78	959.39	790.79
$C_{60}O_2$ cis-1[a]	C_s		944.03	
C_{120}	D_{2h}	419.53	1912.98	1585.35
$C_{120}O$	C_{2v}	399.63	1877.17	1549.31
$C_{120}O_2$(**A**) cis-1, syn[b]	C_1	422.36	1860.76	1526.76
$C_{120}O_2$(**B**)[c]				
[6,6-5,6-6,6] syn[d]	C_{2v}	430.97	1812.67	1477.44
[6,6-5,6-6,6] anti	C_s	418.78	1853.47	
[5,6-6,6-6,5] syn[e]	C_{2v}	423.74	1838.13	
[5,6-6,6-6,5] anti	C_{2h}	415.86	1942.62	
$C_{120}O_2$(**C**)[f]	D_{2h}		1856.91	1527.17

[a] The lowest-energy regioisomer of the bis(epoxide). Other isomers have energies 2−4 kcal/mol higher. [b] The lowest-energy form. Data for other regioisomers, defined by relative positions of furanoid bridge and epoxy group (Figure 5), are summarized in Figure 7. [c] Regioisomers defined by furanoid−cyclobutane−furanoid bridge junctions and relative orientation of oxygens. [d] Isomer 1 in ref 7, most consistent with ^{13}C NMR. [e] Isomer 2 in ref 7. [f] Two C−O−C bridges between C_{60} [6,6] junctions result in a six-membered 1,4-dioxane ring.

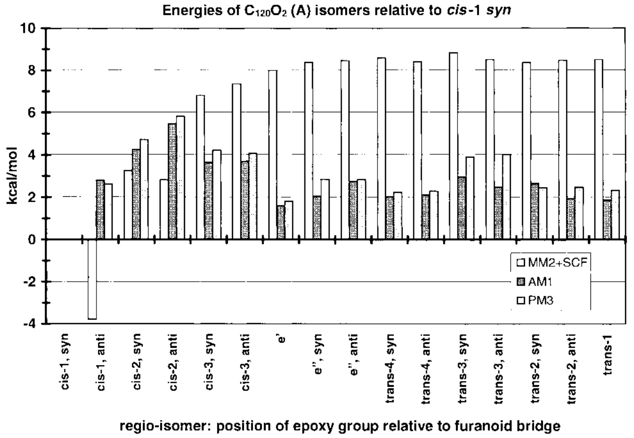


Figure 7. Calculated energies for optimized structures of all possible isomers of $C_{120}O_2$(**A**). The minimized energies obtained with the MM2+SCF force field and with the semiempirical methods AM1 and PM3 are presented graphically and expressed as differences relative to the cis-1 syn isomer (Figure 6).

distribution that was between those expected for thermodynamically and kinetically controlled processes.

Taken together, all of the modeling results for $C_{120}O_2$(**A**) indicate that cis-1 syn (which is consistent with the NMR) is energetically favorable and should predominate in the product mixture but that cis-1 anti and the e and trans isomers (which are less consistent with the NMR) should also be present in comparable amounts because they have similar statistical probabilities and similar or only slightly higher energies. Surprisingly, we could isolate only one HPLC fraction containing $C_{120}O_2$(**A**) and representing ca. 40% of all dimeric and trimeric species containing two oxygens. The NMR data indicate that only a single major species plus a second minor component are present. A reasonable explanation for the relatively high regioisomeric purity of our $C_{120}O_2$(**A**) preparation is as follows. The cis-2 syn, cis-3, e, or trans isomers, which could be produced in our reaction mixture, still have a well-exposed epoxy group that can react further with a neighboring C_{60} molecule (present in excess in our reaction mixture), for example, to give $C_{180}O_2$ trimers with two furanoid bridges and an L- or V-like appearance.[18] However, modeling indicates that in the cis-1 syn, cis-1 anti, and cis-2 anti isomers the epoxy group is close to and partially shielded by the second fullerene cage so that reaction with another C_{60} is sterically hindered, especially for the anti isomers. We have already discussed the observed yields of dimeric and trimeric products on the basis of simple statistics and concluded that about half of the dimer species **A** are converted to trimers. This would provide a mechanism for eliminating e and trans isomers of **A** from the product mixture, for example, resulting in several possible trimeric products (three fractions were isolated) and a dimeric fraction **A** consisting of only the two cis-1 isomers (assuming cis-2 forms are unlikely).

We have also attempted to synthesize $C_{120}O_2$(**A**) by a different method that we expected would result in a variety of isomers: namely, the reaction of $C_{120}O$ with ozone under conditions analogous to those used for the ozonolysis of C_{60}. However, HPLC analysis showed that only the breakdown of $C_{120}O$ occurred under these conditions, perhaps due to the lability of the C−C bridging bond. An alternative reaction scheme that might avoid the conversion to trimeric species would be the use of a mild chemical oxidizer such as *m*-chloroperoxybenzoic acid. This method was used by Balch et al.[12] to produce $C_{60}O_2$ from C_{60}, and they obtained a mixture of isomers with the cis-1 form predominating.

Modeling studies have also been performed for eight possible **B** isomers, four of which have been presented in Table 2. The first structure listed features [6,6] junctions at the furanoid bridges and has a significantly lower energy compared with all other structures (see also ref 11). It represents the structure preferred on the basis of ^{13}C NMR.[7] Owing to the length of the C−O−C portion of a furanoid bridge, the axis connecting the two fullerene cages acquires a kink (e.g., $C_{120}O$). Therefore, the syn orientation of two furanoid bridges is favored over the anti, since their induced kinks coincide without additional strain. It is interesting that the energy of the preferred **B** isomer, formed at high temperature, is significantly lower than the energies of the **A** isomers (ca. 50 kcal/mol), which disappear at high temperature. This suggests that the formation of **B** requires a higher activation energy but gives a more stable product, which, as we have found, also dissociates less readily in the mass spectrometer. Mechanistically, it is quite straightforward for the cis-1 anti form of **A** (but not syn) to rearrange to the preferred **B** isomer by opening of the proximal epoxide bond closest to the furanoid bridge on the one cage followed by cycloaddition to the accessible cis-1 bond of the other cage. In the cis-1 anti isomer of **A** the distance between the two carbons, which could close to form the cyclobutane ring, is only 2.85 Å (AM1); the epoxide oxygen is only 3.09 Å from the corresponding *cis*-1 site (see Figure 6). From another point of view the preferred **B** isomer, with syn orientation of two furanoid bridges containing only [6,6] junctions, is the *only* structure that can be formed by a *double* cycloaddition between two $C_{60}O$ molecules (two cis-1 anti additions). Such a reaction could also occur between C_{60} and $C_{60}O_2$ in the cis-1 form.

For comparison we have included in Table 2 a third possible isomer type labeled $C_{120}O_2$(**C**). This structure, which has an energy very similar to that for the **A** class, contains a six-membered 1,4-dioxane bridge involving one [6,6] junction in each of two C_{60} units. Formally, this isomer can be obtained by inserting an oxygen atom into each of the C−C bridges of C_{120}. In the energy-minimized structure the dioxane ring adopts a boat form, resulting in C_{2v} molecular symmetry with four equivalent sp^3 carbons. The symmetry planes of each C_{60} unit intersect at the O−O axis at an angle of 135°. However, through the dynamics of ring inversion along the O−O axis the effective symmetry will be increased to D_{2h}. In any event this structure is not consistent with the NMR data for isomer **B**.

The above energetic and mechanistic arguments lead to the conclusion that the two isomers detected by NMR in the isolated $C_{120}O_2$(**A**) fraction are most likely the cis-1 adducts in syn and anti forms. The question then arises: can we make further use of the ^{13}C NMR chemical shift data not only to determine molecular symmetry but also to confirm a particular isomeric form? The cis-1 configuration of the two furanoid bridges in $C_{120}O_2$(**B**) has been established.[7,11] Evidence supporting a cis-1 configuration for isomer **A** can be found in the chemical shifts of the epoxy sp^3 carbons. Values of 82.3 and 78.4 ppm have been measured[12] for the cis-1 isomer of the bis(epoxide) $C_{60}O_2$ and compare reasonably well with our assignments of 85.361 and 80.197 (Table 1) for the epoxy group of **A**. From a more theoretical standpoint, we have used the SpecTool program to make the following a priori predictions for sp^3 carbons: C_{120} (calcd 69.5; obsd 76.22); $C_{60}O$ (calcd 82.9; obsd 90.18); $C_{120}O$ (calcd 87.0 and 63.9; obsd 99.0 and 78.9); $C_{120}O_2$(**B**) (calcd 86.5 and 66.6; obsd 92.11 and 72.19). These are the best estimates for the most complex fused-ring models that could be handled by the program (e.g., 12 rings for C_{60}), and the calculated values are generally too low by ca. 6−15 ppm. However, the predicted shift *difference* between the two carbons of the furanoid bridge moiety is in error by only 3.0 ppm for $C_{120}O$ and <0.1 ppm for $C_{120}O_2$(**B**). Attempts to calculate a priori shifts for $C_{120}O_2$(**A**) isomers were not successful because of software problems encountered with sufficiently large model structures. Therefore, we used SpecTool data to calculate a set of shift increments (α, β, γ, δ effects) for replacing a double bond with an epoxy group as an adduct to $C_{120}O$ and an analogous set of increments for the furanoid bridge unit as an adduct to $C_{60}O$. These increments were then applied to the known sp^3 shifts for $C_{60}O$ and $C_{120}O$. The corresponding predictions for the cis-1 syn form of isomer **A** were 102.5 and 98.6 for furanoid C−O−C carbons, 78.5 and 74.8 for C−C carbons, and 95.9 and 84.6 for epoxy carbons. For cis-1 anti the corresponding predictions were 98.6 and 94.9, 82.4 and 74.8, and 88.3 and 85.7. Comparing these predictions with the measured chemical shifts for the major isomer (Table 1), we find rather poor agreement and no fully consistent and convincing evidence clearly favoring either the syn or anti form. Only the observed shifts of 78.8 and 77.8 ppm for the furanoid C−C bridging carbons agree better with predictions for the syn form

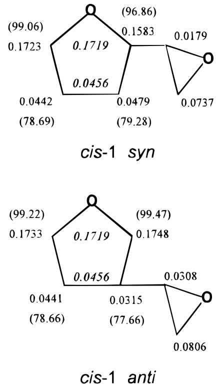


Figure 8. Schematic presentation of the sp^3 carbon skeleton in $C_{120}O_2$-(**A**). Each carbon site is labeled with its Mulliken atomic charge, as calculated by AM1, and the values for the symmetrical furanoid structure in $C_{120}O$ are given in italics. The predicted furanoid carbon chemical shifts, based on the atomic charges (see text), are given in parentheses.

(78.5 and 74.8) rather than the anti form. Unfortunately, data for appropriate model compounds are lacking, and the applicability and reliability of simple shift increment methods are severely limited for systems with multiple rings or highly strained structures. Thus, an unequivocal assignment of the syn or anti form for **A** cannot be made on the basis of predicted sp^3 carbon shifts.

We have taken a second approach to the analysis of the ^{13}C NMR spectra of the fullerene oxides by considering a possible correlation between chemical shifts and Mulliken atomic charges calculated by AM1, for example. Several different linear correlation functions have been developed in the literature, each correlating the shift of a given carbon type in closely related structures to some calculated measure of charge or electron density. For example, Lazzeretti and Taddei[19] correlated shifts in substituted benzenes with total charges calculated by CNDO, and Sardella[20] found that chemical shift *differences* in π-systems were proportional to atom−atom polarizabilities. In Figure 8 we present schematically the sp^3 skeleton and the calculated atomic charges for the cis-1 isomers of $C_{120}O_2$(**A**) together with the values for $C_{120}O$ (in italics). Assuming that there is a linear correlation between charge and shift for the furanoid carbons in $C_{120}O$ (99.0, 78.9 ppm), we calculate a slope of 159.14 ppm per unit charge, which can be used to predict the shifts for the furanoid carbons in the cis-1 syn and anti isomers of **A** (numbers in parentheses in Figure 8). The predictions for the syn isomer are in better agreement with the experimental data for the major isomer of **A** (Table 1). The minimum rms deviations for observed vs calculated shifts are 1.76 for cis-1 syn and 2.90 for cis-1 anti. In an analogous manner we find rms deviations of 2.69 for cis-2 syn and 2.71 for cis-2 anti (data not shown). Other possible isomers such as the e or trans forms have charges that differ only slightly from the values calculated for $C_{120}O$ and are, therefore, not compatible with the observed chemical shift dispersion. The data of Figure 8 also indicate that the charges for the epoxy carbons cannot be used to calculate reasonable absolute shift values via the formula used for the furanoid carbons.

The chemical shifts of the sp^2 carbons in fullerene derivatives also represent potential structural information that has not been widely exploited to date. Our AM1 and PM3 calculations indicated that the cis-1 bonds in dimeric fullerenes have significantly higher charge polarization, i.e., the difference in atomic charges for the two carbon sites, than is found for the other [6,6] double bonds. The cis-1 bonds are also significantly shorter. In general, the proximal carbon next to a bridging sp^3 carbon has a negative charge while the distal carbon has a smaller negative or a positive charge. For example, for the C_{120} fullerene dimer[21] we find the mean proximal minus distal charge difference for cis-1 bonds to be −0.0332. In the ^{13}C NMR spectrum of C_{120} a high- and a low-frequency-shifted signal appear widely separated from the bulk of the sp^2 signals (151.42 and 139.02 ppm). We assign these to the proximal and distal carbons, respectively, of the eight equivalent cis-1 bonds, in agreement with appropriate chemical shift predictions from SpecTool. For $C_{120}O$ the 8-fold symmetry of cis-1 bonds is split by the furanoid bridge to give two pairs of high- and low-frequency-shifted ^{13}C NMR resonances (153.58, 136.36 and 150.92, 137.61 ppm), which we associate with the calculated cis-1 charge differences of −0.0466 (syn) and −0.0414 (anti), respectively. If the molecular symmetry is reduced to C_1, then we expect a separate pair of resonances for each cis-1 bond; in other words, each of the four cis-1 resonances in $C_{120}O$ should effectively split into four resolved resonances in a derivative such as $C_{120}O_2$(**A**). We find that the largest charge difference in **A** is −0.052 for cis-1 syn and −0.054 for cis-1 anti, consistent with the larger maximum shift difference found for **A** (major isomer, 18.62 ppm; minor isomer, 19.61 ppm) compared to $C_{120}O$. From the data for the major **A** isomer in Table 1, we see that only *three* carbon resonances appear in each of the ranges 153−155 and 136−136.5 while *four* signals are found in the ranges 149−151.5 and 137−138.5. Note that each of these ranges contains one of the cis-1 signals for $C_{120}O$. Thus, we conclude that in $C_{120}O_2$(**A**) one of the cis-1 bonds between sp^2 carbons is missing and has been replaced by an epoxy group. We rule out the high-energy cis-2 isomers of **A** because (a) eight pairs of carbon resonances associated with cis-1 bonds would be present and (b) in this case the cis-1 bond adjacent to the epoxy group has a calculated charge difference of ca. −0.070, which should result in an even larger shift difference than expected for the cis-1 isomers of **A**.

Finally, we have examined this empirical correlation between shift difference and charge difference graphically in Figure 9. For $C_{60}O$, C_{120}, and $C_{120}O$ the assignment of the outlying carbon resonances to the cis-1 bonds is, in our opinion, reasonably secure. We assume that the syn bond in $C_{120}O$, with the larger charge difference, corresponds to the most outward-lying pair of resonances (largest possible shift difference) and that the anti bond gives the next inward-lying pair of signals. Similarly, we include two data points for $C_{120}O_2$(**B**), which has two cis-1 bonds adjacent to each furanoid bridge. If we take the fullerene oxides ($C_{60}O$, $C_{120}O$, $C_{120}O_2$(**B**)) as reference compounds, a linear regression ($y = mx + b$) applied to their data gives $m = -521 \pm 44$ and $b = -7.7 \pm 1.6$ ($r^2 = 0.978$). The data point for C_{120} (no oxygen in the bridge) deviates somewhat from this regression line. We have also included in Figure 9 five data points for the major isomer of $C_{120}O_2$(**A**), whereby the five largest carbon shift differences (pairs of resonances labeled 1−5 in Figure 3A) have been simply assigned in numerical order to the five largest charge differences calculated for cis-1 bonds. When the AM1 charge differences for the syn configuration are used, these data points (shaded squares) fit quite well to the reference regression line. On the other hand, when the shift data for the major isomer are plotted vs charge data for the anti configuration (data points ×), a poorer correlation is obtained. Finally, shift differences for the putative cis-1 resonances of the minor isomer (peaks labeled * in Figure 4) vs charge differences for the anti isomer (data points +) also fall close to the regression line. This analysis of sp^2 chemical shifts provides

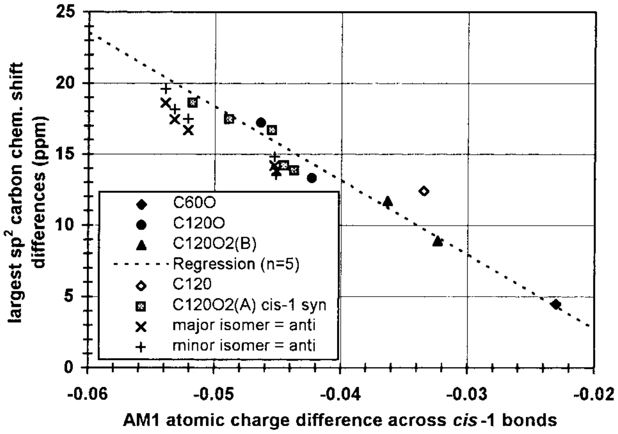


Figure 9. Empirical correlation of the largest possible ^{13}C NMR chemical shift differences between sp^2 resonances (for the most outward-lying pairs of high- and low-field-shifted signals) vs the Mulliken atomic charge differences across the most highly polarized cis-1 double bonds (see text for details). The dashed regression line is for the five reference data points for $C_{60}O$, $C_{120}O$, and $C_{120}O_2$(**B**) ($r^2 = 0.978$, $F = 136.8$, $p = 0.0013$). For $C_{120}O_2$(**A**) the shift differences derived from the pairs of signals labeled 1−5 in Figures 3 and 4 were used and showed better agreement with the regression line when correlated with the five largest charge differences in the cis-1 syn isomer (shaded squares) and less agreement when the largest charge differences in the anti isomer were used (×). The correlation of the largest shift differences for the minor isomer with anti charge differences is also shown (+).

further support for a cis-1 syn structure for the major isomer of $C_{120}O_2$(**A**) and is consistent with an anti configuration for the minor isomer.

We are further pursuing this somewhat novel charge-vs-shift approach for analyzing the ^{13}C NMR spectra of fullerene derivatives. For example, we find that the cis-1, cis-2, and trans-4 isomers of $C_{60}O_2$, whose C_s symmetry is consistent with the NMR spectrum presented by Balch et al.,[12] can be unequivocally distinguished by their unique patterns of charge distribution in the [6,6] double bonds. On the basis of our correlation method, only the pattern for cis-1 is consistent with the NMR spectrum, and this isomer was confirmed by X-ray structure analysis.[12]

Summary

We have characterized two dimeric [60]-fullerene oxide products with the formula $C_{120}O_2$. Product **A** is formed along with $C_{120}O$ at 200 °C in $C_{60}/C_{60}O/C_{60}O_2$ mixtures, while **B** is produced during the thermolysis of $C_{120}O$ at $T > 300$ °C. Both compounds can be formed, for example, by the reaction of two $C_{60}O$ molecules via the [3 + 2] cycloaddition of an epoxy group of one cage across a cis-1 double bond next to the epoxy group in the second cage. For **A** one such cycloaddition gives one furanoid bridge linking C_{60} and $C_{60}O$ cages with two possible orientations of the bridging oxygen (syn and anti) relative to the remaining epoxy group. ^{13}C NMR detected two isomers with C_1 symmetry in product **A**, in 4:1 ratio, and the NMR data together with molecular modeling results provide strong evidence for cis-1 syn as the major and lowest-energy isomer. The minor isomer could not be characterized completely by NMR, but the data at hand are consistent with the cis-1 anti structure. The other possible isomers of **A** (cis, e, and trans forms) can be formed with very similar energies, but apparently the remaining sterically accessible epoxy group reacts with a neighboring C_{60} molecule to give trimeric $C_{180}O_2$, of which three HPLC fractions have been detected but only characterized by MS.

At higher temperatures the unique and more stable product **B** is formed by a double cycloaddition to give two furanoid bridges containing [6,6] junctions in cis-1 configuration. In addition, these bridges are fused to a cyclobutane bridge with [5,6] junctions. This structure has C_{2v} symmetry, confirmed by ^{13}C NMR, and has the lowest energy of all possible structures containing two furanoid bridges. Raman spectroscopy was also found to be quite useful for characterizing the different bridging configurations for **A** and **B**.

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