Structure and Properties of the Fullerene Dimer C_{140} Produced by Pressure Treatment of C_{70}

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A [2+2] cycloaddition cap-to-cap C₇₀ dimer with C_{2h} molecular symmetry was synthesized in high yield by pressure treatment of polycrystalline C₇₀ at 1 GPa and 200 °C. It was separated from unreacted monomers by chromatography and characterized by ¹³C NMR, Raman, and infrared spectroscopy, and other methods. Remarkably, only one isomer was produced out of the five possible [2+2] cycloaddition products which have equally low formation energies according to semiempirical modeling calculations. The dimer obtained is the one favored when C₇₀ molecules adopt an ordered packing with parallel D_5 axes. The intercage bonding in C₁₄₀, its thermal stability, and intercage vibrational modes are similar to those found for the C₆₀ dimer, C₁₂₀. Both dimers photodissociate to the monomers in solution, probably via excited triplet states. The UV absorption and fluorescence properties of C₁₄₀ are not very different from those of C₇₀, suggesting only weak electronic interactions between the two cages of C₁₄₀. In comparison, the pressure-induced dimerization of C₆₀, under the conditions used for C₇₀, results mainly in C₆₀ oligomers and polymeric chains, but the dimer C₁₂₀ could be isolated at low yield when short reaction times (≤ 5 min) were used.

1. Introduction

In recent years a large amount of data¹ have been collected on polymeric C₆₀ phases obtained by applying high pressure and temperature²⁻⁴ or by irradiation with UV-visible light.^{5,6} The polymerization reaction can be described formally as a [2+2] cycloaddition across parallel double bonds (hexagon-tohexagon junctions) in neighboring C_{60} cages. At a relatively moderate pressure of about 1 GPa and a temperature of 300 °C, linear chains of C₆₀ molecules are formed,^{7,8} whereas the application of higher pressure and temperature produces twodimensional networks of bonded molecules.⁹ The polymeric structures are metastable at ambient pressure, reverting at elevated temperature (~ 200 °C) to monomeric C₆₀. The dimer C₁₂₀ has been proposed as an initial intermediate in the polymerization process.¹⁰ This "shortest-chain polymer" was recently synthesized in a mechanochemical reaction¹¹ and by applying pressure to C_{60} -[bis(ethylenedithio)tetrathiafulvalene]₂ crystals.¹² According to vibrational spectroscopy, C₁₂₀ is also formed in significant yields by light irradiation of pure C_{60} at 100 °C,⁶ and by a fast pressure treatment.¹⁰

In principle, polymerization by cycloaddition across reactive double bonds is also possible for C_{70} and other fullerenes. Up to now, only a few studies concerning the polymerization of C_{70} have appeared, in part with controversial results. Rao et

al.13 observed insolubility of C70 films after long irradiation with visible/UV light, but no changes in their vibrational spectra. The first attempt to polymerize C_{70} under pressure (at pressures of 5 and 7.5 GPa and temperatures up to 1100 K) uncovered no Raman signatures of polymerization.14 However, later, Iwasa et al.¹⁵ and Premila et al.¹⁶ reported IR and X-ray diffraction spectra¹⁵ showing strong structural changes in solid C₇₀ after treatment at 5 GPa and 200-300 °C and at 1-7.5 GPa and 750 °C, respectively. Similar to C_{60} polymers, these materials reverted to C70 by heating at ambient pressure. However, the nature of the putative polymeric structures generated in these studies remained unclear. After treating C₇₀ at very high pressures and temperatures (up to 12.5 GPa and 1500 °C), Blank et al.¹⁷ found new super-hard phases and tentatively assigned them to three-dimensionally polymerized C70 and to a disordered carbon state. Considering the treatment conditions used in these previous studies, one might conclude that polymerization of C₇₀, in comparison with that of C₆₀, is very inefficient at moderate pressures and temperatures. However, Soldatov et al. recently showed that C_{70} readily polymerizes similarly to C_{60} at pressures and temperatures as low as 1 GPa and 200-300 °C.¹⁸ A comparison of the corresponding Raman spectra with those obtained from C₁₂₀ and C₆₀ polymers indicated that two predominant structures are formed, depending on the applied pressure: C₇₀ dimers at pressure around 1 GPa and C₇₀ chains at 2 GPa.¹⁸ The latter hypothesis has very recently been supported by X-ray crystal analysis.¹⁹

It has been shown that C_{120} and other dimeric fullerenes, e.g., $C_{120}O$, $C_{120}O_2$, and $C_{130}O$, are soluble, in particular in *o*-dichlorobenzene, and can be separated by chromatography.^{11,20–22} Our hypothesis was that the same approach could be applied to

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Figure 1. HPLC chromatogram of an *o*-dichlorobenzene solution of polycrystalline C_{70} treated at ~1 GPa and 200 °C (Cosmosil Buckyprep column, elution with toluene, optical detection at 330 nm).

 C_{140} as well. As described in this work, we have indeed succeeded in dissolving and separating C_{140} from polycrystalline C_{70} following treatment at ca. 1 GPa and ca. 200 °C. Thus, we provide unambiguous proof for the formation of C_{140} at high pressure, and, perhaps more remarkable, we demonstrate that only a single isomer is obtained.

2. Experimental Details

2.1. Pressure Synthesis of C₁₄₀. A simple piston-cylinder pressure cell (6 mm diameter) made of hardened steel was used for the synthesis. About 50 mg of polycrystalline C₇₀ powder (chromatographically purified in our lab to a level of >99%) was loaded into the cell and compacted by applying 0.1-0.2 GPa pressure with a hand press. Loading and compaction were carried out in an argon glovebox to minimize the possible oxidation of C₇₀. After loading, the cell was transferred to a laboratory hydraulic press in which 1 GPa pressure was applied while the temperature of the cell was increased to 200 °C and held for 30 min. Subsequently, the cell was cooled to room temperature within about 10 min, and the pressure was then released.

The resulting material was dissolved in o-dichlorobenzene (ODCB) with the aid of an ultrasonic bath to a concentration of about 2 mg/mL, with less than 5 wt % remaining as an insoluble residue. According to high-performance liquid chromatography (HPLC, Cosmosil Buckyprep column 20 × 250 mm, elution with toluene at 18 mL/min), the solution contained predominantly unreacted C_{70} and C_{140} (Figure 1). A small shoulder in front of the C140 peak probably was due to a minor C_{140} isomer(s) with a total contribution of about 5%, as estimated from the peak areas. No other peaks were observed up to a retention time >120 min, and no peaks were detected for the oxides $C_{70}O_x$, x = 1-3, which would follow the C_{70} peak. C_{140} was separated from C70 with a yield of 20-30 wt % with respect to the starting material by two-stage flash chromatography on alumina (activity I) using chloroform and ODCB to elute C₇₀ and C_{140} , respectively. Powder samples of C_{140} (purity >95%; the main impurity was C_{70}) were prepared by evaporating the solvent and drying the residue under a vacuum.

2.2. Preparation of Other Dimeric Fullerenes. Pressure Synthesis of C_{120} . The C_{60} dimer, C_{120} , and the dimeric oxides $C_{120}O$ and $C_{120}O_2$ were used for comparative studies. They were prepared as described in refs 11, 20, and 21, respectively. C_{120} was also prepared for the first time using the conditions applied to C_{70} , i.e., C_{60} powder was subjected to pressure and temperature of ca. 1 GPa and 200–220 °C for just a few minutes, followed by ultrasonic extraction with ODCB and chromatographic separation on alumina. A short treatment time appears to be crucial. The largest yields were obtained in the following manner. The pressure was initially set to 0.2 GPa, and the cell

was heated to the desired temperature. Then, the pressure was increased to ca. 1 GPa within seconds; after about 1 min, the cell was quickly cooled (initial cooling rate ca. 20 °C/min) and the pressure released. The product comprised 15-20% unreacted C₆₀, ca. 3 wt % of extracted C₁₂₀, and an insoluble residue of higher C_{60} oligomers and polymeric chains (see Discussion). Longer treatment resulted in a decrease in the yield of C_{120} and an increase in the insoluble portion. The dimerization/polymerization of C_{60} under the above conditions appears to be strongly promoted by interstitial gases in the starting material. The pressure synthesis of C120 was successful with a C60 powder sample that had been stored for a long period of time under air or nitrogen. With a powder that had been freshly annealed at 250 °C in 10⁻⁶ mbar vacuum, practically no dimerization/ polymerization of C₆₀ was observed. The FT-Raman, IR, and UV-visible absorption spectra obtained from C₁₂₀ extracted from the pressure-polymerized C₆₀ were equivalent to those obtained from C₁₂₀ obtained by a mechanochemical reaction.¹¹ The purity of the dimeric derivatives was estimated by HPLC and Raman spectroscopy to be >95%.

2.3. Spectroscopy. For ¹³C NMR, a saturated solution (ODCB) of C_{140} (ca. 0.5 mg) enriched to ca. 7% in ¹³C was prepared in a 5-mm NMR tube. Nondeuterated ODCB (0.2 mL) contained ca. 16 mM Cr(acac)₃ for paramagnetic relaxation enhancement. The spectrum was acquired at 125.76 MHz and 30 °C with a Bruker AM-500 FT-NMR spectrometer using a J-modulated spin-echo method for suppression of solvent CH carbons, as described in detail previously.23 A 2-mm capillary with acetone- d_6 provided a deuterium lock signal. Data acquisition parameters were as follows: spectral width $= 25\ 000\ Hz$; 90° pulse = 7.7 μ s; half echo time delay = 3.05 ms; relaxation delay = 1.9 s, acquisition time = 0.655 s for 32 K data points; repetition time = 2.56 s. Successive blocks of 20 000 transients (14.2 h) were stored separately. Identical conditions were used to acquire a control spectrum of the ODCB + $Cr(acac)_3$ solvent. Data processing was performed using Bruker's WIN NMR software. A total of eight data blocks (114 h) were added for the C_{140} spectrum, and six blocks (85 h) were added for the solvent-control spectrum. As shown in Figure 2, the sp² carbon region was analyzed using a Lorentz-Gauss line shape transformation for resolution enhancement (Bruker parameters: LB = -2.5 Hz, GB = 20%) and zero-filling to 64K, while the sp³ region was examined with sensitivity enhancement (LB = 2.5Hz). Chemical shifts were calibrated relative to the C1 carbon of ODCB at 132.53 ppm, which gives a C_{60} shift of 142.83 ppm. The C₁₄₀ and solvent spectra were baseline-corrected and compared via a dual display routine, and the difference spectrum was computed. In this way all signals from solvent, impurities, and intermodulation distortion artifacts could be clearly identified. With the acquisition conditions used, the sp² signals gave relatively uniform intensities (integrals) per carbon atom, whereas the sp³ carbon signals were significantly reduced, presumably because of a longer T_1 at these sites.

IR and Raman spectra were obtained with a resolution of 2 cm⁻¹ from powder samples (pressed in pellets with 3-mm diameter for the far-IR or embedded in KBr pellets for the mid-IR measurements) on a Bruker Equinox 55S spectrometer equipped with a FRA106 FT-Raman module and an Nd:YAG laser for excitation at 1064 nm. No decomposition of C₁₄₀ due to the intense irradiation (~10 W/cm²) at 1064 nm was detected. The presented Raman spectra are corrected for luminescence background, but not for the wavelength-dependent spectrometer response.



Figure 2. 125.76 MHz ¹³C NMR spectrum of a saturated solution of C_{140} (enriched to ca. 7% in ¹³C) in ODCB + Cr(acac)₃. The sp² region (signals 1–35) is shown with resolution enhancement, the sp³ region (signals 36,37) with sensitivity enhancement. The labels p1–p5 mark the positions expected for the five signals of D_{5h} C₇₀ with respective carbon counts of 10, 10, 20, 20, 10. The solvent ODCB gives three large offscale resonances with corresponding ¹³C satellites, whereby the residual signals from solvent CH groups are out of phase because of the suppression technique used (see Experimental Details). The signals marked "a" (artifacts) were detected in a control spectrum obtained from the solvent alone.

Matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) time-of-flight (TOF) mass spectrometry were performed on home-built instruments.^{24,25} A pulsed N₂ laser for desorption/ionization and 9-nitroantracene as a matrix were used for MALDI. For ESI, a solution of C₁₄₀ in ODCB was sprayed with nitrogen as a nebulizing and drying gas in an Analytica ESI source.

UV-vis absorption spectra were measured on a Hitachi U-2000 spectrometer. Fluorescence emission and excitation spectra were recorded on a Spex Fluorolog-3 spectrometer (450 W xenon lamp, R928 photomultiplier tube) and were corrected for the wavelength-dependent instrumental response. The photomultiplier tube operated up to ca. 850 nm, and the emission correction was found to be reliable up to ca. 800 nm. The fluorescence of C_{70} extends into the near-infrared up to ca. 1000 nm,²⁶ and the fluorescence of C_{140} apparently does the same (Figure 7); therefore, the presented emission spectra can serve for qualitative comparisons between C_{140} and C_{70} .

2.4. Photodissociation Quantum Yield. We found that in ambient room light, C_{140} and C_{120} in dilute solutions undergo photodissociation to C_{70} and C_{60} , respectively. To estimate the quantum yield of photodissociation, φ_{PD} , i.e., the ratio of dissociated molecules to photons absorbed, dilute solutions in ODCB were irradiated at 514 nm with an Ar–ion laser and subsequently analyzed by HPLC calibrated for C_{70} and C_{60} (see above; elution was with xylene instead of toluene in the case of C_{140}/C_{70} to shorten the retention times). The absolute

irradiation laser intensity was measured using a Coherent 200 power meter. The values of $\varphi_{\rm PD}$ at other wavelengths were estimated relative to $\varphi_{\rm PD}$ at 514 nm by irradiating the solutions in the Spex Fluorolog-3 spectrometer. To determine the effect of dissolved oxygen, the solutions were irradiated either in air or under anaerobic conditions after careful degassing in a vacuum. The estimated error in the determination of $\varphi_{\rm PD}$ is $\pm 30\%$. All measurements, if not stated otherwise, were performed at room temperature.

3. Results

Our pressure treatment of polycrystalline C_{70} at ~ 1 GPa and 200-220 °C resulted in \sim 30-50% conversion of C₇₀ into dimers, according to the Raman, IR, and HPLC analysis. The rest of the material consisted mainly of unreacted C70. A small portion (<5 wt %), insoluble in ODCB, is tentatively attributed to higher C₇₀ oligomers. The reaction yield did not depend strongly on the treatment time, which was varied from several minutes to several hours. However, the yield of C₁₄₀ decreased dramatically when the applied pressure and temperature were lower than 0.8 GPa and 180 °C, respectively. The 30-50% conversion of C₇₀ achieved in this study is less than the ca. 80% conversion estimated in a previous study,¹⁸ where similar pressure and temperature were applied. It is conceivable that the lower efficiency was due to a relatively inhomogeneous distribution of the pressure in our simple pressure cell. On the other hand, residual C₇₀ molecules may help the dissolution of the material, acting as "spacers" between the less soluble dimer molecules.

3.1. Chromatography. The HPLC shows, essentially, a single product peak at a retention time of 43 min and a peak of unreacted C_{70} at 14 min (Figure 1). Under similar conditions, the retention times for C_{60} and C_{120} are 8 and 15 min, and for the dimeric oxides $C_{120}O$ and $C_{120}O_2$, ca. 15 and 16.5 min, respectively. However, the elution of the heterodimeric oxide $C_{130}O$ containing both C_{60} and C_{70} cages is retarded to ~30 min.²² This trend suggests that the peak at 43 min is a C_{70} dimer and not a trimer.

3.2. Mass Spectrometry. Only an ion peak of C_{70} at m/z 840 could be observed in the negative and positive MALDI– TOF and in the negative ESI–TOF mass spectra of C_{140} . Evidently, there is complete dissociation of the dimer molecules/ ions under the MS conditions. The same problem was encountered for C_{120} .¹¹ On the other hand, the dimeric fullerene oxides C_{120} O, C_{120} O₂, and C_{130} O, with stronger cage-to-cage furanoid links readily yield dominant parent ion peaks in the negative MALDI–TOF mass spectra.^{20–22}

3.3. ¹³C NMR Measurements. C₁₄₀ is only poorly soluble in ODCB, but is even less so in CS2 or other solvents. Therefore, a saturated solution of C_{140} (enriched to ca. 7% in ¹³C) in ODCB was used for the NMR measurements. The ¹³C NMR spectrum of C₁₄₀ is shown in Figure 2; the 37 assigned resonances are numbered and listed in Table 1. Only one (dominant) C140 isomer was found. Based on the S/N in the spectrum, if another isomer were present, its mole fraction would have to be less than $\sim (2 \times 10^{-3}) n$ (where *n* is the number of symmetry-related carbon sites). The only impurity detected could be assigned to C_{70} , which has five nonequivalent carbon sites, denoted as 1-5in Figure 3. These sites lie on planes perpendicular to the long axis of the "rugby ball" cage and are expected to give five ¹³C NMR signals in the ratio 1:1:2:2:1 at the positions labeled p1p5 in Figure 2.27 Resolved resonances for p1-p4 were detected (Table 1), although the signal for p5 could not be observed because of interference from the residual C3,6 signal from

TABLE 1: ¹³C NMR Data for C_{140} in *o*-Dichlorobenzene at 30 °C^{*a*}

peak nr	ppm	integral	peak nr	ppm	integral
1	155.733	4.06	19,20	146.821	5.90
2	152.224	4.01	21	145.882	3.63
3	151.519	3.85	22	145.810	4.44
4	151.267	2.20	p4	145.001	2.45
5	151.201	5.05	23	143.644	4.17
6	150.865	3.83	24	143.434	4.27
7	150.732	3.90	25	143.288	4.62
8	150.494	5.04	26	142.914	3.93
9	150.326	3.30	27	142.809	3.88
p1	150.291	1.52	28	141.868	4.00
10	150.218	4.27	29	140.523	4.02
11	149.718	4.23	30	140.280	3.95
12	149.313	4.53	31	134.281	3.58
13	148.978	4.93	32	133.355	6.11^{b}
14	148.637	3.63	ODCB(1,2)	132.530	
15	148.518	4.24	33	131.766	3.50
р3	147.750	3.07	34	131.105	3.90
16	147.468	4.27	35	130.978	3.86
17	147.263	4.19	p5	(130.5)	nd
p2	147.047	2.18	36	71.177	0.93 ^c
18	146.973	4.33	37	67.826	1.51^{c}

^{*a*} Chemical shifts were calibrated relative to ODCB(1,2) = 132.53, which corresponds to TMS = 0 and C₆₀ = 142.83 ppm. Peak integrals are relative to peak nr 28, defined as 4.00. For sp² carbons, 33 signals represent 4 carbons each, while signals nr 4 and 19,20 (in boldface) represent 2 and 4+2 carbons, respectively. The signals labeled p1-p5 (italic) are from C₇₀; the expected chemical shifts²⁷ are 150.33, 147.03, 147.73, 145.03, and 130.53 (in benzene-*d*₆, corrected to C₆₀ = 142.83 ppm). ^{*b*} This integral contains a contribution from a solvent artifact signal. ^{*c*} The observed integrals are less than expected (2.0) due to partial saturation of sp³ carbons under our measurement conditions.



Figure 3. Structure of the D_{5h} C_{70} cage showing the labeling scheme used to define sites in C_{70} dimers. There are five basic nonequivalent carbon types in C_{70} representing "lines of latitude" from "pole" (or cap) to "equator" in the "northern hemisphere" (1–5) and the corresponding sites in the "southern hemisphere" (1–4'). The numbering follows a zigzag course about a reference "line of longitude". The letters a, b, c, etc., are used to distinguish sites at a given latitude moving from west to east. We define dimer configurations in terms of bridges between northern hemispheres so that numbers with primes denote sites in the opposite hemisphere remote from the bridging site.

ODCB. Based on the signal integrals, the sample contains C_{70} and C_{140} in a molar ratio of ca. 0.15:1.0, i.e., about 7% of the C_{70} cages were present as monomers.

The five C_{140} isomers of lowest energy (see Discussion) are shown in Figure 4. The nomenclature used here is (a,b)/(c,d) C_{140} to denote a dimer having a-b and c-d intracage bonds and a-c and b-d intercage bridging bonds, where a, b, c, and d are the corresponding carbon sites on the C_{70} cages. In each cage of (1,2)/(2,1) C_{2h} C_{140} (structure I in Figure 4), there are four different carbons on the σ_h symmetry plane: the (1,2) sp³ carbons in the bridge and two sp² carbons from the corresponding 1', 2' sites remote from the bridge. Altogether, there are 66 sp² carbons that are not on the σ_h symmetry plane, and these form 33 pairs of distinguishable sp² sites in each cage. Therefore, for isomer I we expect 33 sp² signals with intensity 4C, two



Figure 4. PM3-optimized geometries for the five energetically favorable C_{70} dimers. The nomenclature is defined in the text and in Figure 3. Dimer I [(1,2)/(1,2) $C_{2h} C_{140}$] is produced by the pressure treatment of solid C_{70} at ~1 GPa and ~200 °C.



Figure 5. FT-IR absorption spectra of C_{70} (top) and its dimer C_{140} (bottom). The scaling of the absorption in the far-IR region to that in the mid-IR region is only approximate.

sp² signals with intensity 2C, and two sp³ signals with intensity 2C. The closely related isomer II, denoted (1,2)/(1,2) $C_{2\nu}$ C₁₄₀ (Figure 4), has the same pattern of distinguishable carbon sites. Thus, the observed NMR spectrum is consistent with either of these isomers. Note that the equatorial carbons p5 are unique in C70 and exhibit a large upfield shift compared to the other sites. Thus, for the dimer one expects 30 signals distributed around the positions p1-p4 and five signals with intensity 4C near the position for p5. In Figure 2, the signals 31-35 have been assigned to the five p5 sites after detailed comparison with the ODCB control spectrum in which the impurity/artifact signals at the positions labeled "a" could be identified. The two sp² signals numbered "4" and "20" with intensity 2C are expected to represent carbons of types p1 and p2, which are remote from the bridge and little perturbed by it; their chemical shifts are in fact close to the values for p1 and p2 in C70.

In (3,3a)/(3,3a) $C_{2h} C_{140}$ and (3,3a)/(3a,3) $C_{2\nu} C_{140}$ (structures III and IV, respectively, in Figure 4), the symmetry plane is perpendicular to and bisects the bridge plane. The four bridging carbons are equivalent and would give one sp³ signal of intensity 4C. Two sp² carbons of types p1 and p2 (proximal to the bridge) and two of types p1' and p2' (distal to the bridge) are on the symmetry plane and would give four signals of intensity 2C, whereas the remaining 32 sp² signals would have intensity 4C. This is clearly not consistent with the observed NMR spectrum. Finally, the (1,2)/(3,3a) $C_1 C_{140}$ isomer (structure V) can be ruled out because it has no equivalent carbons and would give four sp³ signals and 136 sp² signals.

3.4. Vibrational Spectroscopy. Figures 5 and 6 show FT-IR and FT-Raman spectra of C_{140} and C_{70} . A typical FT-Raman pattern of a C_{70} powder sample after the treatment at ca. 1 GPa and 200 °C is presented in Figure 6. This pattern and its IR counterpart (not shown) are essentially superpositions of the corresponding spectra of C_{70} and C_{140} . As usual for fullerene derivatives with weakly disturbed fullerene cages,^{28a} C_{140} demonstrates peaks in the same regions as C_{70} , but with splittings and shifts due to the reduced molecular symmetry and weak vibrational interactions between the covalently bonded C_{70} cages. For instance, this results in the appearance of



Figure 6. FT-Raman spectra, obtained with Nd:YAG laser excitation at 1064 nm, from a sample of C_{70} before (top) and after (middle) treatment at ca. 1 GPa and 200 °C and from the purified dimer C_{140} (bottom).



Figure 7. Electronic absorption and fluorescence (FL) spectra of C_{70} (bottom) and its dimer C_{140} (top) in ODCB. The absorption spectra were measured with 10 μ M solutions. The FL emission spectra (450-nm excitation) were obtained with solutions with optical density 0.2. The FL excitation spectrum (dotted line, shifted for clarity) was obtained with a 1 μ M solution of C_{140} .

originally silent modes or an increase in weak modes in the far-IR spectrum (Figure 5).

Compared to C70, new low-frequency Raman peaks appear in the spectrum of C_{140} at 89, 118, and 129 cm⁻¹. The peaks are attributed to intercage vibrational modes where the heavy fullerene cages move more or less as rigid units. Six such modes, which originate from the coupled translational and rotational motions of the two cages, are a common feature for the dimeric fullerene molecules and have been studied in detail, both experimentally and theoretically.^{22,29-32} The frequencies and relative spectral intensities of these modes depend on the exact nature of the bridge between two fullerene cages. The C₆₀ dimer C_{120} (D_{2h} molecular symmetry) exhibits three Raman-active intercage modes³² at 96 (the strongest peak due to the stretchinglike vibration), 127, and 139 cm⁻¹ (Figure 8). Three further intercage modes of C120 (two IR-active and one silent) are expected below 50 cm⁻¹. The corresponding three remaining vibrations in C₁₄₀ should also appear at very low frequencies, and are therefore inaccessible in our measurements (see Discussion). Note that the relative peak intensities of the intercage vibrations in the Raman spectra of C₁₄₀ and C₁₂₀ are similar (Figures 6 and 8), and that their respective frequencies ν (89,



Figure 8. FT-Raman spectra obtained from C_{60} (top), its dimer C_{120} (bottom), and samples of C_{60} after treatment for a few minutes ("short") and for 1 h ("long") at ca. 1 GPa and 220 °C.

118, and 129 for C_{140} vs 96, 127, and 139 cm⁻¹ for C_{120}) are proportional to $M^{-1/2}$, where *M* is the cage mass, as expected in the harmonic oscillator approximation. This indicates that both dimers have the same type of the intercage bonding.

As for C_{120} ,³² we observed slight differences in the vibrational spectra of different samples of C_{140} , which may be attributed to differences in local molecular orientations and intermolecular interactions in those samples. For instance, we observed a shift of the stretching-like intercage vibration, to 87 cm⁻¹, in the Raman spectrum of a well-crystallized C_{140} powder that probably contained a substantial number of interstitial solvent molecules.

3.5. Electronic Absorption and Fluorescence. The light absorption spectrum of C_{140} resembles that of C_{70} (Figure 7), but the bands are broadened and shifted, and the onset is at a longer wavelength (ca. 690 nm) compared to C₇₀ (ca. 640 nm). This difference can be attributed to the reduced molecular symmetry and a smaller HOMO-LUMO gap for the dimer.¹³ The molar absorptivity of C_{140} is larger than that of C_{70} by approximately a factor of 2 (Figure 7). Both the monomer³³ and the dimer exhibit weak fluorescence (FL) which is somewhat red-shifted and structureless for the dimer (Figure 7). The FL yield of C_{70} is 5.9 \times 10⁻⁴ in toluene, not very different in other solvents and independent of the excitation wavelength.33 Using a solution of C70 in toluene as a reference, approximately the same FL yield was estimated for C₇₀ in ODCB. The FL yield of the dimer is about a factor of 2 higher in ODCB (Figure 7). It is interesting to note that the FL yield of C_{120} in different solvents is also larger than that of C_{60} by a factor of $3.^{34}$ The FL spectrum of C_{140} is essentially independent of the excitation wavelength (320-650 nm) and practically the same in ODCB, 1-methylnaphthalene, and CS₂. The above similarities between C₁₄₀ and C₇₀ suggest that there is only moderate perturbation of the ground and excited electronic states in C₇₀ upon dimerization.

3.6. Photodissociation. A characteristic process involving excited electronic states was observed for C₁₄₀, namely its photodissociation (PD) to C₇₀ upon irradiation in the range of 400–600 nm. The quantum yield of PD, φ_{PD} , is quite low: 5 × 10⁻⁵ for a 10 μ M solution of C₁₄₀ in ODCB. It does not

depend significantly on the irradiation wavelength in the range probed, indicating that PD occurs from a low-lying excited state. Dissolved oxygen strongly reduces φ_{PD} , which increased to ca. $2-3 \times 10^{-3}$ when the C₁₄₀ solution was degassed. This result suggests that C₁₄₀ dissociates via the excited triplet state. Assuming that the latter is quenched to the ground state in about 1 μ s by dissolved oxygen (ca. 1 mM in air-saturated aromatic solvents³⁵) at the diffusion-limited rate constant of ca. 10⁹ M⁻¹s⁻¹, one can estimate from the increase in φ_{PD} for degassed solutions that the intrinsic lifetime of a triplet state of C₁₄₀ in ODCB is about 50 μ s. For comparison, the intrinsic lifetime of a triplet state of C₇₀ is \geq 12 ms in toluene.³⁶ Despite the low value of φ_{PD} in air, prolonged photolysis or exposure of C₁₄₀ solutions to daylight resulted in complete dissociation of the dimer to C₇₀ (confirmed by HPLC).

An interesting question is whether the other dimeric fullerenes are light-sensitive. In disagreement with a previous report about the photochemical stability of C_{120} ,³⁴ we found that the C_{60} dimer also photodissociates to monomeric C_{60} with approximately the same quantum efficiency as C_{140} when irradiated at 400 nm. The φ_{PD} values of 6×10^{-5} and 7×10^{-4} were estimated for, respectively, air-saturated and degassed C_{120} solutions in ODCB (ca. 5 μ M). The decrease in φ_{PD} upon admittance of air likely is due to the same triplet-quenching mechanism proposed for C_{140} . The estimated intrinsic lifetime for the triplet state of C_{120} in ODCB is about 10 μ s. This agrees well with the triplet-state lifetime for C_{120} in toluene of ≥ 10 μ s, as obtained from transient absorption measurements.³⁴ For comparison, a significantly longer lifetime of 133 μ s has been reported for the triplet state of C_{60} in toluene.³⁷

In contrast to C_{140} and C_{120} , we found no HPLC or spectroscopic evidence for the photodecomposition of the dimeric fullerene oxides $C_{120}O$ and $C_{120}O_2$ over the 400–600 nm range.

3.7. Thermal Stability. In general, fullerene polymers revert back to the monomeric state at ambient pressure and elevated temperature, and, as expected, C_{140} decomposes thermally to C_{70} . A detailed study of the depolymerization kinetics for different polymeric C_{70} materials will be published elsewhere.^{18,38} Here we only wish to emphasize that C_{140} and C_{120} show similar behavior. For example, a powder sample of C_{140} (in KBr pellet) decomposes by first-order kinetics with $\tau = 65 \pm 5$ min at 150 °C, as determined from intensity changes of the characteristic IR bands of C_{140} and C_{70} . At the same temperature, C_{120} decomposes in the solid state to C_{60} by first-order kinetics with $\tau = 43$ min, according to dilatometric measurements.³⁸

4. Discussion

4.1. Structure of C₁₄₀. Our ¹³C NMR, Raman, HPLC, and other results show that the main product of the pressure–temperature treatment of solid C₇₀ at 1 GPa and 200 °C is the dimer C₁₄₀. It is reasonable to expect that C₁₄₀ is formed by a [2+2] cycloaddition across double bonds to give a fourmembered ring as a cage-to-cage bridging unit, in complete analogy with the reaction of C₆₀ to form C₁₂₀ and polymeric C₆₀.³⁹ Indeed, remarkable similarities are observed in those properties of C₁₄₀ and C₁₂₀ that are primarily determined by the nature of the intercage bonding. In particular, the photoand thermal dissociation properties and intercage vibrational modes in the Raman spectra are similar for the two dimers.

In I_h C₆₀, there are only two types of bonds, generally represented as "single" and "double" bonds in modeled structures.^{28b} Each bond serves as the junction between two

 TABLE 2: Semi-Empirical Modeling (PM3) of C₇₀ Dimers

 Formed by [2+2] Cycloaddition Containing a Cyclobutane

 Intercage Bridge

C ₁₄₀ isomer ^a	symmetry	relative energy ^b (kJ/mol)	bridge bond lengths ^c inter-/intracage (Å)
(1,2)/(2,1)	C_{2h}	0	1.547/1.601
(1,2)/(1,2)	C_{2v}	0.0	1.547/1.601
(3,3a)/(3,3a)	C_{2h}	-0.5	1.555/1.578
(3,3a)/(3a,3)	C_{2v}	-0.3	1.554/1.579
(1,2)/(3,3a)	C_1	-0.2	1.551;1.551/1.600;1.579
(1,2)/(3a,3)			
(3,3a)/(4,5)	C_1	73	1.553;1.563/1.576;1.610
(3a,3)/(4,5)			
(4,4i)/(4,4i)	C_{2h}	74	1.561/1.636
(1,2)/(5,5a)	$C_{\rm s}$	93	1.555;1.554/1.592;1.692
(1,2)/(5a,5)			
(2,3)/(3,2)	C_2	160	1.549/1.630
(5,5a)/(5,5a)	D_{2h}	550	1.523/1.624

^{*a*} The nomenclature is described in the text and in Figure 3; the first five isomers are those depicted in Figure 4; isomers listed as pairs are enantiomers. ^{*b*} Calculated from PM3 heats of formation; the relative energy for two moles of C_{70} is 159 kJ. ^{*c*} For C_{120} , the results are 1.549/ 1.598 Å.

TABLE 3: Bond Types and Lengths in D_{5h} C₇₀

bond	length (Å) (PM3) ^a	code	general type	approx bond order
1-1	1.457	hp-hh	single	1
1 - 2	1.386	hh-pp	double	2
2 - 3	1.453	hp-hh	single	1
3-3	1.374	hĥ-pp	double	2
3 - 4	1.463	hp-hh	single	1
4 - 4	1.426	hp-hh	aromatic	1.5
4 - 5	1.412	hĥ-hp	aromatic	1.5
5 - 5	1.463	hh-hh	single	1

 a The PM3 values of bond lengths in C₇₀ presented here for illustrative purposes are in good agreement with experimental and ab initio theoretical data.^{28b}

rings, hexagon or pentagon (h or p), and connects the vertexes of two other rings. The two types of bonds can be defined in terms of a junction-vertexes letter code, i.e., hp-hh and hh-pp (or simply as hp and hh type) with bond lengths of 1.457 and 1.384 Å, respectively (PM3 calculations). The hh-type double bonds are the reactive centers for C_{60} dimerization, oxidation, and many other reactions.⁴⁰ Thus, for C_{60} there is only one possible [2+2] reaction across *hh*-type bonds, leading to the $D_{2h} C_{120}$ dimer.

The D_{5h} C₇₀ molecule has a total of eight distinguishable C–C bonds^{28b} which can be classified as shown in Table 3. Only two of these, 1-2 and 3-3, are "double" bonds analogous to those in C₆₀, and these sites in the cap region are almost exclusively the ones involved in cycloadditions.⁴⁰ In contrast, the equatorial region contains "single" bonds (3-4 and 5-5)and "aromatic" bonds of intermediate length (4-4 and 4-5); this region is relatively inert to addition reactions, although minor cycloadducts of benzyne across the 4-5 and 4-4 bonds of C70 have been reported.41 Therefore, the number of chemically accessible [2+2] C140 isomers is expected to be limited to those involving 1-2 or 3-3 bonds, i.e., the five structures I-V shown in Figure 4 and Table 2. In agreement with previous semiempirical MNDO results,42 our semiempirical PM3 calculations Gaussian 98W PC software package⁴³) gave essentially equal heats of formation for these five isomers (Table 2). We expanded the calculations to include several other [2+2] C₁₄₀ isomers involving addition across single or aromatic type bonds and obtained substantially higher energies (Table 2). The belt-tobelt (5,5)/(5,5) D_{2h} isomer was found to be the most energetically

unfavorable dimer, with a PM3 energy of +550 kJ/mol relative to I (+940 kJ/mol, according to tight-binding molecular dynamics calculations¹³).

Remarkably, our ¹³C NMR and HPLC results indicate that only one C_{140} isomer (\geq 95%) is produced by the high-pressure synthesis. The NMR spectrum is consistent only with the (1,2)/(2,1) C_{2h} or the (1,2)/(1,2) $C_{2\nu}$ isomer (structures I and II in Figure 4). These two isomers should have the same basic pattern of carbon chemical shifts, with only minor differences in the actual shift values (based on PM3 atomic charges) so that it is not possible to assign structure I or II on an a priori basis. Some of the features of the ¹³C NMR spectrum can be explained on the basis of the PM3 modeling results. The atomic (Mulliken) charges on the bridging sp³ carbons were found to be q = 0.0636and 0.0616 for carbons 1 and 2 in isomer I, 0.0661 and 0.0591 for carbons 1 and 2 in isomer II, and 0.0636 for C₁₂₀. The corresponding chemical shift for C₁₂₀ is 76.22 ppm, which is close to the shifts measured for C_{140} (71.18 and 67.83 ppm). The "center of gravity" for sp2 chemical shifts is shifted downfield in both C₁₄₀ and C₁₂₀, consistent with the negative average charge on sp² carbons. For p5 type carbons in C_{70} , q =+0.0289, and the values for I and II are in the range 0.0232-0.0315; this is consistent with the appearance of NMR signals 31-35 in the relatively narrow range of 131-135 ppm near the position of p5 in C_{70} . On the basis of atomic charge, stronger perturbations occur in the dimer for carbons of types 3 and 4, consistent with the broad range of chemical shifts observed from 140 to 152 ppm. In each cage of C_{140} two sp² carbons of type 1 and two of type 3 are attached to the bridging sp³ carbons, and their charges show the strongest perturbations compared to C_{70} (q = ca. -0.033 vs +0.0052 and -0.029 vs +0.0062, respectively). For C_{120} the corresponding carbons have q =-0.0366, resulting in one isolated resonance at low field (151.43 ppm). For C_{140} there is an analogous isolated resonance at 155.73 ppm (5.5 ppm downfield of the position p1) which can be tentatively assigned to the type 1 sp² carbons attached to the bridge. Similarly, resonance 2 may correspond to the type 3 carbons attached to the bridge (downfield shift of 4.5 ppm compared to p3). Finally, the PM3 calculations predict that the 1' and 2' carbons located on the symmetry plane of the dimer have minor but opposite perturbations in charge (< 0.001 units); this is consistent with the small and opposite shifts in the twocarbon resonances 4 and 20 relative to p1 and p2.

The appearance of a single C_{140} isomer out of the five possible and energetically equivalent structures I-V (equivalent for isolated molecules in a vacuum) must be due to some additional kinetic and/ or energetic constraints imposed in the solid state under high pressure. The situation would be clear if dimerization of C₇₀ were to occur under ambient conditions. Indeed, the general features of the phase diagram of C₇₀ at normal pressure are fairly well understood. There are two orientational ordering transitions in C₇₀ on cooling from the high-temperature facecentered cubic/hexagonal close-packed (fcc/hcp) phase that have freely rotating molecules: the freezing of the tumbling motion at $T_{01} \sim 350$ K and the freezing of the uniaxial rotations of the molecules around their long axes and complete ordering at T_{02} $\sim 280~{
m K}.^{44}$ The intermediate phase is a rhombohedral (rh) or deformed hcp phase, with the long axes of the molecules aligned in parallel along [001] hcp/[111] fcc. In the intermediate and low-temperature phase, short intermolecular contacts between reactive double bonds of C70 are realized only for the (1,2) bonds of neighboring C70 molecules in stacked layers.13,44 The uniaxial rotations of the molecules in the intermediate phase can readily bring these bonds into a parallel orientation, which is favorable for dimerization. Such close and favorable intermolecular contacts are not available for two (3,3) bonds or a (3,3) and (1,2) combination. It was for this reason that Rao et al.¹³ proposed a cap-to-cap (1,2)/(2,1) $C_{2h} C_{140}$ isomer as the single possible dimer in the room-temperature photopolymerization of C_{70} . This unique structure would also be consistent with our results. However, above $T_{01} \sim 350$ K, tumbling rotations of the C_{70} molecules could bring all reactive bonds into reaction contact, and the formation of all five energetically favorable C_{140} isomers would be expected.

The formation of a single C₁₄₀ isomer by high-pressure treatment at ~ 200 °C (470 K) suggests that the orientational ordering favorable for (1,2)/(2,1) bonding is preserved at 1 GPa pressure even at elevated temperatures. Although very little is yet known about the structure and dynamics of C70 under high pressure, this suggestion is consistent with the strong effects of pressure on the orientational phase transitions of C₇₀ observed by Kawamura et al.⁴⁵ and Samara et al.⁴⁶ Despite quantitative discrepancies, their results agree with regard to a large shift of the rh-to-fcc transition temperature under pressure (≥300 K/GPa). This implies that the application of ~ 1 GPa pressure would preserve the orientational ordering in C₇₀ up to much higher temperatures than were applied in this work. According to the data of Soldatov and Sundqvist,47 the molecules rotate uniaxially at p,T conditions of our experiment, i.e., they possess sufficient mobility for the spatial adjustment of (1,2)/(2,1) bonds required for dimerization.

Strong support for the (1,2)/(2,1) C_{2h} C_{140} isomer is also provided by a very recent study of the polymerization of a C_{70} single crystal at 2.0 GPa and 570 K.¹⁹ X-ray diffraction analysis established the formation of "zigzag" chains of C_{70} molecules having the expected (1,2)/(2,1) intermolecular bonding.¹⁹ This result also suggests that the orientational anisotropy and uniaxial rotations favorable for (1,2)/(2,1) bonding can be preserved in pressurized crystalline C_{70} even at 2.0 GPa and at temperatures much higher than $T_{01} \sim 350$ K.

Another approach to isomer assignment involves comparing experimental and theoretical vibrational spectra. This approach is feasible for fullerenes because the van der Waals intermolecular forces in bulk samples are weak and result in relatively small perturbations of the molecular vibrations.^{28a} For example, quantum molecular dynamics simulations of Raman spectra have been successfully applied to isomers of the odd-numbered dimeric fullerene C_{119} .⁴⁸ However, the vibrational modes on the two cages in dimeric fullerenes interact only weakly with each other.³¹ Consequently, very similar in-cage modes are expected for the C_{140} isomers I–V, especially for the closely similar pairs I, II or III, IV.

The intercage vibrations might be expected to be more isomer-specific. In any event, the corresponding Raman spectra are much simpler to analyze in the region below 200 cm⁻¹ than above 200 cm⁻¹, where there is a large and increasing density of the on-cage vibrations. It has been shown that the PM3 method quite accurately predicts the low-frequency vibrations in C₁₂₀ and other dimeric fullerenes.²² Therefore, we have calculated the intercage vibrational frequencies for the PM3optimized C_{140} isomers I-V and (5,5)/(5,5) D_{2h} C_{140} by this method (Table 4). The Raman-active intercage vibrations for (1,2)/(2,1) C_{2h} C₁₄₀ are calculated to occur at 87 (the stretchinglike vibration), 122, and 134 cm⁻¹ and closely match the Raman features observed at 89, 118, and 129 cm⁻¹. The other three intercage modes of this dimer are IR-active and are predicted to occur at 20, 22, and 32 cm⁻¹. However, such low frequencies were inaccessible for our Raman/IR measurements. Unfortu-

TABLE 4: PM3 Modeling of C₁₄₀ Isomers: Calculated Intercage Vibrations

C ₁₄₀ isomer	sym	calculated intercage vibrations (cm ⁻¹)					
(1,2)/(2,1)	C_{2h}	20 (A _u)	22 (A _u)	32 (B _u)	87 (A _g)	123 (B _g)	134 (Ag)
(1,2)/(1,2)	C_{2v}	21 (A ₂)	$22(B_1)$	32 (A ₁)	88 (A ₁)	123 (A ₁)	133 (B ₂)
(1,2)/(3,3a)	C_1	20	22	32	87	120	134
(3,3a)/(3,3a)	C_{2h}	20 (A _u)	22 (A _u)	33 (B _u)	85 (Ag)	$120 (B_g)$	134 (A _g)
(3,3a)/(3a,3)	C_{2v}	20 (A ₂)	$22(B_1)$	33 (A ₁)	88 (A ₁)	117 (A ₁)	134 (B ₂)
(5,5)/(5,5)	D_{2h}	9 (A _u)	$24 (B_{1u})$	$34 (B_{2u})$	88 (A _g)	121 (B _{1g})	127 (B _{2g})

nately, no significant differences were predicted for the intercage vibration frequencies of C_{140} isomers, including the energetically unfavorable (5,5)/(5,5) D_{2h} isomer (Table 3). This probably is due to the closely similar geometries of the four-membered intercage ring in isomers I–V. Thus, for C_{140} an isomer assignment on the basis of calculated intercage vibration frequencies is not possible.

The two NMR-consistent dimers I and II have different symmetries and should, therefore, have different Raman vs IR activities for the intercage modes. For isomer I ,with a center of symmetry in the bridge, the vibrations observed in the Raman spectrum at 89, 118, and 129 cm⁻¹ should be IR-inactive, whereas for isomer II these vibrations, belonging to the A₁ and B₁ symmetry class (Table 3), should be IR-active. We found no IR features in this frequency range for C₁₄₀ (ca. 4 mg pressed in a 3-mm-diameter pellet), and this result would be consistent with the C_{2h} isomer. However, the expected (calculated) IR intensities for the intercage modes of the C₁₄₀ isomers are very low, and the poor sensitivity of our spectrometer in the far-IR region does not allow us to make an unambiguous structure assignment on the basis of the vibrational spectra alone.

The experimental spectroscopic results and calculations presented here and discussed above provide firm evidence that C_{140} produced at high pressure has either structure I or II. The evidence available concerning phase transitions and molecular packing in the solid state allow us to conclude that the C_{140} produced in our experiments is most likely the (1,2)/(2,1) C_{2h} isomer (structure I).

4.2. Photodissociation of C_{140} **and** C_{120} **.** We have frequently mentioned that C_{140} and C_{120} have very similar properties due to the structural similarities of the intercage bonding. Remarkable parallels can be found in the photophysical properties of the dimers relative to the monomers. The photophysics of C_{120} have been studied in detail by Ma et al.,³⁴ who concluded that the C_{60} dimer can be thought of as a pair of C_{60} derivatives, each with one functionalized double bond. In other words, there is no significant electronic interaction between the two cages in either the ground or the excited state. The similarities in the absorption and fluorescence properties of C_{140} and C_{70} indicate that the model of independent cages applies in this case as well.

Especially interesting is the observation of the photodissociation of C₁₂₀ and C₁₄₀ into monomeric C₆₀ and C₇₀. We found essentially the same, relatively low photodissociation quantum yield for both dimers (about 5×10^{-5} for the air-saturated dilute ODCB solutions irradiated at 400-600 nm). In contrast, Ma et al.³⁴ reported no effects of photoirradiation on the absorption and fluorescence spectra of C120, i.e., no photodissociation, using approximately the same wavelengths reported here. The reason for this disagreement with our results is not clear. Obviously, our HPLC analysis is much more sensitive and specific for monitoring low-yield photodissociation. However, the conversion of a substantial part of the dimers into monomers was also accompanied by notable changes in our absorption spectra. We believe that photodissociation proceeds via an excited triplet state for both dimers. The photodissociation yield increased in deoxygenated solutions for both C140 and C120, and this allowed us to estimate the intrinsic triplet-state lifetimes of about 50 μ s for C_{140} and 10 μ s for C_{120} . If one assumes that the efficiency of intersystem crossing to the triplet state is high (about unity for monomeric C₆₀ and C₇₀),⁴⁹ then dissociation must be only a minor decay channel for the triplet state of the dimers. The main decay may be due to intercage excitation quenching. Although it substantially decreases the triplet-state lifetime of C_{140} relative to C_{70} (≥ 12 ms in toluene³⁶) and of C_{120} relative to C₆₀ (133 μ s in toluene³⁷), such intercage quenching with k_q $\leq 10^5 \,\mathrm{s}^{-1}$ would be quite slow on a photophysical time scale.³⁴ Again, this suggests moderate electronic interactions between the two linked cages in the dimers. The nature of these interactions remains to be understood. The results for the C_{60} dimer have shown no evidence for the formation of a singlet or triplet excimer-like state.³⁴ In other words, electronic (photo)excitations seem to be essentially localized on one of the fullerene cages. Etheridge and Weisman have reported the formation of a triplet C70 excimer through encounters between triplet- and ground-state C₇₀ molecules in toluene.³⁶ However, the structure of the C_{70} excimer may be different from that of C_{140} , and the triplet state of the dimer may be of a localized character like that of C120. To clarify this and other aspects of the photophysics of the C70 dimer, further time-resolved absorption and fluorescence studies would be very helpful.

The triplet-state dissociation of the C_{60} and C_{70} dimers is expected to be the reverse of [2+2] cycloaddition of the monomers via the excited triplet state. The latter reaction has been proposed for the photopolymerization of solid C₆₀ and $C_{70}\!^{\,\,,5,13}$ The observation of dimer dissociation is important because it gives additional support to this proposal. Obviously, the overall efficiencies of the photoinduced [2+2] ring formation and decomposition can strongly depend on the reaction conditions. In general, however, these efficiencies seem quite low for the fullerenes both in the solid state and in solution. Our results show that the [2+2] C₆₀ and C₇₀ dimers photodissociate in (deoxygenated) solution with a quantum yield of the order of 10^{-3} . No reverse photocycloaddition has been observed in deoxygenated C₆₀ solutions,⁵⁰ probably because of its very low yield. The photophysics is evidently much more complicated in solid fullerenes, where not only intramolecular, but also intermolecular electronic processes determine the photoexcitation relaxation.⁵¹ The cycloaddition of C₆₀ molecules seems to be only a minor relaxation channel. Nevertheless, a long and intense photoirradiation of C₆₀ films yields a well-polymerized material.⁵ Apparently, photocycloaddition prevails over possible photodissociation in solid C₆₀. In contrast to C₆₀, there is little evidence for photopolymerization in solid C70. Its efficiency appears to be very low.¹³ This difference between C_{60} and C_{70} has been attributed to the smaller number of reactive double bonds in C₇₀.¹³ We believe that, apart from structural differences, the photophysics behind photopolymerization may also play an important role.

4.3. Dimerization of C₇₀ and C₆₀ under Pressure. In the pressure-induced dimerization of solid C₆₀ and C₇₀, we observed considerable analogy but also significant differences between these two fullerenes. Both C₆₀ and C₇₀ dimerize at 1 GPa and

200-220 °C, and the resulting dimers have been isolated and characterized as individual compounds. However, in contrast to C_{140} , the yield of C_{120} dramatically decreased with increasing treatment time, as illustrated in Figure 8. C₁₂₀ shows characteristic peaks at 1463 cm⁻¹ (shifted pentagonal pinch mode, which occurs at 1468 \mbox{cm}^{-1} in $C_{60})$ and the strong intercage vibration peak at 96 cm⁻¹. Polymerization of C₆₀ and C₁₂₀ to higher C₆₀ oligomers and polymeric chains⁷ (characteristic Raman peak at 1458 cm⁻¹) is relatively fast and after an hour depletes most of the C_{60} and C_{120} . In fact, the hypothesis that under high pressure/temperature C60 initially forms dimers which then readily transform into higher oligomers or polymeric chains has already received strong support based on vibrational spectroscopy studies.^{1,6,10} According to the Raman and IR spectra (the latter not shown), the short-time treated C₆₀ contains a high fraction of C_{120} (~30 wt %). However, we could dissolve only ~ 3 wt % of C₁₂₀ by sonication in ODCB. Conceivably, most dimer molecules were intercalated in a matrix of higher oligomers and could not be easily released to the solvent.

Treatment of solid C₇₀ at 1 GPa and 200–220 °C yields 30– 50% C₁₄₀ and only a small amount of insoluble (in ODCB) residue, which is tentatively assigned to higher C₇₀ oligomers. The product composition does not depend significantly on the treatment time. Thus, in contrast to C₆₀, the polymerization of C₇₀ appears to be kinetically "frozen" at the dimer stage under our conditions. The efficient formation of C₇₀ polymeric chains appears to require substantially higher pressures of \geq 2.0 GPa and temperatures of 250–300 °C.^{18,19} One possible explanation for this behavior is that the formation of extended and ordered polymeric structures is simply more difficult in C₇₀ because of its lower symmetry and the lower number of reactive double bonds. However, this does not adequately explain why there are few C₇₀ trimers and other oligomers (insoluble residue) in the C₇₀/C₁₄₀ material.

An additional complication for fullerene polymerization may arise from the presence of intercalated (interstitial) gases. We found that the dimerization/polymerization of C₆₀ under short pressure treatment at 1 GPa and 200-220 °C proceeds efficiently for samples stored for a long time in air or nitrogen, i.e., for samples containing some amount of intercalated gas, but is inefficient for samples freshly annealed in a vacuum and containing only a small, if any, amount of intercalated argon due to handling in a glovebox. In contrast to C_{60} , the dimerization of C₇₀ did not depend in this fashion on the sample history. It is well-established that interstitial gases, even at low occupation numbers, can notably affect the phase diagram, molecular rotations, and other physical properties of C₆₀ and C70.1,46 However, their influence on the polymerization reaction has not yet been studied. In general, interstitial gases would be expected to hinder the interactions between fullerene molecules and the polymerization, but our results suggest that there are more interesting effects which deserve further investigation.

Summary

We have shown that at a pressure of 1 GPa and a temperature of 200 °C, solid C_{70} reacts to form a single dimeric species with high yield. The dimer was isolated by HPLC and characterized by ¹³C NMR, vibrational, UV–visible absorption, and fluorescence spectroscopy. Semiempirical PM3 calculations predicted that the five possible isomers involving [2+2] cycloaddition across the short double bonds in C_{70} should have essentially equal energy. The preferential formation of a single C_{140} isomer indicates that orientational ordering of C_{70} monomers with parallel D_5 axes is the determining factor and that this ordering is preserved under 1 GPa pressure even at temperatures well above 200 °C, in agreement with previous results.^{45,46} In this ordered phase, the uniaxial rotations of C_{70} monomers along D_5 axes⁴⁷ place the (1,2) double bonds in antiparallel juxtaposition so that the cap-to-cap (1,2)/(2,1) dimer with C_{2h} symmetry (isomer I in Figure 4) can be readily formed. This structure, which is consistent with all spectroscopic data, was proposed earlier for the room-temperature photopolymerization of C_{70} .¹³ The only other structure consistent with the NMR data is the (1,2)/(1,2) C_{2v} isomer II, but this geometry would require a parallel juxtaposition of (1,2) double bonds with the symmetry axes of neighboring C_{70} monomers at angles of ca. 120°, which in turn requires a disordered state.

The C_{70} dimer is structurally analogous to the [2+2] cycloaddition C_{60} dimer C_{120} .¹¹ Vibrational spectroscopy studies have suggested that C_{60} dimers can initially form under high pressure and temperature, but that these species are rapidly transformed into higher C_{60} oligomers and polymers.^{1,10} We were able to isolate C_{120} from solid C_{60} treated under the same conditions used to prepare C_{140} when the reaction time was limited to ≤ 5 min. However, even short treatment resulted in an insoluble residue as the major product, attributed to higher C_{60} oligomers and polymeric chains, whose yield increased at the expense of C_{120} as treatment time was increased.

 C_{140} and C_{120} feature the same intercage bonding (fourmembered ring) and exhibit close correspondence in many properties. Thus, C₁₂₀ exhibits characteristic Raman peaks at 96, 127, and 139 cm⁻¹ for intercage vibrations, which are shifted to 89, 118, and 129 cm⁻¹, respectively, in C_{140} according to the factor $(60/70)^{1/2}$, exactly as expected for the effect of cage mass. Both dimers thermally decompose to the monomers with similar kinetic parameters, and both show little interaction between the two fullerene cages in the ground and excited electronic states. Finally, both dimers photodissociate to the respective monomers with a quantum yield of the order of 10^{-3} in deoxygenated solutions (400-600 nm irradiation). It is likely that photodissociation occurs via the excited triplet state of the dimers and is, therefore, the reverse of the triplet-state [2+2]cycloaddition of the monomers-a reaction proposed for the photopolymerization of solid C₆₀ and C₇₀.

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