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Resolution and Configurational Stability of the Chiral Fullerenes C_{76}, C_{78}, and C_{84}: A Limit for the Activation Energy of the Stone–Wales Transformation

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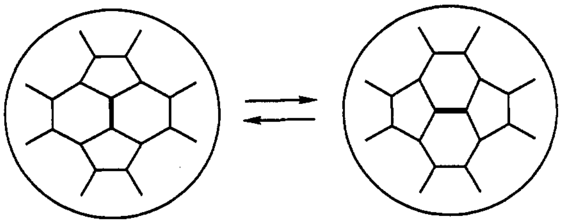
Abstract: Chiral fullerenes C_{76}, C_{78}, and C_{84} were kinetically resolved by asymmetric osmylation providing three optically active allotropes of elemental carbon. The circular dichroism spectra of D_3 C_{78} and D_2 C_{84} are more detailed than the corresponding UV–vis spectra. Optically active C_{76} and C_{84} are configurationally stable under conditions approaching their limit of thermal (600–700 °C) and photochemical (193 nm) stability. Given the potential racemization of D_2 C_{84} by two consecutive Stone–Wales pyracylene transformations, the configurational stability of C_{84} at 700 °C sets a limit for the activation energy of the Stone–Wales transformation of >83 kcal/mol.

The contact-arc vaporization of carbon produces the higher fullerenes as discrete sets of isomers. Of thousands of geometrically possible fullerene structures, C_{76}, C_{78}, and C_{84} form as one,[1] three, and two[2] isomers, respectively. Both thermodynamic and kinetic controls have been proposed to account for this selectivity. These mechanisms rely on pyracylene rearrangements to migrate pentagons to equilibrate intermediates[3] or intact fullerenes (eq 1).[4] Known as the Stone–Wales transformation[5] in the fullerene literature, this rearrangement is related to arene rearrangements studied by Scott, e.g. the automerization of naphthalene (eq 2).[6] These transformations formally involve the rotation of a C_2 unit (in bold) by 90° and may involve carbene intermediates. In order to test for the equilibration of intact fullerenes, we kinetically resolved chiral fullerenes by asymmetric osmylation and subjected the optically active fullerenes to thermolysis and photolysis conditions. Optically active C_{76} and C_{84} were found to be configurationally stable under conditions approaching their limit of thermal and photochemical stability. These results establish that the activation energy for the Stone–Wales transformation is >83 kcal/mol for D_2 C_{84} and that this rearrangement is not photochemically induced at 193 nm.



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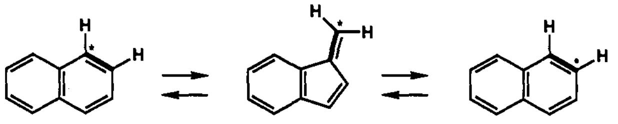
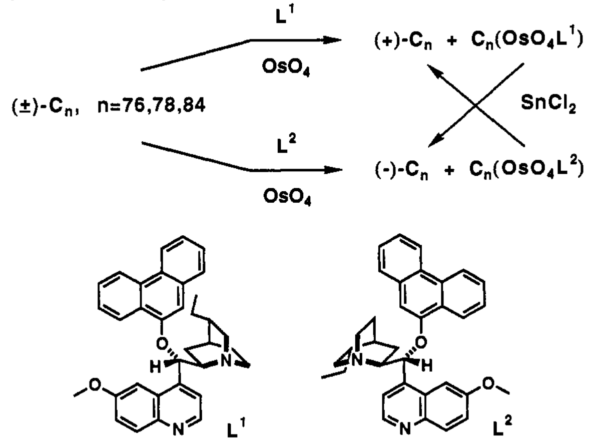


(2)

Scheme 1. Kinetic Resolution of Chiral Fullerenes by Asymmetric Osmylation[a]



[a] (+)- and (–)- refer to the signs of the CD traces at 375 nm.

We recently described the kinetic resolution of C_{76} by asymmetric osmylation, providing the first optically active allotrope of a pure element.[7,8] We have extended this technology to C_{78} and C_{84} (Scheme 1). Partial osmylation[9] of the purified racemic fullerenes[10] with OsO_4 and Sharpless[11] cinchona alkaloid ligands L^1 or L^2 gave optically active fullerenes (kinetically resolved recovered starting materials) and diastereomerically

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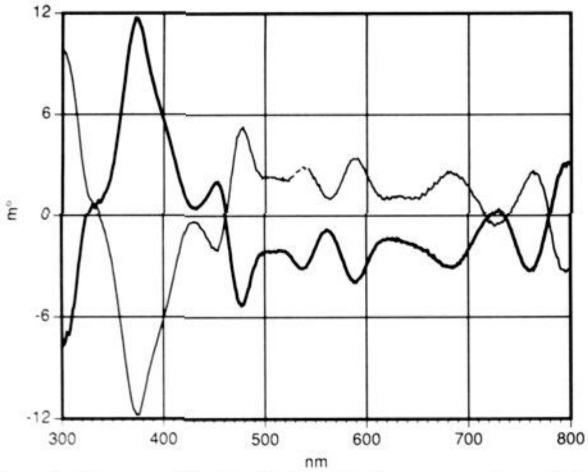

Figure 1. CD spectra of C_{78} kinetically resolved by asymmetric osmylation with L^1: recovered enantiomer after ca. 40% conversion (bold trace) and regenerated enantiomer after ca. 40% conversion (thin trace, scaled by a factor of 1.5), recorded in toluene. Maxima and minima: 333 (sh), 373, 453, 479, 538, 588, 684, 729, 760, 790 nm.

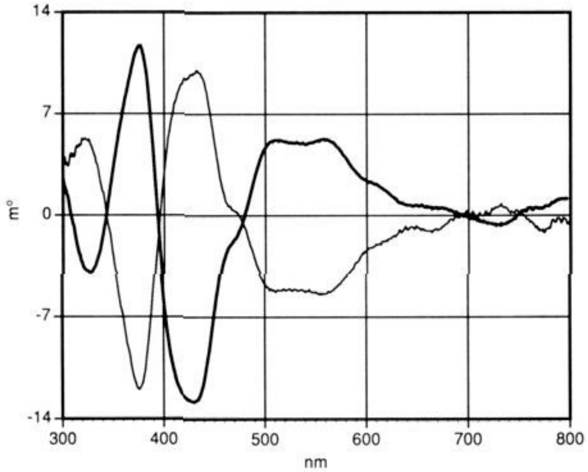

Figure 2. CD spectra of C_{84} kinetically resolved by asymmetric osmylation with L^1: recovered enantiomer after ca. 73% conversion (bold trace) and regenerated enantiomer after ca. 32% conversion (thin trace, scaled by a factor of 4), recorded in toluene. Maxima and minima: 327, 376, 430, 466 (sh), 511, 558, 610 (sh), 665, 731 nm.

enriched osmate esters. Reduction of the osmate esters with $SnCl_2$ regenerated fullerenes enriched in the opposite enantiomer as the initially recovered fullerenes. Circular dichroism (CD) spectra of both enantiomers of kinetically resolved C_{78} and C_{84} are shown in Figures 1 and 2. Since C_{78} and C_{84} each form with only one chiral isomer,[2] these spectra represent single isomers, i.e. D_3 C_{78} and D_2 C_{84}. For D_3 C_{78}, CD peaks at 373, 479, 684, 729, and 760 nm correspond to UV–vis peaks[4a] at 362, 472, 700, 734, and 757 nm. The CD spectra of C_{78} and C_{84} show considerably more structure than the corresponding UV spectra.[4a,12] CD spectra obtained in this way should aid in the analysis of the electronic structures of higher fullerenes, especially since CD spectra show only chiral isomers, unobscured by achiral isomers.

Table 1. UV–Vis Data for Thermolyzed and Photolyzed C_{76}

	absorbance of C_{76}		
λ (nm)	original solution	heated at 600 °C (ratio, %)	irradiated at 193 nm (ratio, %)
330	2.034	0.941 (46)	1.153(57)
400	1.084	0.488 (45)	0.604 (56)
426	0.914	0.414 (45)	0.511(56)
480	0.465	0.193 (42)	0.252(54)
524	0.305	0.129 (42)	0.174 (57)

The kinetic resolution of fullerenes by asymmetric osmylation appears to be general and provides a class of optically active all-carbon molecules with novel chiral π-systems. The kinetic resolution of C_{84} is remarkable considering the roundness of this molecule. While the enantiomers of C_{76} show a pronounced handedness, especially in the vicinity of the most probable reaction site,[7] the calculated structure of D_2 C_{84} is nearly spherical.[13]

Of the geometrically possible fullerene isomers of C_{84}, 24 satisfy the isolated pentagon rule.[14] The D_2 and D_{2d} isomers observed by NMR[2] are believed to be a thermodynamic mixture[2b,15] of the two most stable isomers[13] which can equilibrate by a single Stone–Wales transformation. Accordingly, the enantiomers of D_2 C_{84} can be interconverted by two Stone–Wales transformations (Figure 3). Transformation of the shaded pyracylene unit of one enantiomer of D_2 C_{84} gives achiral D_{2d} C_{84}, which can then be transformed to either the original or the mirror image enantiomers of D_2 C_{84} by transforming one or the other of its shaded pyracylene units. Thus the racemization of C_{84} is a test for the Stone–Wales transformation. For comparison, the enantiomers of C_{76} cannot be interconverted via isolated pentagon isomers and should be more configurationally stable.

To test for fullerene racemization and the Stone–Wales transformation under conditions simulating fullerene formation, we subjected enantiomerically enriched C_{76} and C_{84} to high temperatures and far-UV irradiation. The fullerenes were purified by HPLC before and after treatment. The extent of fullerene recovery was determined by UV–vis spectroscopy, and the preservation or loss of enantiomeric purity was determined by CD spectroscopy, both measured at multiple wavelengths. The fullerenes were heated under vacuum in quartz, which is fairly inert in high-temperature arene rearrangements.[6c] After heating C_{76} for 2 h at 600 °C, 44(2)% of the C_{76} was recovered and the recovered sample showed 49(1)% of the original optical activity (Tables 1 and 2). After heating C_{84} for 2 h at 700 °C, 28(1)% of the C_{84} was recovered and the recovered sample showed 30(1)% of the original optical activity (Tables 3 and 4). The specific

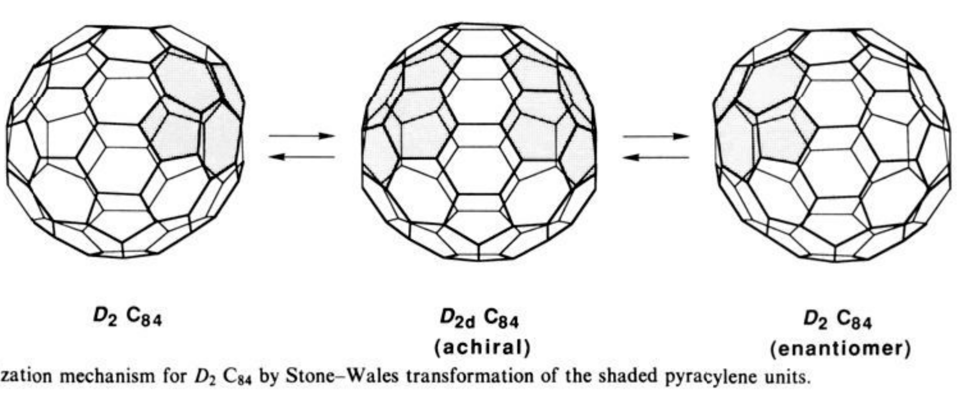

Figure 3. Racemization mechanism for D_2 C_{84} by Stone–Wales transformation of the shaded pyracylene units.

Table 2. CD Data for Thermolyzed and Photolyzed C_{76}

	$\Delta\epsilon$ (m°) C_{76}		
λ (nm)	original solution	heated at 600 °C (ratio, %)	irradiated at 193 nm (ratio, %)
326	2.51	1.20 (48)	1.31 (52)
395	13.23	6.63 (50)	7.28 (55)
455	3.83	1.87 (49)	2.55 (67)

Table 3. UV-Vis Data for Thermolyzed and Photolyzed C_{84}

	absorbance of C_{84}			
λ (nm)	original sample	heated at 600 °C (ratio, %)	heated at 700 °C (ratio, %)	irradiated at 193 nm (ratio, %)
400	1.284	0.757 (59)	0.377 (29)	0.578 (45)
428	0.982	0.573 (58)	0.282 (29)	0.439 (45)
464	0.654	0.373 (57)	0.179 (27)	0.287 (44)
490	0.534	0.304 (57)	0.145 (27)	0.234 (44)

Table 4. CD Data for Thermolyzed and Photolyzed C_{84}

	$\Delta\epsilon$ (m°) C_{84}			
λ (nm)	original sample	heated at 600 °C (ratio, %)	heated at 700 °C (ratio, %)	irradiated at 193 nm (ratio, %)
378	10.40	6.24 (60)	3.24 (31)	5.00 (48)
470	−2.07	−1.52 (73)	−0.64 (31)	−0.96 (46)
518	4.24	3.03 (71)	1.28 (30)	2.24 (53)
562	4.55	2.88 (63)	1.32 (29)	2.71 (60)

CD intensities did not change within experimental error upon thermolysis, indicating that neither C_{76} nor C_{84} racemizes at these temperatures.

The fullerenes were photolyzed in oxygen-free hexane at 193 nm with an excimer laser. After photolysis, 56(1)% of the C_{76} was recovered and the recovered sample showed 58(8)% of the original optical activity (Tables 1 and 2). Photolysis of C_{84} yielded 44(1)% recovered C_{84} with 52(6)% of the original optical activity (Tables 3 and 4). The specific CD intensities did not change within experimental error upon laser irradiation, indicating that neither C_{76} nor C_{84} racemizes photochemically at 193 nm.

Thus C_{76} and C_{84} are configurationally stable under thermal and photochemical conditions approaching their limits of chemical stability. Considering the error limits of the UV-vis and CD measurements, C_{84} maintains at least 94% of its enantiomeric purity after heating at 700 °C for 2 h. Given the structural assignment for D_2 C_{84},[2,13,15] this sets a limit for the activation energy of the Stone-Wales transformation of >83 kcal/mol. Thus the Stone-Wales transformation is not particularly facile and has an activation energy significantly higher than the rearrangement of azulene to naphthalene (ca. 52 kcal/mol),[6b,c] at least on the order of the automerization of naphthalene (86 kcal/mol).[6a,d] It would be interesting to see if the Stone-Wales transformation as detected by the racemization of C_{84} is facilitated by metal surfaces, as metals affect the morphology of arc-generated carbon nanostructures.[16]

Experimental Section

General Procedures. Fullerene extract was purchased from Nick Holden, Polygon Enterprises, Waco, TX. The higher fullerenes were obtained from the extract by two successive column chromatographies on alumina (15-100% toluene in hexanes and 20-100% toluene in hexanes), followed by preparative HPLC on a 10-mm-i.d. Regis Buckyclutcher I column (65-70% toluene in hexanes). Fullerenes C_n, n = 76, 78, and 84, were obtained pure with respect to n according to analytical HPLC (4.6-mm-i.d. Regis Buckyclutcher I column, 60% toluene in hexane) and FAB mass spectroscopy. UV-vis spectra were recorded on a Hewlett Packard diode array spectrometer (model 8452A) with 1.0-cm cells, and CD spectra were recorded on a J-500 C JASCO spectropolarimeter with a 1.0-cm-path-length cell. UV-vis and CD spectra were recorded in HPLC grade toluene. For the photolysis experiments, 700 mL of HPLC grade hexane was washed consecutively with three 100-mL portions of concentrated H_2SO_4, three 100-mL portions of 3 N NaOH, and three 100-mL portions of distilled water, followed by passage through 400 g of basic alumina (activity 1) and distillation.

Resolution of C_{84}. A 39.2 μM stock solution of C_{84} was prepared from 1.980 mg (1.96 μmol) of C_{84} and 50.0 mL of toluene. A 15-mL portion of this stock solution (590 nmol) was concentrated to 5.0 mL, cooled to −10 °C, and treated with a solution of 180 μg (700 nmol) of OsO_4 and 1.7 mg (3.5 μmol) of hydroquinidine 9-phenanthryl ether (L^1) in 600 μL of toluene. The resulting solution was stirred at −10 °C for 24 h and passed through a short silica gel column with toluene to elute the unreacted C_{84}. The toluene was removed in vacuo, and the C_{84} was purified by HPLC (10-mm-i.d. Regis Buckyclutcher I column, 70% toluene in hexanes). UV-vis spectral analysis indicated ca. 32% conversion.[17]

The osmate ester was eluted from the silica column with 10% pyridine in $CHCl_3$, and the solvent was removed in vacuo. The product was reduced back to C_{84} by dissolving in 2.0 mL of pyridine and treating with 500 μL of a 8.86 mM solution of $SnCl_2{\cdot}2H_2O$ in pyridine. This mixture was sonicated for 10 min, concentrated in vacuo, and extracted with toluene under sonication. The toluene solution was filtered, concentrated, and purified by HPLC (10-mm-i.d. Regis Buckyclutcher I column, 70% toluene in hexanes). The purified material was identical to the original C_{84} sample according to HPLC and UV-vis spectroscopy. The CD spectrum was recorded in 2.0 mL of toluene (Figure 2).

The unreacted C_{84} after ca. 32% conversion was further osmylated with 940 nmol of OsO_4 and 4.7 μmol of L^1, bringing the total conversion up to ca. 73%.[17] The purified material was identical to the original C_{84} sample according to HPLC and UV-vis spectroscopy. The CD spectrum was recorded in 2.0 mL of toluene (Figure 2).

Resolution of C_{78}. Using the methodology described for C_{84}, ca. 400 nmol of C_{78}[18] was treated with 400 nmol of OsO_4 and 2.0 μmol of L^1 at −10 °C for 21 h. UV-vis spectral analysis indicated ca. 40% conversion.[18] The CD spectra of the unreated and regenerated C_{78} were recorded in 2.0 mL of toluene (Figure 1).

Resolution of C_{76}. Using the methodology described for C_{84}, 1.0 μmol of C_{76} was treated with 1.1 μmol of OsO_4 and 5.0 μmol of L^1 in 15 mL of toluene at −10 °C for 18 h. The unreacted starting material after 68% conversion was used for the racemization experiments. (The CD spectra of unreacted and regenerated C_{76} resolved by this technique appear in ref 7).

Thermal Racemization Experiments. Purified recovered C_{84} from kinetic resolutions run to 70-87% conversion was dissolved in 10.0 mL of toluene, and the UV-vis and CD spectra of this stock solution were measured. A 2.00-g portion of this solution was reduced in volume in vacuo and quantitatively transferred to a 0.6- × 11-cm quartz tube by repetitively pipetting small amounts of the solution into the bottom of the tube and removing the solvent with a stream of argon. The quartz tube was evacuated to 5×10^{-5} mmHg for 1 h with gentle heating, back-filled with argon, and reevacuated to 5×10^{-5} mmHg with gentle heating. This evacuation-purge cycle was repeated a total of three times before sealing the tube under dynamic vacuum. Quartz tubes containing optically active C_{76} were prepared similarly.

The sealed tubes were placed in an oven at 300 °C, and the temperature was increased at a rate of 200 °C/h. The tubes were maintained at the specified temperature for 2.0 h, at which time they were removed from the oven and cooled to room temperture. The samples were extracted with toluene while sonicating for up to 5 h. The toluene solutions were concentrated, and the fullerenes were purified by HPLC (10-mm-i.d. Regis Buckyclutcher I column, 70% toluene in hexanes). The reisolated fullerenes were identical to the original samples according to HPLC and UV-vis spectroscopy. The solvent was removed in vacuo, and toluene was added to the residue for a total weight of 2.00 g. This solution was then analyzed by UV-vis and CD spectroscopies under the same conditions used for the unheated stock solutions (Tables 1-4).

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(17) Assuming equal molar extinction coefficients for both isomers of C_{84}.

(18) Assuming the molar extinction coefficients for the three isomers of C_{78} equals 11 500 L mol^{-1} cm^{-1} at 528 nm, the measured value for the major isomer.[4a]

Photolysis Experiments. Toluene solutions of enantiomerically enriched C_{76} and C_{84} quantified by UV–vis and CD spectroscopy as describedabove, 2.00 g of each solution, were concentrated and gently heated undervacuum at 1×10^{-3} mmHg for 20 h. These samples were dissolved in250 mL of purified hexane with sonication and warming. The hexane solutions were degassed by sparging with argon for 2 h and transferred to a 250-mL photocell capped at both ends with Suprasil windows. With stirring, each solution was irradiated for 7 min at 193 nm with a Lambda Physik excimer laser (model EMG 201 MSC, ArF) operating at 50 mJ/pulse at 2 Hz. The solvent was removed in vacuo, and the fullerenes were purified by HPLC (10-mm-i.d. Regis Buckyclutcher I column, 70% toluene in hexanes). The reisolated fullerenes were identical to the original samples according to HPLC and UV–vis spectroscopy. The solvent was removed in vacuo, and toluene was added to the residue for a total weight of 2.00 g. This solution was analyzed by UV–vis and CD spectroscopies under the same conditions used for quantification before photolysis (Tables 1–4).

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