## Reports

## Fullerene Isomerism: Isolation of $C_{2\nu}$ - $C_{78}$ and $D_3$ - $C_{78}$

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Early reports on the formation of the higher fullerenes  $C_{76}$ ,  $C_{78}$ ,  $C_{84}$ ,  $C_{90}$ , and  $C_{94}$  by resistive heating of graphite stimulated theoretical calculations of possible cage structures for these all-carbon molecules. Among the five fullerene structures with isolated pentagons found for  $C_{78}$ , a closed-shell  $D_{3k}$ -isomer was predicted to form preferentially. Two distinct  $C_{78}$ -isomers were formed in a ratio of ~5:1 and could be separated by high-performance liquid chromatography. The carbon-13 nuclear magnetic resonance (NMR) spectrum of the major isomer is uniquely consistent with a  $C_{2\nu}$ -structure. The NMR data also support a chiral  $D_3$ -structure for the minor isomer. The isolation of specifically these two isomers of  $C_{78}$  provides insight into the stability of higher fullerene structures and into the mechanism for fullerene formation in general.

HEN MACROSCOPIC QUANTITIES of  $C_{60}$  (1) and the oblong  $D_{5h}$ -C<sub>70</sub> were isolated (2) and characterized in pure form (3-9), the isolation of enriched samples of C76/C78 and C84 from the soot obtained by resistive heating of graphite under inert atmosphere was also reported (10). Improved chromatographic separation methods later led to the isolation of highly enriched samples of these allcarbon molecules (11-14), but it was only recently (15) that a third molecular form of carbon, C<sub>76</sub>, could be isolated and characterized in pure form. The <sup>13</sup>C NMR spectrum of this molecule was uniquely consistent with a chiral  $D_2$ -symmetrical fullerene structure that obeys the isolated pentagon rule (IPR). This structure had also been predicted in theoretical work by Manolopoulos (16) who applied a spiral algorithm (17) combined with the IPR to the search for reasonable fullerene structures. Fowler and Manolopoulos subsequently found the five IPR-satisfying structures for C<sub>78</sub> (Table 1) (18) and predicted on the basis of qualitative molecular orbital (MO) theory that the closed-shell  $D_{3h}$ -isomer would be the most stable isomer.

We isolated the  $C_{78}$ -fraction from the toluene extract of the carbon produced through resistive heating of graphite under helium by methods previously described (11, 15): (i) the crude extract was separated

chromatographically on neutral alumina into the fractions C<sub>60</sub>, C<sub>70</sub>, and higher fullerenes; (ii) the higher fullerenes (0.1 g)were separated on a second alumina column with hexane-toluene elution to yield three fractions, (I) C<sub>70</sub>, (II) C<sub>76</sub> and C<sub>78</sub>, and (III) the major component C<sub>84</sub>; and (iii) the final step was threefold purification by high-performance liquid chromatography (HPLC) of fraction II, performed on a Vydac 201-TP-510 column (C18 reversed phase, 250 mm, 10-mm internal diameter) (13, 19). After most of the  $C_{76}$  was removed with a 70:30 CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN eluant mixture, chromatography with a 1:1 toluene-CH<sub>3</sub>CN mixture provided two highly enriched fractions of two C78-isomers. A final run with toluene-CH<sub>3</sub>CN led to the fractions shown by the HPLC profiles in Fig. 1, A to C. In HPLC assays with various solvent mixtures, the purity was

**Fig. 1.** (**A** to **C**) HPLC profiles of (A) a mixture of  $C_{76}$  (retention time  $t_R = 9.08 \text{ min}$ ),  $C_{2\nu}$ - $C_{78}$  ( $t_R = 9.67 \text{ min}$ ), and  $D_3$ - $C_{78}$  ( $t_R = 10.30 \text{ min}$ ); (B) pure  $C_{2\nu}$ - $C_{78}$ , and (C) pure  $D_3$ - $C_{78}$ . Experimental conditions: Vydac 201 TP 510 C-18 reversed-phase column of dimensions 25 cm by 1 cm, particle size, 5  $\mu$ m; eluant, toluene-acetonitrile 1:1; pressure, 1000 psi; flow rate, 6 ml/min; and ultraviolet detection at 310 nm. (**D** and **E**) Laser-desorption time-of-flight mass spectra recorded for (D)  $C_{2\nu}$ - $C_{78}$  and (E)  $D_3$ - $C_{78}$ . Spectrum D corresponds to the HPLC profile in (B) and spectrum E corresponds to (C). In addition to  $C_{76}$ ,  $C_{74}$ , and  $C_{72}$  peaks resulting from  $C_{20}$ -fragment losses, spectrum D contains minor  $C_{60}$  and  $S_{70}$  peaks from previous calibration runs and spectrum E shows  $C_{84}$  as a minor impurity in the  $D_3$ - $C_{78}$  isomer.

**Table 1.** The five IPR-satisfying isomeric structures of  $C_{78}$ , the number of independent resonances in their <sup>13</sup>C NMR spectra, the gasphase heats of formation  $\Delta H_f^{\circ}$  (298 K), and the differences in  $\Delta H_f^{\circ}$  calculated with the molecular mechanics program MM3. (MM3 calculates a heat of formation of 573.8 kcal mol<sup>-1</sup> for  $C_{60}$ .)

Struc- ture	<sup>13</sup> C NMR lines (intensity)	$\Delta H_{\rm f}^{\rm o}$ (kcal mol <sup>-1</sup> )	$\Delta(\Delta H_{\rm f}^{\rm o})$ (kcal mol <sup>-1</sup> )
$\begin{array}{c} & \\ & C_{2\nu} \\ & D_{3} \\ & C_{2\nu'} \\ & D_{3h} \\ & D_{3h'} \end{array}$	$\begin{array}{c} 18 \ (4 \ \mathrm{C}) \ + \ 3 \ (2 \ \mathrm{C}) \\ 13 \ (6 \ \mathrm{C}) \\ 17 \ (4 \ \mathrm{C}) \ + \ 5 \ (2 \ \mathrm{C}) \\ 5 \ (12 \ \mathrm{C}) \ + \ 3 \ (6 \ \mathrm{C}) \\ 5 \ (12 \ \mathrm{C}) \ + \ 3 \ (6 \ \mathrm{C}) \end{array}$	695.7 697.8 694.3 702.3 697.8	1.4 3.5 0.0 8.0 3.5

assessed to be >98%. The first fraction yielded ~2 mg of the major isomer, and the second fraction yielded ~0.2 mg of the minor  $C_{78}$ -isomer. Mass spectrometric analysis (laser desorption time-of-flight) of each fraction (Fig. 1, D and E) verified that both contain material of  $C_{78}$  chemical formula with >98% purity.

The structures of the two isomers were elucidated by <sup>13</sup>C NMR spectroscopy. The spectrum of the purified major isomer, recorded in CS2 with Cr(acac)3 (acac, acetylacetonate) as a relaxant after 71,000 scans, shows 18 large peaks of nearly equal intensity and 3 small peaks, each with one-half the intensity of the major ones (Fig. 2 and Table 2). This spectrum is thus uniquely consistent with one of the two  $C_{2\nu}$ -symmetrical, IPRsatisfying fullerene structures calculated by Manolopoulos and Fowler for C<sub>78</sub> (Table 1) (18). As in  $C_{70}$  (20) and  $C_{76}$  (15), each C atom in C<sub>78</sub> lies in one of three distinct environments. Five resonances, four of higher and one of lower intensity, originate from C atoms lying at the intersection of three hexagons ("pyrene"-like) and show the largest



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shielding near 130 ppm. A total of nine resonances, eight of higher and one of lower intensity, originate from C atoms in the bonds between two five-membered rings (5MR) in pyracylene substructures. In analogy to  $C_{70}$  and  $C_{76}$ , these signals should be the most deshielded near 150 ppm. The remaining seven peaks, six of higher and one of lower intensity, are due to C atoms at corannulene sites, as defined by the intersection of one 5MR and two 6MRs but not connected to another 5MR. The symmetry elements and the location of the three different types of C atoms in  $C_{2\nu}$ -C<sub>78</sub> are shown in Fig. 3, A to C. The molecule is depicted with a remarkably flat face shaped by a coronene subunit facing the viewer (Fig. 3A), in a view perpendicular to the symmetry plane (Fig. 3B), and in a view onto one of the two identical caps (Fig. 3C). If a paper model of  $C_{2\nu}$ - $C_{78}$  is put on its flat coronene base, it resembles a helmet or a turtle's shell.



The small amount of minor  $C_{78}$ -isomer that we isolated was insufficient to record a <sup>13</sup>C NMR spectrum of the pure compound. However, after the spectra of pure  $C_{76}$  and  $C_{2\nu}$ - $C_{78}$  were known, structural evidence for the minor  $C_{78}$  isomer was obtained by subtraction from the spectrum of a concentrated  $CS_2$  solution containing a mixture of  $C_{76}$ ,  $C_{2\nu}$ - $C_{78}$ , and the minor



**Fig. 2.** Expanded view of the fullerene region in the <sup>13</sup>C NMR spectrum of 1.6 mg of  $C_{2\nu}$ - $C_{78}$  in CS<sub>2</sub>, taken at 125.6 MHz, with acctone as an internal lock. In addition to the fullerene resonances, the full spectrum from 0 to 220 ppm only shows the acetone peaks near 30 and 206 ppm and the solvent peak near 190 ppm.

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isomer of  $C_{78}$  in a ratio of ~5:5:1. This spectrum showed 13 resonances of approximately equal intensity in addition to the 19 equally intensive resonances of  $D_2$ - $C_{76}$ (15) and the 21 resonances of  $C_{2\nu}$ -C<sub>78</sub> (Table 2). Of the five calculated IPRsatisfying fullerene structures for C<sub>78</sub>, only the chiral  $D_3$ -structure (Table 1) is in agreement with the observed spectrum. A more detailed analysis of the NMR data provides additional support for the assignment of the  $D_3$ -structure to the minor C<sub>78</sub>-isomer. A view onto one of the three symmetry-related, smoothly curved faces in D3-C78 that are capped by two triphenylene caps is shown in Fig. 3D. It indicates both the location of the pyrene- and corannulene-type C sites that are assembled on each face. There are three different pyrene-type sites in the molecule, and three distinctively upfield-shifted resonances be-



**Fig. 3.** (A to C) Views of  $C_{2\nu}$ - $C_{78}$  (A) onto the flat face shaped by a coronene subunit, (B) perpendicular to the symmetry plane, and (C) onto one of the two caps. The starred C atoms are corannulene-type sites, and the C atoms marked by a circled × are pyrene-type sites. (D) View of  $D_3=C_{78}$  (A) onto one of the three symmetry-related, smoothly curved faces that shows corannulene-type sites as starred atoms and pyrene-type sites marked by a circled ×.

tween 132 and 135 ppm are observed in the spectrum. We tentatively assign the four signals between 136 and 141 ppm to the four corannulene-type sites and the six residual, least-shielded resonances to the six pyracylene-type sites in the molecule.



The two  $C_{78}$ -isomers differ considerably in their optical properties. A solution of the  $C_{2\nu}$ isomer (in CH<sub>2</sub>Cl<sub>2</sub>) is chestnut brown, whereas a solution of the  $D_3$ -compound has a more golden-yellow color. The electronic absorption spectra of the two molecules are distinctively different (Fig. 4). Whereas the longest wavelength band in the  $C_{2\nu}$ -isomer appears at ~700 nm with the end-absorption tailing to ~900 nm, the  $D_3$ -isomer shows a set of distinct bands between 700 and 850 nm.

Why do the experimental results differ from the calculations by Manolopoulos and Fowler, who predicted the preferential formation of the  $D_{3h}$ -isomer (18), and why do

**Table 2.** Line positions in the <sup>13</sup>C NMR spectra of  $C_{2\nu}$ - $C_{78}$  and  $D_3$ - $C_{78}$  in CS<sub>2</sub>. Centers of gravity in the spectra: C<sub>60</sub>, 143.2; C<sub>70</sub>, 145.0; C<sub>76</sub>, 142.7; C<sub>2\nu</sub>-C<sub>78</sub>, 141.9; and D<sub>3</sub>-C<sub>78</sub>, 141.1.

	$C_{2\nu}$ - $C_{78}$		D <sub>3</sub> -C <sub>78</sub> *
δ (ppm)	Integrated intensity	Carbons (no.)	δ (ppm)
132.31	4.1	4	132.18
132.63	2.3	2	132.90
133.98	4.2	4	134.85
136.49	3.9	4	139.55
137.67	3.9	4	140.45
138.08	3.9	4	140.82
138.39	6.7†	4	140.91
138.41		4	141.83
142.19	1.7	2	142.88
143.34	4.2	4	144.53
143.89	3.9	4	145.45
144.49	4.5	4	148.14
144.72	4.5	4	149.45
144.89	4.1	4	
144.99	1.9	2	
145.96	3.8	4	
146.04	4.7	4	
146.12	4.2	4	
146.99	4.1	4	
147.56	4.6	4	
147.62	4.7	4	

\*The integrated intensities are not inconsistent with 13  $\times$  6 C signals; high uncertainties of individual values are due to a poor signal-to-noise ratio of the small resonances of  $D_3$ -C<sub>78</sub> in the spectrum.  $\dagger$ Two peaks.

we observe the formation specifically of the  $C_{2\nu}$ - and  $D_3$ -isomers? The latter question of isomeric preference was until now irrelevant in fullerene chemistry, because only one IPRsatisfying structure exists for C<sub>60</sub> and C<sub>70</sub>. The prediction of  $D_{3h}$ -C<sub>78</sub> as the most stable structure was predominantly based on the qualitative MO theory calculation of a large gap between the highest occupied MO and the lowest unoccupied MO; it allows no comparative estimate of the strain among the IPRsatisfying isomers. We performed MM3 forcefield calculations (21, 22) on the five IPRsatisfying C78 fullerene structures and found that the two isolated isomers are much more



Fig. 4. Optical spectra recorded in  $CH_2Cl_2$  for (A)  $C_{2\nu}$ - $\hat{C}_{78}$  and (B)  $D_3$ - $C_{78}$  (path length of 1 cm). Absorption maxima  $\lambda$  (nanometers) and absolute extinction coefficients  $\varepsilon$  (liter mol<sup>-1</sup> cm<sup>-1</sup>) for  $C_{2\nu}$ - $C_{78}$ :  $\lambda$  696 ( $\varepsilon$  3,400); 638 (4,000); 528 (11,500); 424 (23,800); 390 shoulder (sh) (25,500); 368 sh (30,300); 359 (30,800); 325 (42,700); and 308 sh (44,400). Absorption maxima of D<sub>3</sub>-C<sub>78</sub> (λ) 820, 768, 757, 734, 700, 472, 362 sh, 356, 322, and 276. The concentration of the  $D_3$ - $C_{78}$  sample is unknown.

stable than the one predicted by qualitative MO theory (Table 1). Also, model building clearly shows that the  $D_{3h}$ -isomer with three flat coronene faces separated by rather sharp edges is much more strained than the  $C_{2\nu}$ isomer, which has only one quasi-planar coronene face (Fig. 3) and a more uniform curvature over two thirds of the helmet-shaped ball surface. Strain is better delocalized in the  $C_{2\nu}$ than in the  $D_{3h}$ -isomer.

Beyond energetics and stability, an explanation for the formation specifically of  $C_{2\nu}$ - and  $D_3$ - $C_{78}$  became apparent when we explored possible mechanisms of interconversion among the five C78 fullerene structures. The predicted  $D_{3h}$ - and the observed dominant  $C_{2\nu}$ -isomers are closely related: They are interchangeable by 90° rotation of a single  $C_2$ -unit in the pyracylene rearrangement (Fig. 5), which was first suggested by Stone and Wales (23) for C<sub>60</sub> and subsequently proposed as the first step in the degradation of  $C_{60}$  to smaller fullerenes through consecutive  $C_2$ -losses (24). The pyracylene rearrangement is a general interconversion route on the C78 fullerene hypersurface; as many as four isomers of C78 are interchangeable in single-step rearrangements (Eq. 1):

$$D_{3h} \rightleftharpoons C_{2\nu} \rightleftharpoons C_{2\nu'} \rightleftharpoons D_{3h'} \qquad (1)$$

In the  $D_{3h}$ -structure, the orientation of all three central pyracylene subunits (Fig. 5) generates a central circular acene of nine fused benzene rings. A single pyracylene rearrangement leads to the  $C_{2\nu}$ -structure (Fig. 5), a second to the  $C_{2\nu}$ '-structure, and a third to the  $D_{3h}$ '-structure. In the latter isomer, all three central pyracylenes now take the orientation shown in Fig. 5 for the  $C_{2\nu}$ -structure. The caps in all four fullerenes are structurally identical (Fig. 3C) and remain unaffected by the rearrangement. In contrast, no similar simple interconversion is possible between any of the four isomers in Eq. 1 and the chiral  $D_3$ -isomer that we isolated as the minor component. It becomes clear that two fullerene C78-forming channels are active in the production process. One leads into the manifold of four isomers shown in Eq. 1 and ultimately, under thermodynamic control during the "cooling period" of the production process



Fig. 5. Interconversion between the  $C_{2\nu}$ - and  $D_{3h}$ -isomers of C78 through the 4epyracylene rearrangement.

(10), to exclusively the most stable  $C_{2\nu}$ -isomer (25). A second product channel leads to the minor  $D_3$ -product, which can be isolated because there exists no good mechanism for conversion into the more stable  $C_{2\nu}$ -isomer. We believe that we have discovered a general selection rule for predicting which isomers of the higher fullerenes have a high probability for isolation. This rule should facilitate their structural characterization, particularly since the number of IPR-satisfying fullerene isomers increases rapidly with larger molecular size. For C<sub>84</sub>, Manolopoulos and Fowler calculated 24 isomers, and this number increases to 46 for C<sub>90</sub> (26). As illustrated above for C78, molecular mechanics calculations in combination with the analysis of isomer interconversions should allow us to predict how many product channels exist for a higher fullerene and which isomers one can expect to isolate.

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   Although the large difference in MM3 heat of forma-
- tions,  $\Delta(\Delta H_{\rm f}^{\rm o}) = 6.6$  kcal mol<sup>-1</sup>, between the  $C_{2\nu}$ . and  $D_{3h}$ -isomers is a significant value, the calculated difference of 1.4 kcal mol<sup>-1</sup> between the  $C_{2\nu}$ -isomers is not very large, and the stability sequence among the two  $C_{2\nu}$ -isomers might actually be reversed.
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