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Absolute Configuration of D_2-Symmetric Fullerene C_{84}

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The number of chiral fullerene isomers predicted by the isolated pentagon rule[1,2] (IPR) rapidly increases with the number of carbon atoms.[3] For example, while there is a single chiral isomer of C_{76}, there are already 10 of C_{84} and 75 of C_{92}. It has early been recognized[4] that electronic circular dichroism (CD) spectra of inherently chiral fullerenes depend sensitively on the electronic structure. However, extensive use for structure elucidation has largely been prevented by the difficulty of obtaining enantiomeric resolution on the experimental side, and by a lack of reliable theoretical predictions. Recently, Diederich and co-workers[5] have introduced a promising strategy for the isolation of enantiomerically pure fullerenes based on the separation of diastereomeric Bingel adducts. At the same time, the development of time-dependent density functional theory (TDDFT)[6] has led to a computational method permitting large-scale simulation of absorption and CD spectra with often quantitative accuracy.[7,8] In the present communication, we assign the experimental CD spectra of D_2-C_{84}[5] by means of TDDFT calculations. In contrast to semiempirical methods,[5,9] TDDFT is accurate enough to determine the absolute configuration of D_2-C_{84}.

Preparation of pure D_2-C_{84} was achieved only in 1998.[10] Assignment of the structure based on the experimental ^{13}C NMR spectrum is difficult since there are four D_2-symmetric IPR isomers with the same NMR pattern.[10,11] However, the good agreement between the experimental IR spectrum[12] and recent DFT calculations[13] indicates that the observed D_2-C_{84} is the isomer shown in Figure 1. This assignment is strongly supported by the present results.

Figure 2 shows the simulated CD spectrum[14] compared to the experimental one by Diederich and co-workers.[5] Considering the systematic error inherent in the method as well as experimental inaccuracies, agreement between the simulation and experiment is surprisingly good. All features of the experimental spectrum are qualitatively reproduced by the calculations. We assign the bands at wavelengths larger than 450 nm to the most intense transitions in Table 1. Below 450 nm, the spectrum becomes increasingly dense, and assignment to individual states is no longer possible.

The absolute configuration of fullerenes is conveniently characterized by using the configurational descriptor system proposed by Thilgen, Herrmann, and Diederich.[18] The calculated CD spectrum belongs to the (^fA) enantiomer, while for (^fC)-D_2-C_{84}, one would obtain the spectrum reflected at the abscissa. Thus, there can be little doubt that the experimental spectrum belongs to the enantiomer with (^fA) configuration.

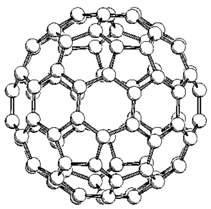

Figure 1. Calculated equilibrium structure of (^fA)-D_2-C_{84}.

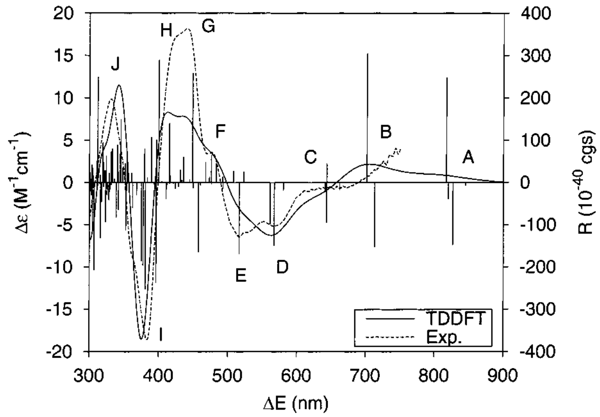

Figure 2. Simulated CD spectrum of (^fA)-D_2-C_{84} compared to experiment. ϵ denotes the molar decadic absorption coefficient, R the rotatory strength, and ΔE the excitation energy. Calculated $\Delta\epsilon$ values were scaled by 1/14 to match the experimental intensities.

Table 1. Assignment of the CD spectrum of (^fA)-D_2-C_{84}[a]

feature	transition	ΔE/nm	R/10^{-40} cgs
A	1 B_3	827	−148
	2 B_1	817	248
B	3 B_1	713	−153
	3 B_3	702	305
C	4 B_1	644	45
	3 B_2	643	−96
D	5 B_1	567	−150
	5 B_2	561	−99
E	5 B_3	516	−170
F	7 B_3	483	46
	8 B_3	476	65
	8 B_1	467	48
G	9 B_1	457	−165
	10 B_3	449	259

[a] ΔE and R denote calculated excitation energies (blue-shifted by 0.4 eV) and rotatory strengths.

Our conclusions are not affected by the observation that we were not able to reproduce the experimentally observed intensities. In fact, the simulated spectrum in Figure 2 had to be scaled by a factor 1/14 to fit the experimental data. While errors in calculated rotatory strengths of individual excited states can reach 50% or more due to vibronic coupling, solvent effects, and inaccuracies of TDDFT, a deviation by a global factor of more than 2−4 is uncommon. In exploratory calculations for C_{76}, we find similar intensities as in C_{84}, and good agreement with experiment.[19] There is no obvious reason TDDFT should fail to predict absolute CD intensities in

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C_{84}. Continued experimental as well as theoretical effort will be necessary to resolve this discrepancy.

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