SUPPORTING INFORMATION

Is C_{50} a superaromat? Evidence from electronic structure and ring currents calculations†

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Spherical parentages: D_3 isomer

Percentages for S (L=0, Table S1), P (L=1, Table S1), D (L=2, Table S2), F (L=3, Table S3) and G (L=4, Table, S4) spherical harmonics overlap with all HMOs have been calculated, however only the significant ones are displayed, which coincide with the shells. The sum over the overlap percentages of one HMO and the spherical harmonics of the same L is indicated in the rightmost columns, and the total overlap percentage of one spherical harmonic with the *shell* HMOs is shown on the last row of each table.

MO	s	p_x	p_y	p_z	$\sum$ (%)
1	100	0	0	0	100
2	0	11.223	88.537	0	99.78
3	0	88.552	11.216	0	99.77
4	0	0	0.023	99.734	99.76
$\sum$ (%)	100	99.775	99.753	99.734	

Table S1 Overlap percentage of D_3 isomer molecular orbitals 1, 2, 3 and 4 with the real spherical harmonics Y_0^{00} (s), Y_1^{11} (p_x), $Y_1^{1,-1}$ (p_y) and Y_1^{10} (p_z).

MO	d_{z^2}	d_{yz}	d_{xz}	d_{xy}	$d_{x^2-y^2}$	$\sum$(%)
5	0.004	12.525	54.685	27.838	7.3821	102.43
6	0.051	52.534	13.3	6.5967	30.015	102.50
7	0.012	20.615	12.21	25.253	37.52	95.610
8	0.015	13.085	18.631	39.558	24.333	95.623
9	99.363	0.064	0.001	0	0	99.430
$\sum$ (%)	99.445	98.823	98.827	99.246	99.250	

Table S2 Overlap of D_3 isomer molecular orbitals 5, 6, 7, 8 and 9 with the real spherical harmonics Y_2^{20} (d_{z^2}), $Y_2^{2,-1}$ (d_{yz}), Y_2^{21} (d_{xz}), $Y_2^{2,-2}$ (d_{xy}) and Y_2^{22} ($d_{x^2-y^2}$).

MO	f_{z^3}	$f_{y(3x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{z(x^2-y^2)}$	f_{xyz}	f_{yz^2}	f_{xz^2}	∑(%)
10	28.725	75.821	0	0.028	0	0.045	0	104.62
11	0	0	0.034	16.732	80.308	2.402	7.101	98.060
12	0.014	0.03	0	69.983	8.8705	9.387	1.579	98.387
13	0	0	97.881	0	0.0323	0	0	97.914
14	68.819	22.677	0	0.007	0	0.11	0	91.616
15	0.035	0	0	1.271	0.0554	12.923	76.1937	96.038
16	0.084	0	0	7.829	6.619	73.294	13.247	95.519
∑ (%)	97.677	98.528	97.915	95.85	95.885	98.161	98.1207	

Table S3 Overlap of D_3 isomer molecular orbitals 10, 11 , 12 ,13, 14, 15 and 16 with the real spherical harmonics Y_3^{30} (f_{z^3}), $Y_3^{3,-3}$ ($f_{y(3x^2-y^2)}$), Y_3^{33} ($f_{x(x^2-3y^2)}$), Y_3^{32} ($f_{z(x^2-y^2)}$), $Y_3^{3,-2}$ (f_{xyz}), $Y_3^{3,-1}$ (f_{yz^2}) and Y_3^{31} (f_{xz^2}).

MO	g_{z^4}	g_{z^3x}	g_{z^3y}	$g_{z^2(x^2-y^2)}$	g_{z^2xy}	g_{zx^3}	g_{zy^3}	$g_{x^4+y^4}$	$g_{xy(x^2-y^2)}$	∑(%)
17	0	0	0	0.002	0.079	89.754	0	0.001	0.046	89.88
18	0.002	0.081	0.895	66.7979	3.079	0.002	0.11	25.790	1.216	97.97
19	0	2.481	0.067	3.078	65.660	0.014	0.018	1.209	25.84	98.36
20	96.854	0.01	0.337	0	0	0	0.057	0	0	97.25
21	0	0.018	0.005	4.471	18.475	0.063	0	12.442	51.159	86.63
22	0	0.001	0.04	18.47	4.459	0.034	0	51.196	12.442	86.62
23	0.069	18.654	47.601	0.135	0.309	0	14.505	0.264	0.132	81.66
24	0.055	35.707	30.633	0.197	0.488	0	13.993	0.317	0.257	81.64
25	0.03	23.353	0.425	0.092	0.421	0	64.123	0.056	0.205	88.70
∑(%)	97.01	80.30	80.00	93.24	92.97	89.86	92.80	91.27	91.29	

Table S4 Overlap of D_3 isomer molecular orbitals 17-25 with the real spherical harmonics Y_4^{40} (g_{z^4}), Y_4^{41} (g_{z^3x}), $Y_4^{4,-1}$ (g_{z^3y}), Y_4^{42} ($g_{z^2(x^2-y^2)}$), $Y_4^{4,-2}$ (g_{z^2xy}), Y_4^{43} (g_{zx^3}), $Y_4^{4,-3}$ (g_{zy^3}), Y_4^{44} ($g_{x^4+y^4}$) and $Y_4^{4,-4}$ ($g_{xy(x^2-y^2)}$).

Spherical parentages: D_{5h} isomer

Analogous calculations have been performed for the D_{5h} isomer.

MO	*s*	p_x	p_y	p_z	∑ (%)
1	100	0	0	0	100
2	0	54.517	45.361	0	99.87
3	0	45.36	54.517	0	99.87
4	0	0	0	99.97	99.97
∑ (%)	100	99.87	99.87	99.97	

Table S5 Overlap percentage of D_{5h} isomer molecular orbitals 1, 2, 3 and 4 with the real spherical harmonics Y_0^{00} (s), Y_1^{11} (p_x), $Y_1^{1,-1}$ (p_y) and Y_1^{10} (p_z).

MO	d_{z^2}	d_{yz}	d_{xz}	d_{xy}	$d_{x^2-y^2}$	∑(%)
5	0	0	0	3.429	94.00	97.43
6	0	0	0	94.008	3.428	97.43
7	99.125	0	0	0	0	99.12
8	0	53.939	45.7	0	0	99.63
9	0	45.708	53.947	0	0	99.65
∑ (%)	99.12	99.64	99.64	97.43	97.43	

Table S6 Overlap of D_{5h} isomer molecular orbitals 5, 6, 7, 8 and 9 with the real spherical harmonics Y_2^{20} (d_{z^2}), $Y_2^{2,-1}$ (d_{yz}), Y_2^{21} (d_{xz}), $Y_2^{2,-2}$ (d_{xy}) and Y_2^{22} ($d_{x^2-y^2}$).

$\|MO>$	f_{z^3}	$f_{y(3x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{z(x^2-y^2)}$	f_{xyz}	f_{yz^2}	f_{xz^2}	$\sum$(%)
10	99.367	0	0	0	0	0	0	99.36
11	0	27.807	65.134	0	0	0	0	92.94
12	0	65.131	27.802	0	0	0	0	92.93
13	0	0	0	98.318	1.093	0	0	99.41
14	0	0	0	1.092	98.317	0	0	99.40
15	0	0	0	0	0	40.019	58.041	98.06
16	0	0	0	0	0	58.025	40.002	98.02
$\sum$ (%)	99.367	92.938	92.936	99.4101	99.4101	98.044	98.043	

Table S7 Overlap of D_{5h} isomer molecular orbitals 10, 11 , 12 ,13, 14, 15 and 16 with the real spherical harmonics Y_3^{30} (f_{z^3}), $Y_3^{3,-3}$ ($f_{y(3x^2-y^2)}$), Y_3^{33} ($f_{x(x^2-3y^2)}$), Y_3^{32} ($f_{z(x^2-y^2)}$), $Y_3^{3,-2}$ (f_{xyz}), $Y_3^{3,-1}$ (f_{yz^2}) and Y_3^{31} (f_{xz^2}).

$\|MO>$	g_{z^4}	g_{z^3x}	g_{z^3y}	$g_{z^2(x^2-y^2)}$	g_{z^2xy}	g_{zx^3}	g_{zy^3}	$g_{x^4+y^4}$	$g_{xy(x^2-y^2)}$	$\sum$(%)
17	0	0	0	0	0	0	0	0.172	94.203	94.37
18	0	0	0	0	0	0	0	94.204	0.173	94.37
19	0	48.139	44.136	0	0	0	0	0	0	92.27
20	0	44.127	48.129	0	0	0	0	0	0	92.25
21	0	0	0	0	0	92.434	0.896	0	0	93.33
22	0	0	0	0	0	0.897	92.437	0	0	93.33
23	0	0	0	2.928	88.754	0	0	0	0	91.68
24	0	0	0	88.752	2.927	0	0	0	0	91.67
25	0	0	0	0	0	0	0	0	0	0
$\sum$ (%)	0	92.26	92.26	91.68	91.68	93.33	93.33	94.37	94.37	
26	92.161	0		0	0	0	0	0	0	92.161
$\sum$ (%)	92.161	92.266	92.26	91.68	91.68	93.33	93.33	94.37	94.37	

Table S8 Overlap of D_{5h} isomer molecular orbitals 17-26 with the real spherical harmonics Y_4^{40} (g_{z^4}), Y_4^{41} (g_{z^3x}), $Y_4^{4,-1}$ (g_{z^3y}), Y_4^{42} ($g_{z^2(x^2-y^2)}$), $Y_4^{4,-2}$ (g_{z^2xy}), Y_4^{43} (g_{zx^3}), $Y_4^{4,-3}$ (g_{zy^3}), Y_4^{44} ($g_{x^4+y^4}$) and $Y_4^{4,-4}$ ($g_{xy(x^2-y^2)}$).

CASSCF results for D_{5h}

The energy differences between A and B D_{5h} isomers obtained from various CASSCF calculations are shown in Table S9. In order to recover a possible stable structure lying between A and B, a series of CASSCF (6,6) 6-31 g calculations (ground state and averaged to the first two singlet states) have been performed. The geometries used are such that:

$$X_i = \lambda X_A + (1-\lambda)X_B$$

Where X_n (n = A, B, I) are, respectively, the coordinates of A, B and the intermediate structure. The resulting energies are shown in Fig. S1.

GS CASSCF	Basis set	E_{A-B} (kcal/mol)
6,6	STO-3G	13.04
	6-31G	7.96
18,12	STO-3G	7.69
	6-31G	3.05

Table S9 Energy difference between A and B isomers of D_{5h} for ground state CASSCF(6,6) and (18,12) with STO-3G and 6-31G basis sets.

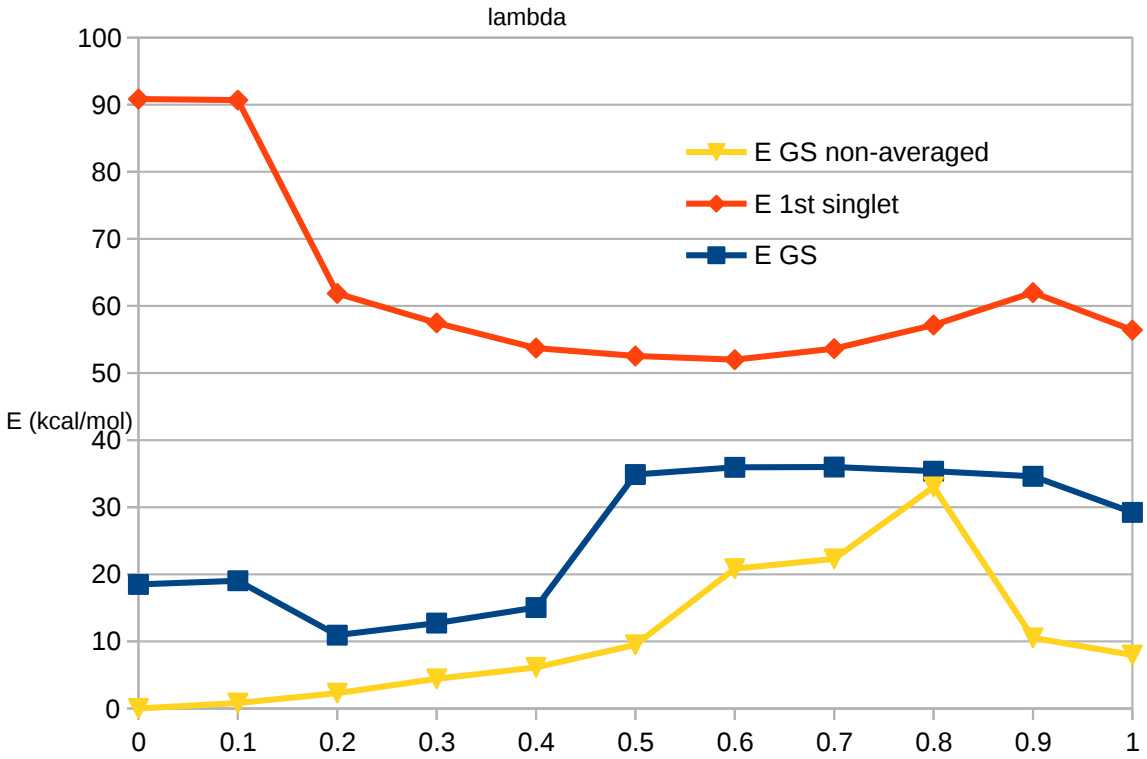

Fig. S1 GS and state average CASSCF(6,6) energies for A, B and their interpolated geometries.