Electronic Supporting Information:

Core-electron contributions to the molecular magnetic response

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Table S1. Energy gaps in eV between the lowest occupied σ-orbital and the highest occupied core-electron orbital ($\Delta_{L\sigma\text{-}Hcore}$) computed at PBE0-D3/def2-TZVP level.

Molecule	$\Delta_{L\sigma\text{-}Hcore}$
Benzene	254.2
Corannulene (C_{5v})	252.4
Corannulene (D_{5h})	252.0
C_{60}	252.0
[14]helicene	252.7

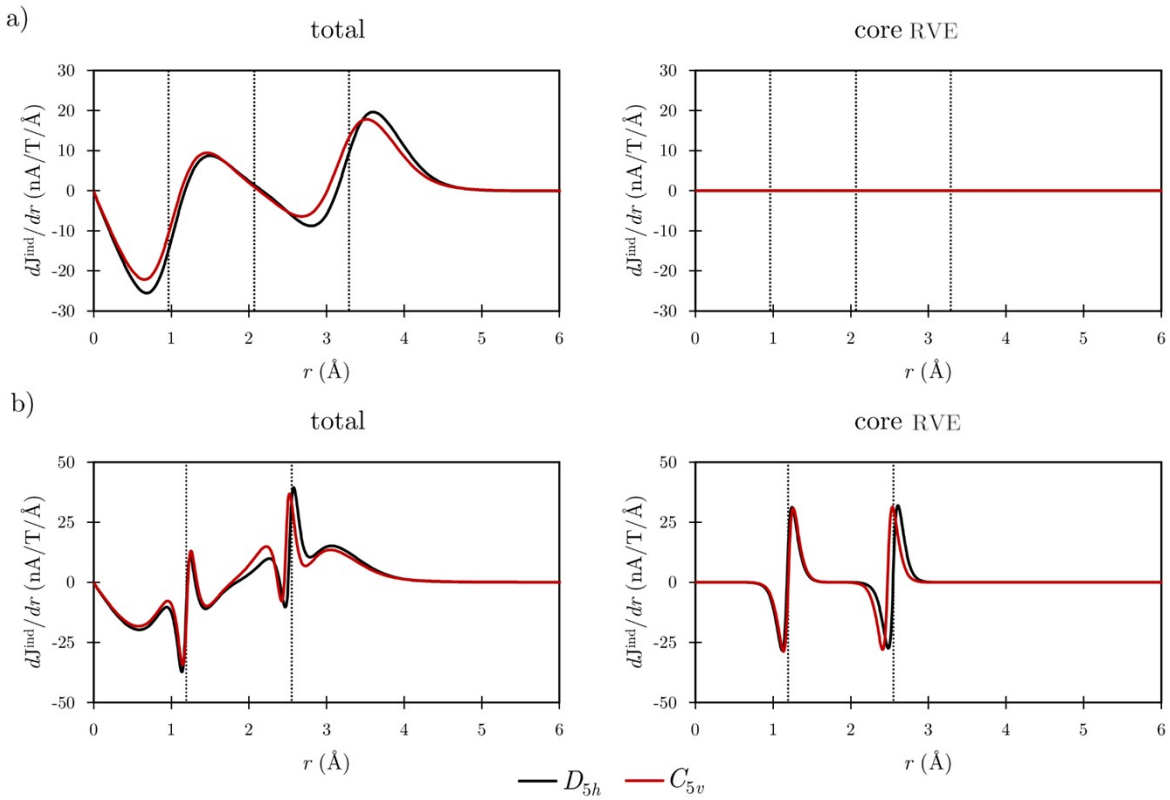

Figure S1. dJ^{ind}/dr plots computed along a plane crossing: a) the C-C bonds and b) the carbon nuclei for corannulene isomers. The vertical dotted lines show the *r* values corresponding to a) the innermost C-C bond, the center of the 6-MR and the outermost C-C bond, respectively. In b), the dotted lines correspond to the carbon nuclei.

Table S2. GIAO-CMO analysis of $B^{ind}_z(0)$ and NICS(0) values (in parentheses) in ppm calculated at the PBE0/TZ2P level with ADF's NMR module at the center of benzene, the centers of 5-MR and 6-MR rings of corannulene structures (D_{5h} and C_{5v}), the center of C_{60} cage, and the centers of each 6-MR of [14]helicene labeled from A to G from the outermost to the middle ring.

Molecule		core CMO	core RVE	σ CMO	σ RVE	core + σ	π	Total
Benzene		-12.37	0.03	34.20	21.81	21.83	-36.84	-15.01
		(-4.28)	(-0.44)	(21.06)	(17.22)	(16.78)	(-24.66)	(-7.88)
Corannulene D_{5h}	5-MR	-22.91	0.18	54.42	31.32	31.50	29.34	60.84
		(-7.95)	(-0.37)	(28.51)	(20.92)	(20.55)	(-7.61)	(12.95)
	6-MR	-15.90	0.18	40.68	24.60	24.78	-24.37	0.41
		(-5.50)	(-0.32)	(21.84)	(16.67)	(16.34)	(-20.94)	(-4.60)
Corannulene C_{5v}	5-MR	-22.16	0.35	33.21	10.71	11.05	41.30	52.36
		(-8.65)	(-0.29)	(13.10)	(4.74)	(4.45)	(4.70)	(9.14)
	6-MR	-16.27	0.08	31.44	15.09	15.17	-18.64	-3.47
		(-6.56)	(-0.33)	(17.64)	(11.41)	(11.08)	(-17.34)	(-6.26)
C_{60}		-28.62	-0.03	8.76	-19.84	-19.86	15.56	-4.30
		(-28.64)	(-0.02)	(8.78)	(-19.84)	(-19.86)	(15.57)	-4.29)
[14]helicene	A	-19.03	-0.05	8.38	-10.61	-10.65	-10.00	-20.65
		(-7.24)	(-0.40)	(6.14)	(-0.70)	(-1.10)	(-9.14)	(-10.24)
	B	-21.95	-0.03	9.52	-12.39	-12.42	1.12	-11.30
		(-8.91)	(-0.41)	(5.55)	(-2.96)	(-3.36)	(-4.12)	(-7.49)
	C	-22.63	-0.05	5.70	-10.86	-16.93	5.63	-11.30
		(-9.87)	(-0.42)	(2.78)	(-6.68)	(-7.09)	(-0.18)	(-7.27)
	D	-22.06	-0.02	3.77	-18.26	-18.28	9.15	-9.13
		(-10.55)	(-0.45)	(0.58)	(-9.52)	(-9.96)	(3.61)	(-6.35)
	E	-22.13	-0.05	6.93	-15.15	-15.20	8.90	-6.30
		(-11.79)	(-0.50)	(0.70)	(-10.60)	-11.09	(5.89)	(-5.20)
	F	-23.13	-0.12	4.98	-18.03	-18.15	8.87	-9.28
		(-14.08)	(-0.56)	(0.06)	(-13.46)	(-14.02)	(7.67)	(-6.35)
	G	-24.52	-0.36	-7.75	-31.90	-32.26	20.30	-11.97
		(-15.98)	(-0.62)	(-4.29)	(-19.65)	(-20.27)	(13.28)	(-6.99)