Electronic Supplementary Information (ESI)

for

Aromaticity of strongly bent benzene rings: persistence of a diatropic ring current and its shielding cone in [5]paracyclophane†

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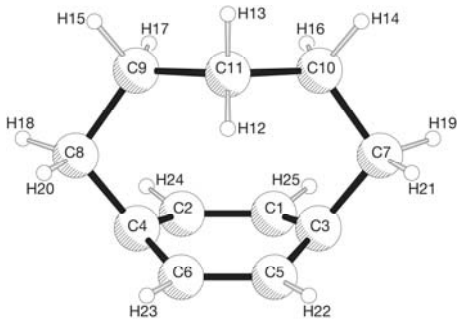
Table S1. RHF/6-31G** cartesian coordinates (in a.u.) for [5]paracyclophane (**1**, Cs symmetry).[a,b]

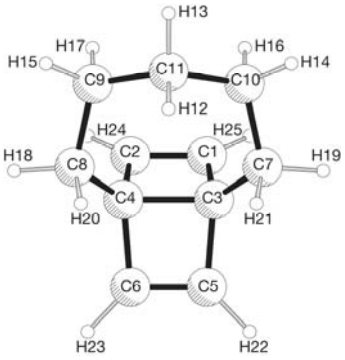


Atom	x	y	Z
C1	1.2957189	2.2875915	-2.2223141
C2	-1.2957189	2.2875915	-2.2223141
C3	2.5592490	0.0038648	-1.7631529
C4	-2.5592490	0.0038648	-1.7631529
C5	1.3165327	-2.2026540	-2.3866116
C6	-1.3165327	-2.2026540	-2.3866116
C7	4.2945874	-0.0797691	0.4925069
C8	-4.2945874	-0.0797691	0.4925069
C9	-2.5877435	0.4693392	2.8753773
C10	2.5877435	0.4693392	2.8753773
C11	0.0000000	-0.9475084	3.3172195
H12	0.0000000	-2.7574002	2.3631237
H13	0.0000000	-1.4018318	5.3179054
H14	3.7639727	0.0836611	4.5163972
H15	-3.7639727	0.0836611	4.5163972
H16	2.2274896	2.4893183	2.9114415
H17	-2.2274896	2.4893183	2.9114415
H18	-5.7854776	1.3335284	0.4639859
H19	5.7854776	1.3335284	0.4639859
H20	-5.1848625	-1.9205230	0.6697054
H21	5.1848625	-1.9205230	0.6697054
H22	2.2850914	-3.9880089	-2.2563028
H23	-2.2850914	-3.9880089	-2.2563028
H24	-2.2969218	4.0539304	-2.0722341
H25	2.2969218	4.0539304	-2.0722341

[a] In this orientation, the *z*-axis is almost perpendicular to the C_1-C_2-C_5-C_6 (benzenoid)-plane (see also Fig. 1). The reference plane for the current-density calculations is parallel to *xy*, at z = -2.30446285 a.u.

[b] RHF/6-31G** total energy: -424.621597 a.u.. The Hessian gives no imaginary frequencies.

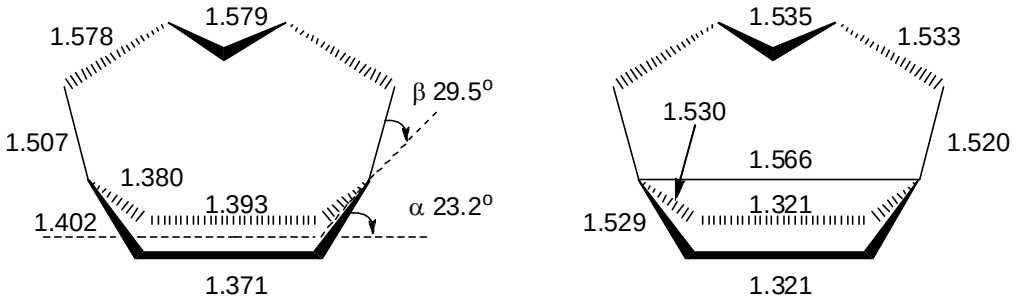
Table S2. RHF/6-31G** cartesian coordinates (in a.u.) for 1,4-pentamethylene Dewar benzene (**2**, C_s symmetry).[a,b]



Atom	x	y	Z
C1	-2.8146390	1.2485978	-2.0283481
C2	-2.8146390	-1.2485978	-2.0283481
C3	0.0176937	1.4796811	-1.5020207
C4	0.0176937	-1.4796811	-1.5020207
C5	1.7092504	1.2480866	-3.8350164
C6	1.7092504	-1.2480866	-3.8350164
C7	0.9391716	3.0711120	0.7049794
C8	0.9391716	-3.0711120	0.7049794
C9	-0.2868389	-2.4775493	3.2620830
C10	-0.2868389	2.4775493	3.2620830
C11	0.5599069	0.0000000	4.5103372
H12	2.6127988	0.0000000	4.6730379
H13	-0.1582350	0.0000000	6.4369156
H14	0.1808326	4.0084643	4.5520212
H15	0.1808326	-4.0084643	4.5520212
H16	-2.3333071	2.4911414	3.0772951
H17	-2.3333071	-2.4911414	3.0772951
H18	0.5999844	-5.0492097	0.2449845
H19	0.5999844	5.0492097	0.2449845
H20	2.9789694	-2.8688999	0.8712550
H21	2.9789694	2.8688999	0.8712550
H22	2.5297992	2.6477014	-5.0605951
H23	2.5297992	-2.6477014	-5.0605951
H24	-4.2511077	-2.6443303	-2.3810120
H25	-4.2511077	2.6443303	-2.3810120

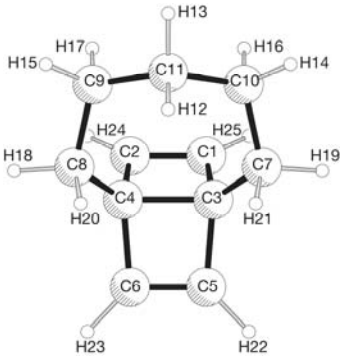
[a] In this orientation, the *z*-axis is almost perpendicular to the C_1-C_2-C_5-C_6 plane (see also Fig. S1).
[b] RHF/6-31G** total energy: -424.603570 a.u.. The Hessian gives no imaginary frequencies.

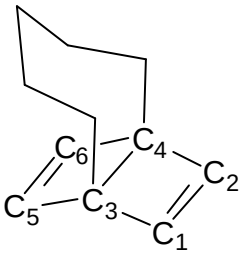
Fig. S1. RHF/6-31G** optimised carbon-carbon bond lengths (in Å) of [**5**]paracyclophane (**1**, C_s symmetry) and its valence isomer 1,4-pentamethylene Dewar benzene (**2**, C_s symmetry).



1 **2**

Fig. S2. CTOCD-*DZ*/6-31G**//RHF/6-31G** π current-density maps for the 1,4-pentamethylene Dewar benzene (**2**, see also Ref. 14 of the paper). Plotting planes (a), (b) and (c) are defined in the diagram – (a) and (b) are planes parallel to the respective halves of the bent Dewar benzene ring at $1a_0$ below the plane of carbon nuclei, and (c) is at $1a_0$ below the four olefinic carbon nuclei of the bent Dewar benzene ring.





(a) plane a: parallel and 1 a_0 below the plane containing C3, C4, C5 and C6

(b) plane b: parallel and 1 a_0 below the plane containing C1, C2, C3 and C4

(c) plane c: parallel and 1 a_0 below the plane containing C1, C2, C5 and C6

(a) (b) (c)