Electronic Supplementary Information

by

The Homotropenylium Cation: A System with a Pinched π Ring Current †

Mark Lillington,[1] Remco W. A. Havenith,[2,3] Patrick W. Fowler,[1]* Jon Baker,[4,‡] and Leonardus W. Jenneskens[5]*

[1]*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.*

[2]*Theoretical Chemistry, Zernike Institute for Advanced Materials, Rijksuniversiteit Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.*

[3]*Ghent Quantum Chemistry Group, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 – Building S3, B-9000 Gent, Belgium.*

[4]*Parallel Quantum Solutions, 2013 Green Acres Road, Suite A Fayetteville, Arkansas 72703, U.S.A.*

[5]*Organic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands.*

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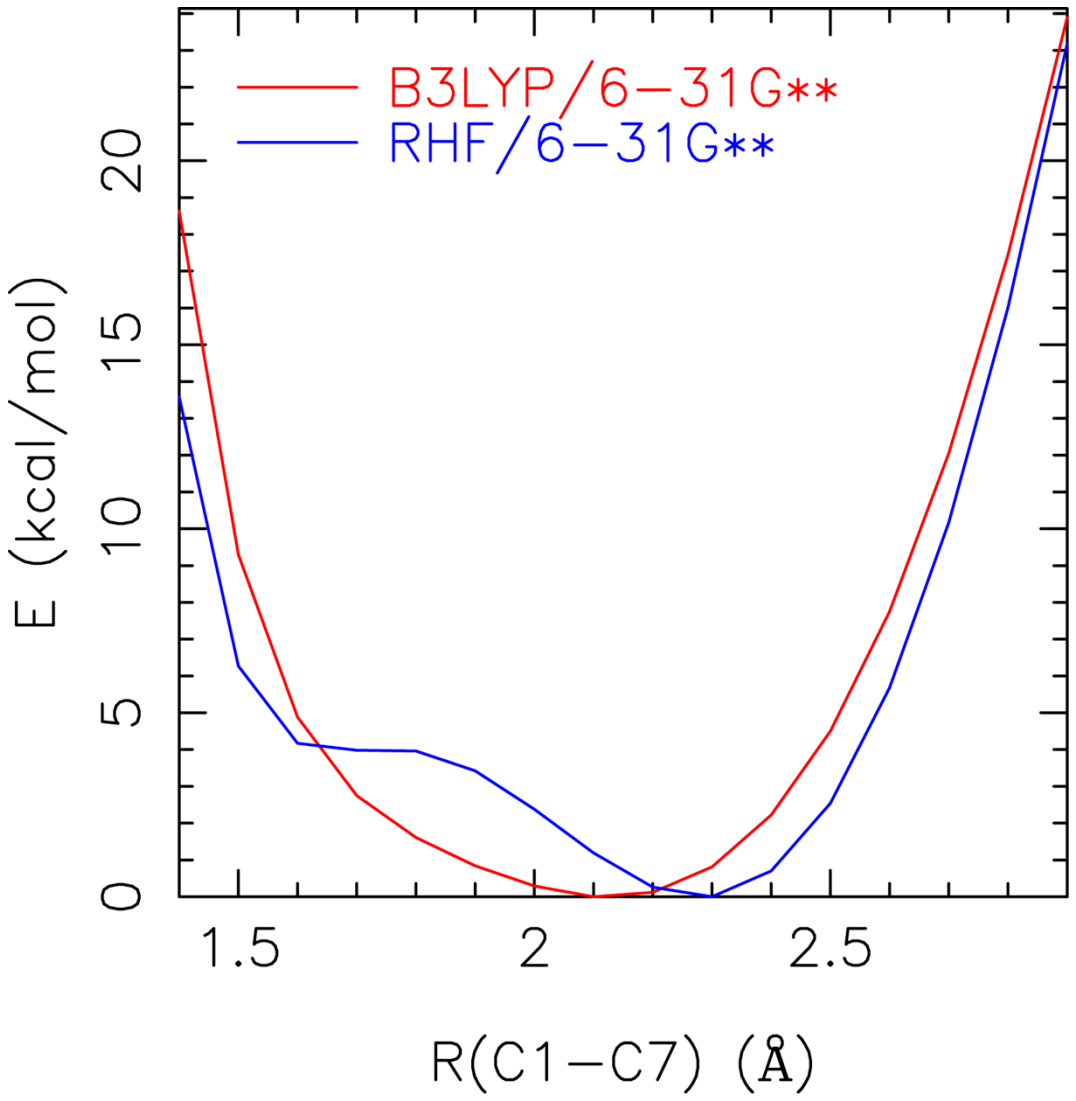

Fig. S1. Variation of the RHF/6-31G** (blue) and B3LYP/6-31G** (red) energy (*E* in kcal/mol), relative to the (global) minimum with *R* (C1···C7) (in Å) distance for the homotropenylium cation (**1**, $C_8H_9^+$). E_{rel} values are scaled either to the global RHF/6-31G** minimum (E_{tot} -307.905291 in Hartree) or the single B3LYP/6-31G** minimum (E_{tot} -309.972227 Hartree)

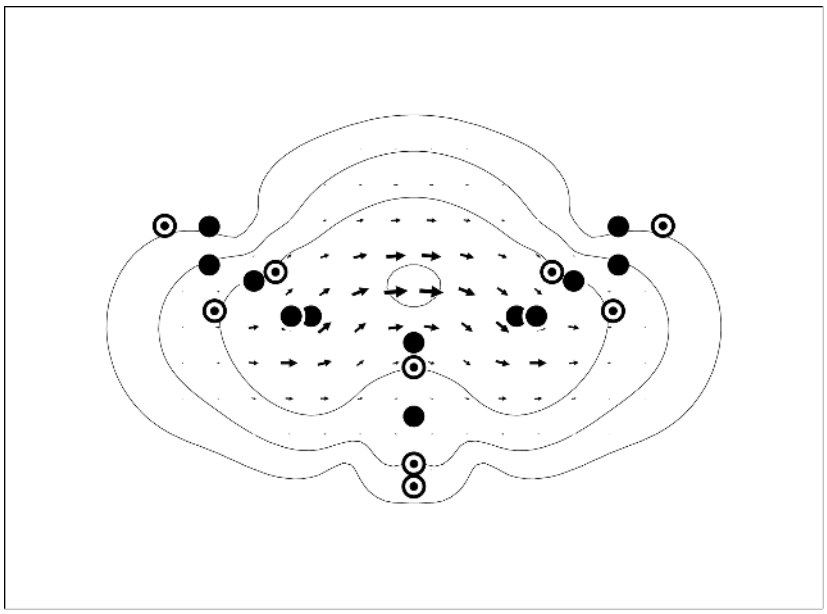

Fig. S2. A current-density map showing the current in the region of the CH_2-bridged gap between C1 and C7 in the B3LYP/6-31G** optimised homotropenylium cation (**1**, $C_8H_9^+$ with *R* (C1···C7) 2.127 Å). The total contributions from the three π-like localised occupied orbitals is shown. The current is mapped in a plane 1 a_0 from C8 *outside* (‘*exo*’) the ring, perpendicular to both the reference plane (C1, C3, C5, C7 (See Fig. 2)) and the C_s symmetry plane. The external magnetic field is parallel to the plotting plane.

Table S1. Salient structural data of (constrained) B3LYP/6-31G** optimised geometries.

R (C1···C7) [a] (in Å)	C1-C2 [b] (in Å)	C1-C8 [b] (in Å)	C2-C3 [b] (in Å)	C3-C4 [b] (in Å)
1.4	1.459	1.508	1.376	1.409
1.5	1.446	1.499	1.379	1.408
1.6	1.434	1.492	1.382	1.407
1.7	1.422	1.487	1.385	1.405
1.8	1.410	1.484	1.389	1.404
1.9	1.400	1.483	1.394	1.404
2.0	1.391	1.485	1.399	1.403
2.1	1.384	1.489	1.404	1.402
2.127 [d]	***1.382***	***1.490***	***1.405***	***1.402***
2.2	1.378	1.494	1.408	1.402
2.3	1.373	1.503	1.412	1.402
2.4	1.369	1.514	1.416	1.402
2.5	1.366	1.528	1.419	1.402
2.6	1.363	1.544	1.421	1.403
2.7	1.361	1.564	1.423	1.403
2.8	1.359	1.588	1.425	1.404
2.9	1.357	1.615	1.427	1.405

Table S1 continued. Salient structural data of (constrained) B3LYP/6-31G** optimised geometries.

R (C1···C7) [a] (in Å)	∑(∠C1)$_i$ [c] (in º)	∑(∠C2)$_i$ [c] (in º)	∑(∠C3)$_i$ [c] (in º)	∑(∠C4)$_i$ [c] (in º)
1.4	345.52	359.98	359.72	359.58
1.5	349.83	359.97	359.58	359.25
1.6	353.43	359.96	359.48	358.95
1.7	356.17	359.95	359.43	358.72
1.8	357.99	359.92	359.40	358.56
1.9	359.07	359.89	359.42	358.44
2.0	359.63	359.86	359.47	358.45
2.1	359.88	359.81	359.53	358.49
2.127 [d]	***359.91***	***359.80***	***359.54***	***358.49***
2.2	359.97	359.74	359.62	358.57
2.3	360.00	359.68	359.70	358.67
2.4	360.00	359.61	359.79	358.81
2.5	360.00	359.55	359.84	358.96
2.6	360.00	359.53	359.90	359.15
2.7	360.00	359.52	359.93	359.30
2.8	360.00	359.55	359.96	359.42
2.9	360.00	359.58	359.97	359.56

[a] *R* (C1···C7): (constrained) distance between C1 and C7 (in Å, see also Fig. 2).

[b] All geometries possess C_s symmetry: C1-C2 (= C6-C7), C2-C3 (= C5-C6) and C3-C4 (= C4-C5).

[c] Sum of valence angles around C1 (= C7), C2 (= C6), C3 (= C5) or C4.

[d] In bold: salient structural data of the fully optimised B3LYP/6-31G** geometry of the homotropenylium cation (**1**, $C_8H_9^+$, E_{tot} = -309.972227 in Hartree).

Table S2. Cartesian coordinates (in a_0) of B3LYP/6-31G** optimised geometry of the homotropenylium cation **1**, $C_8H_9^+$. NIMAG = 0 and E_{tot} -309.972227 Hartree.

Atom	X	Y	Z
C	-0.836527	2.249848	-2.009708
C	-0.836527	2.249848	2.009708
C	0.967071	3.047287	0.000000
C	-0.836527	-0.110810	-3.126228
C	-0.836527	-0.110810	3.126228
C	0.534446	-2.264434	-2.397531
C	0.534446	-2.264434	2.397531
C	1.319569	-3.075547	0.000000
H	-2.164417	3.655687	-2.703245
H	-2.164417	3.655687	2.703245
H	-1.911871	-0.278894	-4.871923
H	-1.911871	-0.278894	4.871923
H	0.845398	-3.639344	3.895865
H	0.845398	-3.639344	-3.895865
H	2.361072	-4.846195	0.000000
H	1.319978	5.075514	0.000000
H	2.724177	1.970098	0.000000

Table S3. Cartesian coordinates (in a_0) of RHF/6-31G** optimised geometry (global minimum) of the homotropenylium cation **1**, $C_8H_9^+$. NIMAG = 0 and E_{tot} -307.905291 Hartree.

Atom	X	Y	Z
C	-0.855297	2.210691	-2.154677
C	-0.855297	2.210691	2.154677
C	0.782656	3.007234	0.000000
C	-0.855297	-0.131234	-3.181172
C	-0.855297	-0.131234	3.181172
C	0.590543	-2.227035	-2.372230
C	0.590543	-2.227035	2.372230
C	1.424043	-2.985638	0.000000
H	-2.088691	3.610051	-2.966452
H	-2.088691	3.610051	2.966452
H	-1.904866	-0.398655	-4.902184
H	-1.904866	-0.398655	4.902184
H	0.988329	-3.577651	3.844299
H	0.988329	-3.577651	-3.844299
H	2.541528	-4.681818	0.000000
H	1.090593	5.024810	0.000000
H	2.578751	2.030887	0.000000

Table S4. Cartesian coordinates (in a_0) of RHF/6-31G** optimised geometry (local minimum) of the homotropenylium cation **1**, $C_8H_9^+$. NIMAG = 0 and E_{tot} -307.898945 Hartree.

Atom	X	Y	Z
C	0.219321	-2.375051	-1.576172
C	0.219321	-2.375051	1.576172
C	-2.073606	-2.673646	0.000000
C	0.739920	-0.134686	-2.984300
C	0.739920	-0.134686	2.984300
C	0.219321	2.328563	-2.400247
C	0.219321	2.328563	2.400247
C	-0.162241	3.372569	0.000000
H	1.058191	-4.078640	-2.292539
H	1.058191	-4.078640	2.292539
H	1.589732	-0.462085	-4.805696
H	1.589732	-0.462085	4.805696
H	0.368775	3.668804	3.919469
H	0.368775	3.668804	-3.919469
H	-0.465092	5.384664	0.000000
H	-2.900296	-4.528666	0.000000
H	-3.395661	-1.131612	0.000000