Cyclooctatetraene in metal complexes – planar does not mean aromatic

by

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Supporting Information

Refcodes corresponding to the crystal structures selected for statistical analysis:

AHAXUC, BUCOFE, COPDCL01, CPTOMN, CPTOMN10, DAFFIA, EDUSUS, EDUTAZ, HETTUW, HETVAE, JUKLOQ, KOVMEN, LAFCIE ,LELCUA, LELCUA, LETQUW, MESQEG, MOBVEE, NEHLER, NEHLOB, NITWES, NUTHEP, QQQDBA01, RAYJIK, ROGDIA, ROGDOG, ROGDUM, ROGFAU, RUGLAG, TALSEE, TIFXAI, TPCHRH, VANXEN, XIQXIF, YEDSEG, YEDSIK, YEDSOQ, YEFZIT, YUHRUO, YUHRUO01

Table S 1. Summarized partial atomic charges corresponding to charges of individual COT rings in complexes under investigations. Values give the idea on the charge transfer between metal centre and COT ligands. (See Figure 1 of the paper for numbering scheme and ring labelling.)

		population scheme				
		Mulliken	**NPA**	**APT**	**CHelpG**	**AIM**
I	*upper lateral ring*	0.28	-0.52	-0.37	-0.38	0.90
	inner ring	-1.51	-1.60	0.31	-0.56	1.15
	lower lateral ring	0.28	-0.53	-0.37	-0.38	0.89
II	*upper ring*	-0.76	-0.05	-0.34	-0.47	0.81
	lower ring	0.15	-0.34	-0.07	-0.25	0.76
III		-0.50	-0.80	0.26	-0.23	0.83
IV		-2.02	-0.28	0.47	-0.05	0.64
V		-0.46	-0.52	-0.19	-0.31	0.55

Table S 2. Geometries and total energies of the systems studied.

COT molecule in tub conformation. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	0.66982	1.56722	0.37287
C	1.56722	0.66982	-0.37287
C	-0.66982	1.56722	0.37287
C	-1.56722	0.66982	-0.37287
C	-1.56722	-0.66982	-0.37287
C	-0.66982	-1.56722	0.37287
C	0.66982	-1.56722	0.37287
C	1.56722	-0.66982	-0.37287
H	1.17078	2.36265	0.92451
H	2.36265	1.17078	-0.92451
H	-1.17078	2.36265	0.92451
H	-2.36265	1.17078	-0.92451
H	-2.36265	-1.17078	-0.92451
H	-1.17078	-2.36265	0.92451
H	1.17078	-2.36265	0.92451
H	2.36265	-1.17078	-0.92451

E=-309.6691568 a.u.

COT molecule in planar conformation. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.537455
C	1.062686	0.000000	2.600141
C	2.422628	0.000000	2.600141
C	3.540704	0.000000	1.482065
C	3.540704	0.000000	-0.082742
C	2.510903	0.000000	-1.112543
C	1.070030	0.000000	-1.112543
H	-0.978815	0.000000	-0.479605
H	-1.081322	0.000000	1.674724
H	0.846410	0.000000	3.668469
H	2.722346	0.000000	3.648124
H	4.530085	0.000000	1.939475
H	4.561773	0.000000	-0.464212
H	2.830255	0.000000	-2.154711
H	0.804440	0.000000	-2.169691

E=-309.6519104 a.u.

I. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	-3.15004	1.48046	-2.06283
C	-0.4209	1.63854	1.62112
C	-0.06865	1.71191	0.26006
C	0.1473	0.707	-0.72951
C	-3.28458	2.45737	-1.05813
C	-3.6142	2.43309	0.30993
C	-3.86842	1.42392	1.25426
C	-3.89096	0.01614	1.22952
C	-3.74665	-0.96155	0.22648
C	-3.52761	-0.92963	-1.16435
C	-3.28458	0.08044	-2.11077
C	-0.25945	0.64646	2.60529
H	-2.76052	1.89086	-2.99077
H	-0.72983	2.5981	2.02458
H	0.02082	2.72384	-0.12556
H	0.29651	1.10685	-1.7268
H	-2.97539	3.44389	-1.39313
H	-3.49552	3.40727	0.77612
H	-3.89045	1.81148	2.26803
H	-3.9231	-0.41379	2.22529
H	-3.70173	-1.96746	0.63123
H	-3.36144	-1.92152	-1.57368
H	-2.97374	-0.32589	-3.06955
H	-0.50298	1.00658	3.60179
Ti	-2.08683	0.67053	-0.13336
C	-0.1473	-0.707	-0.72951
Ti	2.08683	-0.67053	-0.13336
C	0.25945	-0.64646	2.60529
C	0.06865	-1.71191	0.26006
H	-0.29651	-1.10685	-1.7268
C	3.15004	-1.48046	-2.06283
C	0.4209	-1.63854	1.62112
C	3.28458	-2.45737	-1.05813
C	3.6142	-2.43309	0.30993
C	3.86842	-1.42392	1.25426
C	3.89096	-0.01614	1.22952
C	3.74665	0.96155	0.22648
C	3.52761	0.92963	-1.16435
C	3.28458	-0.08044	-2.11077
H	0.50298	-1.00658	3.60179
H	-0.02082	-2.72384	-0.12556
H	2.76052	-1.89086	-2.99077
H	0.72983	-2.5981	2.02458
H	2.97539	-3.44389	-1.39313
H	3.49552	-3.40727	0.77612
H	3.89045	-1.81148	2.26803
H	3.9231	0.41379	2.22529
H	3.70173	1.96746	0.63123
H	3.36144	1.92152	-1.57368
H	2.97374	0.32589	-3.06955

E=-2628.0881223 a.u.

II. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	2.70613	0.83074	-0.60989
C	-1.25978	-1.63503	-0.90136
C	-0.76962	-0.71843	-1.86389
C	-0.76756	0.7056	-1.86911
C	2.76359	-0.57966	-0.69576
C	2.22834	-1.64802	0.05484
C	1.33632	-1.74756	1.13742
C	0.60073	-0.8255	1.90882
C	0.52573	0.57726	1.9804
C	1.16615	1.64508	1.31976
C	2.07443	1.75127	0.25107
C	-2.32004	-1.64514	0.0436
H	3.17498	1.31302	-1.46049
H	-0.84639	-2.62809	-1.05763
H	-0.21054	-1.16769	-2.6811
H	-0.20887	1.14765	-2.69049
H	3.26417	-0.91638	-1.59681
H	2.42708	-2.60957	-0.406
H	1.01573	-2.7691	1.30808
H	-0.16535	-1.30799	2.50474
H	-0.28681	0.91386	2.61429
H	0.74446	2.60558	1.59313
H	2.18454	2.77332	-0.09501
H	-2.49158	-2.64458	0.43856
Ti	0.56422	-0.00045	-0.28799
C	-1.25123	1.62981	-0.91023
C	-3.18067	-0.69827	0.56953
C	-2.30974	1.6494	0.03678
H	-0.83417	2.6203	-1.07298
C	-3.17578	0.70999	0.5672
H	-3.95786	-1.12526	1.19858
H	-2.4747	2.65125	0.42847
H	-3.9496	1.14433	1.19537

E=-1468.9073612 a.u.

III. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	0.52424	-1.51356	-0.53617
H	1.06334	-2.44298	-0.70285
C	0.52415	-0.53541	-1.51599
H	1.06599	-0.70247	-2.44372
C	-0.52413	0.53596	-1.5158
H	-1.06595	0.70337	-2.44348
C	-0.52424	1.51375	-0.53561
H	-1.06334	2.44323	-0.70195
C	0.52424	1.51355	0.53615
H	1.06334	2.44297	0.70284
C	0.52413	0.53539	1.51597
H	1.06596	0.70245	2.44372
C	-0.52415	-0.53597	1.51577
H	-1.06599	-0.70337	2.44345
C	-0.52426	-1.51375	0.53558
H	-1.06337	-2.44323	0.70192
C	5.13911	-0.72467	0.25372
H	5.98655	-0.9167	0.92092
H	5.23057	-1.41771	-0.58948
C	5.13905	0.72493	-0.25341
H	5.98657	0.91708	-0.92049
H	5.23027	1.41798	0.58979
C	3.90033	-0.73174	2.87235
H	3.04429	-0.99912	3.49645
C	3.59178	-2.97786	1.17055
H	4.52226	-3.33345	1.62409
C	3.59162	2.97786	-1.17075
H	4.52212	3.33347	-1.62423
C	3.90061	0.73153	-2.87219
H	3.04463	0.99876	-3.49644
C	-5.13905	-0.72479	-0.25378
H	-5.98657	-0.91668	-0.92094
H	-5.23031	-1.41814	0.58918
C	-5.1391	0.72463	0.25386
H	-5.98657	0.91645	0.92109
H	-5.23049	1.41797	-0.58909
C	-3.90054	-0.73052	-2.87253
H	-3.04456	-0.99757	-3.49685
C	-3.59163	-2.97744	-1.17183
H	-4.52215	-3.3329	-1.62539
C	-3.59174	2.97744	1.17163
H	-4.52225	3.33288	1.62521
C	-3.90041	0.73065	2.87254
H	-3.0444	0.99779	3.49678
P	3.50578	-1.12331	1.09481
P	3.50579	1.12332	-1.09475
P	-3.50578	-1.12292	-1.09522
P	-3.50579	1.12291	1.09517
Ni	1.95796	-0.00001	0.
Ni	-1.95796	0.00001	-0.00002
H	-4.78243	-1.2719	-3.22899
H	4.78249	1.27307	-3.22846
H	4.07151	-0.34148	-2.98238
H	2.7479	3.34948	-1.75696
H	3.50633	3.38723	-0.16183
H	-4.07139	0.34254	-2.98235
H	-2.74793	-3.34886	-1.7582
H	-3.5063	-3.38712	-0.16304

H	3.50664	-3.38708	0.16156
H	2.74802	-3.34964	1.75661
H	4.07113	0.34127	2.98271
H	4.7822	-1.27325	3.22866
H	-3.50648	3.38704	0.16281
H	-2.74803	3.34896	1.75792
H	-4.0712	-0.34241	2.98247
H	-4.78231	1.27201	3.22902

E=-5168.6330236 a.u.

IV. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	1.10899	0.59302	1.61619
H	1.45784	0.94071	2.58842
C	1.11843	-0.82533	1.51726
H	1.45641	-1.30544	2.43491
C	0.44227	-1.78288	0.6425
H	0.6548	-2.80724	0.94796
C	0.39859	1.66057	0.90993
H	0.5824	2.6263	1.3807
C	5.35343	-0.56044	-1.25033
H	6.29894	-1.09157	-1.40449
H	4.84159	-0.5292	-2.21807
C	5.58846	0.86837	-0.73199
H	6.05691	1.49857	-1.49548
H	6.26538	0.85068	0.12901
C	5.436	-2.22568	1.12183
C	3.81793	-3.00182	-1.10465
C	4.55177	3.12276	0.76595
C	3.27964	2.35741	-1.68206
Ni	2.78219	-0.04061	0.68156
P	4.22111	-1.50884	-0.08584
P	3.96937	1.61075	-0.13404
C	-0.35391	-1.70507	-0.45231
C	-0.91684	-0.62591	-1.26666
H	-1.13436	-0.97353	-2.27697
C	-0.93262	0.78912	-1.15909
H	-1.15726	1.28235	-2.10503
C	-0.40052	1.73964	-0.18193
H	-0.72466	2.75491	-0.40991
Ni	-2.69853	0.01655	-0.55696
P	-4.17548	1.52528	0.03953
C	-5.55769	0.58787	0.9049
H	-6.49015	1.16224	0.8986
H	-5.25226	0.48442	1.95154
C	-5.7464	-0.80042	0.27099
H	-6.38666	-1.43892	0.8888
H	-6.23341	-0.70642	-0.70562
P	-4.07689	-1.60515	-0.03977
C	-4.54798	-3.02881	-1.12945
C	-3.74677	-2.4765	1.56204
C	-5.10188	2.41455	-1.30199
C	-3.86685	2.90872	1.23102
H	-0.64168	-2.67904	-0.84801
H	-3.1945	3.63408	0.76865
H	-3.36845	2.51544	2.11883
H	-4.79231	3.41335	1.52493
H	-5.93355	3.00352	-0.90307
H	-5.48775	1.69097	-2.02274
H	-4.41514	3.07837	-1.83142
H	-2.79508	-3.00584	1.48245
H	-3.67535	-3.66939	-1.27301
H	-5.36096	-3.62447	-0.70273
H	-4.85416	-2.65162	-2.10735
H	-4.54175	-3.18404	1.81669
H	-3.64615	-1.74263	2.36383
H	3.29563	-3.72871	-0.47955
H	4.71503	-3.4679	-1.52375
H	3.14391	-2.71603	-1.91413
H	4.91104	-2.90248	1.79923

H	6.23714	-2.77436	0.61725
H	5.87098	-1.42484	1.72261
H	3.96281	3.08893	-2.12427
H	2.32765	2.83649	-1.44429
H	3.07589	1.56759	-2.40763
H	3.68263	3.72393	1.04116
H	5.22775	3.73175	0.15772
H	5.06267	2.82711	1.68457

E=-5168.6430754 a.u.

V. Geometry optimized at B3LYP/6-311++G(d,p) level of theory.

C	1.59895	0.54578	-1.54161
C	2.19698	1.57704	-0.69237
C	3.13646	1.59418	0.28874
C	3.95967	0.58108	0.91308
C	3.90008	-0.77339	1.00289
C	2.99016	-1.78586	0.5114
C	2.05516	-1.82215	-0.47314
C	1.54292	-0.86465	-1.45444
C	-2.57545	-2.31306	-1.18037
C	-1.19278	-2.90604	1.26229
C	-1.74588	3.11981	-0.86412
C	-0.81749	2.38289	1.75122
C	-2.83167	-0.52134	1.09704
C	-2.99032	0.89193	0.51246
H	1.31742	0.93643	-2.51846
H	1.8223	2.56555	-0.95619
H	3.36217	2.59238	0.65964
H	4.78779	1.01791	1.46811
H	4.68998	-1.20353	1.61583
H	3.12926	-2.74055	1.01535
H	1.59731	-2.80156	-0.60471
H	1.23438	-1.3507	-2.37888
H	-3.78852	-1.0523	1.12852
H	-2.46367	-0.46339	2.12679
H	-3.53429	0.85124	-0.43695
H	-3.56225	1.54063	1.18373
Ni	-0.06727	-0.03528	-0.57633
P	-1.55077	-1.49231	0.12722
P	-1.30693	1.62698	0.13552
H	-2.48026	3.75123	-0.35536
H	-2.14874	2.80503	-1.8287
H	-0.84281	3.70464	-1.04971
H	-0.69142	1.5978	2.49883
H	-1.56081	3.10413	2.10308
H	0.14756	2.87852	1.63103
H	-2.97856	-1.55838	-1.8583
H	-3.39971	-2.88814	-0.74841
H	-1.93995	-2.98113	-1.76523
H	-2.10921	-3.39701	1.60237
H	-0.56894	-3.63406	0.74051
H	-0.63066	-2.54432	2.12488

E=-2739.1612759 a.u.