Substituent Effects in Mono- and Disubstituted 1,3,5,7-cyclooctatetraene Derivatives in Natural and Planar Conformations

by

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Supporting Information

General Information:

The molecular structures were optimized at B3LYP/6-311+G(d) level of theory using Gaussian03 package (**G03 Rev. E.01**). All structures were verified through a vibration analysis. No imaginary frequencies were found for tub-shaped COTs and benzene derivatives. Since planar geometry of COT corresponds to the transition state of this system, the corresponding imaginary frequency was found. Additionally, imaginary frequencies corresponding to out-of-plane vibration of the nitroso group was also found for planar COTs (it resulted from the symmetry restrains forcing planar geometry).

Geometry in angstroms, total energies in a.u.

Table S2. Geometries and total energies of the systems studied.

COT (tub-shaped)

C	0.669819	1.567221	0.372870
C	1.567221	0.669819	-0.372870
C	-0.669819	1.567221	0.372870
C	-1.567221	0.669819	-0.372870
C	-1.567221	-0.669819	-0.372870
C	-0.669819	-1.567221	0.372870
C	0.669819	-1.567221	0.372870
C	1.567221	-0.669819	-0.372870
H	1.170784	2.362653	0.924514
H	2.362653	1.170784	-0.924514
H	-1.170784	2.362653	0.924514
H	-2.362653	1.170784	-0.924514
H	-2.362653	-1.170784	-0.924514
H	-1.170784	-2.362653	0.924514
H	1.170784	-2.362653	0.924514
H	2.362653	-1.170784	-0.924514

E_{total} = -309.6554353

COT (planar)

C	0.671439	1.713641	0.000000
C	1.713641	0.671439	0.000000
C	-0.671439	1.713641	0.000000
C	-1.713641	0.671439	0.000000
C	-1.713641	-0.671439	0.000000
C	-0.671439	-1.713641	0.000000
C	0.671439	-1.713641	0.000000
C	1.713641	-0.671439	0.000000
H	1.108393	2.709836	0.000000
H	2.709836	1.108393	0.000000
H	-1.108393	2.709836	0.000000
H	-2.709836	1.108393	0.000000
H	-2.709836	-1.108393	0.000000
H	-1.108393	-2.709836	0.000000
H	1.108393	-2.709836	0.000000
H	2.709836	-1.108393	0.000000

E_{total} = -309.6382314

COT-NO (tub-shaped)

C	1.703089	0.900286	0.308026
C	1.748170	-0.408891	-0.362513
C	0.645692	1.707938	0.449196
C	-0.730797	1.478147	-0.021946
C	-1.511080	0.420649	0.226936
C	-1.160892	-0.778139	1.004568
C	-0.110766	-1.608487	0.829233
C	0.978592	-1.485779	-0.132758
H	2.575541	-0.535657	-1.060060
H	0.815008	2.681271	0.908489
H	-1.177190	2.310896	-0.563713
H	-2.545366	0.447074	-0.109001
H	-0.135696	-2.529162	1.411132
H	1.239701	-2.408385	-0.649301
N	-2.253341	-1.205863	1.860478
O	-1.963504	-1.968221	2.757353
H	2.667862	1.263860	0.659568

E_{total} = -438.984558

COT-NO (planar)

C	-0.248081	2.573644	0.000000
C	-1.501089	1.810521	0.000000
C	1.055783	2.243163	0.000000
C	1.819265	0.982658	0.000000
C	1.493136	-0.317089	0.000000
C	0.230267	-1.075907	0.000000
C	-1.076978	-0.736572	0.000000
C	-1.837613	0.502561	0.000000
H	-2.364129	2.473269	0.000000
H	1.720328	3.104591	0.000000
H	2.890660	1.166396	0.000000
H	2.335654	-1.005348	0.000000
H	-1.716506	-1.620190	0.000000
H	-2.909193	0.320713	0.000000
N	0.555657	-2.505539	0.000000
O	-0.366613	-3.292489	0.000000
H	-0.433581	3.644623	0.000000

E_{total} = -438.9698114

COT-OH (tub-shaped)

C	1.716805	0.890489	0.299664
C	1.752107	-0.419252	-0.376581
C	0.659612	1.704920	0.455278
C	-0.716925	1.473622	0.005369
C	-1.498015	0.404815	0.225866
C	-1.171686	-0.800290	0.999357
C	-0.104164	-1.598953	0.865540
C	0.978244	-1.478817	-0.123537
H	2.558267	-0.519736	-1.100327
H	0.846880	2.693023	0.881419
H	-1.172150	2.316075	-0.515888
H	-2.524817	0.455930	-0.134912
H	-0.060853	-2.493813	1.485730
H	1.200560	-2.394700	-0.671304
O	2.987808	1.249728	0.679931
H	2.979606	2.132840	1.071927
H	-1.930992	-1.100702	1.721461

E_{total} = -384.8999815

COT-OH (planar)

C	0.045921	1.434801	0.000000
C	-1.322965	0.870452	0.000000
C	1.286096	0.905073	0.000000
C	1.821907	-0.454695	0.000000
C	1.315340	-1.703063	0.000000
C	-0.041914	-2.257100	0.000000
C	-1.282916	-1.738304	0.000000
C	-1.827155	-0.371499	0.000000
H	-2.054398	1.672153	0.000000
H	2.083471	1.649074	0.000000
H	2.909987	-0.434876	0.000000
H	2.071423	-2.484193	0.000000
H	-2.076254	-2.481866	0.000000
H	-2.915270	-0.383541	0.000000
O	-0.099171	2.801442	0.000000
H	0.766734	3.229655	0.000000
H	-0.026774	-3.345574	0.000000

E_{total} = -384.8844673

COT 1,3-disubstituted (tub-shaped)

C	1.676013	0.882115	0.367656
C	1.816695	0.123665	-0.881230
C	0.551907	1.219934	1.014129
C	-0.833127	0.914788	0.628139
C	-1.356052	-0.281713	0.335125
C	-0.651617	-1.571133	0.340982
C	0.468672	-1.923536	-0.314072
C	1.293094	-1.078779	-1.181957
H	2.613713	1.264925	0.769601
H	2.521750	0.548471	-1.598537
H	0.653350	1.849901	1.896775
H	-1.517968	1.761330	0.659572
H	-2.426038	-0.356762	0.155180
H	0.753180	-2.973353	-0.286602
N	-1.450013	-2.623172	0.959086
O	-0.841335	-3.592532	1.350341
O	1.575661	-1.745727	-2.347136
H	2.171964	-1.223102	-2.899303

E_{total} = -514.2271169

COT 1,3-disubstituted (planar)

C	-0.291594	2.516285	0.000000
C	1.021908	1.871648	0.000000
C	-1.572095	2.103591	0.000000
C	-2.232415	0.790705	0.000000
C	-1.808385	-0.481262	0.000000
C	-0.485702	-1.122795	0.000000
C	0.789826	-0.705226	0.000000
C	1.465619	0.596724	0.000000
H	-0.185506	3.598640	0.000000
H	1.823861	2.610518	0.000000
H	-2.293684	2.916594	0.000000
H	-3.315790	0.887404	0.000000
H	-2.590048	-1.236963	0.000000
H	1.509797	-1.522791	0.000000
N	-0.697934	-2.594674	0.000000
O	0.283134	-3.295578	0.000000
O	2.817682	0.342208	0.000000
H	3.320147	1.166948	0.000000

E_{total} = -514.211902

COT 1,4-disubstituted (tub-shaped)

C	2.271319	0.247042	0.478462
C	1.755071	0.190187	-0.904353
C	1.627538	0.681220	1.565050
C	0.234252	1.138932	1.666758
C	-0.855439	0.466325	1.276680
C	-0.929915	-0.820389	0.572872
C	-0.315355	-1.176004	-0.589548
C	0.665700	-0.465623	-1.363613
H	3.308881	-0.073912	0.578750
H	2.194426	0.720486	2.495174
H	0.086435	2.060891	2.226134
H	-1.828911	0.870414	1.547045
H	-0.716806	-2.078826	-1.049048
H	0.578680	-0.538154	-2.445494
N	-2.036268	-1.614696	1.031030
O	-2.036033	-2.787253	0.701924
O	2.584396	0.737850	-1.838916
H	3.297130	1.227981	-1.410046

E_{total} = -514.2321508

COT 1,4-disubstituted (planar)

C	-0.766188	1.812594	0.000000
C	0.656528	2.184505	0.000000
C	-1.447469	0.625829	0.000000
C	-1.046292	-0.737130	0.000000
C	0.118158	-1.457260	0.000000
C	1.526450	-1.077813	0.000000
C	2.209166	0.083218	0.000000
C	1.809892	1.487354	0.000000
H	0.796855	3.264874	0.000000
H	-2.523282	0.771459	0.000000
H	-1.902021	-1.414855	0.000000
H	2.147696	-1.971682	0.000000
H	3.289283	-0.029744	0.000000
H	2.681361	2.139740	0.000000
N	0.019093	-2.892347	0.000000
O	-1.095206	-3.392960	0.000000
O	-1.589012	2.888922	0.000000
H	-1.090743	3.715801	0.000000

E_{total} = -514.2193247

COT 1,5-disubstituted (tub-shaped)

C	1.706603	0.895250	0.298566
C	1.742888	-0.414633	-0.382353
C	0.651990	1.712565	0.442388
C	-0.724068	1.476822	-0.008056
C	-1.504275	0.410874	0.219621
C	-1.159366	-0.788104	0.991401
C	-0.097405	-1.606729	0.846944
C	0.982949	-1.486700	-0.128200
H	2.556735	-0.514459	-1.097187
H	0.835111	2.699915	0.870366
H	-1.181847	2.314518	-0.533068
H	-2.536796	0.443787	-0.119825
H	-0.107174	-2.515752	1.446652
H	1.227667	-2.406997	-0.657238
N	-2.261756	-1.216618	1.841251
O	-1.973933	-1.953772	2.757645
O	2.975341	1.235820	0.693481
H	2.973620	2.106867	1.111882

E_{total} = -514.228461

COT 1,5-disubstituted (planar)

C	-0.105588	2.169413	0.000000
C	-1.397122	1.444719	0.000000
C	1.184261	1.783662	0.000000
C	1.878140	0.493793	0.000000
C	1.519359	-0.800203	0.000000
C	0.233247	-1.501943	0.000000
C	-1.059818	-1.124241	0.000000
C	-1.765518	0.153191	0.000000
H	-2.216616	2.156772	0.000000
H	1.890538	2.614390	0.000000
H	2.956072	0.638431	0.000000
H	2.341214	-1.511279	0.000000
H	-1.736638	-1.978094	0.000000
H	-2.844010	0.014912	0.000000
N	0.505960	-2.957973	0.000000
O	-0.445974	-3.701452	0.000000
O	-0.419007	3.508910	0.000000
H	0.385085	4.043895	0.000000

E_{total} = -514.2135604

C_6H_6

C	0.583046	-1.384636	0.000070
C	1.977563	-1.384608	0.000574
C	2.674847	-0.177229	-0.000095
C	1.977618	1.030463	-0.001029
C	0.583312	1.030430	-0.001422
C	-0.114078	-0.177127	-0.000979
H	0.040489	-2.324645	0.000433
H	2.520057	-2.324684	0.001372
H	3.760187	-0.177219	0.000177
H	2.520407	1.970331	-0.001444
H	0.040601	1.970375	-0.002248
H	-1.199424	-0.176876	-0.001320

E_{total} = -232.3007043

C_6H_5NO

C	-0.243162	-1.348793	0.005793
C	0.860702	-1.176183	0.840016
C	1.551240	0.032513	0.825133
C	1.127762	1.056496	-0.024765
C	0.019734	0.889038	-0.865115
C	-0.662558	-0.318171	-0.845357
H	-0.783193	-2.290180	0.014769
H	1.179158	-1.979237	1.495846
H	2.414614	0.205402	1.458865
H	-0.280780	1.704842	-1.512367
H	-1.523250	-0.467050	-1.489088
N	1.909471	2.264743	0.037197
O	1.547938	3.161048	-0.697568

E_{total} = -361.6305745

C_6H_5OH

C	-0.249064	-1.352301	-0.001528
C	1.147016	-1.334827	-0.001425
C	1.843082	-0.130630	0.001565
C	1.137380	1.073623	0.004474
C	-0.258542	1.067670	0.004408
C	-0.945218	-0.146005	0.001420
H	-0.785891	-2.294660	-0.003863
H	1.701025	-2.268190	-0.003690
H	2.927084	-0.103937	0.001702
H	-0.808553	2.005974	0.006668
H	-2.030581	-0.142287	0.001397
O	1.870884	2.230833	0.007328
H	1.285374	2.997450	0.009707

E_{total} = -307.5429461

$C_6H_5NO_2$ 1,3-disubstituted

C	-1.803350	-0.004561	-0.739783
C	-1.322472	-0.003090	0.578788
C	0.045000	-0.000259	0.820450
C	0.918096	0.001145	-0.269141
C	0.455172	-0.000283	-1.586756
C	-0.917457	-0.003250	-1.814528
H	0.430604	0.000866	1.832783
H	1.173482	0.000894	-2.398404
H	-1.305709	-0.004434	-2.827157
N	2.354921	0.004140	-0.128909
O	2.769045	0.005549	1.010920
H	-2.875203	-0.006693	-0.922794
O	-2.154613	-0.004149	1.660912
H	-3.078618	-0.007757	1.383207

E_{total} = -436.8719546

$C_6H_5NO_2$

C	-0.002870	-1.730019	0.063018
C	-0.004682	-0.904121	1.200886
C	-0.003837	0.470208	1.053903
C	-0.001042	1.029992	-0.231766
C	0.000907	0.202591	-1.361562
C	-0.000118	-1.174996	-1.220950
H	-0.006761	-1.350051	2.192631
H	-0.005231	1.128501	1.914987
H	0.003106	0.665704	-2.342539
H	0.001216	-1.836384	-2.079365
N	0.000144	2.433163	-0.491639
O	-0.000545	3.155556	0.489857
O	-0.003648	-3.084249	0.152522
H	-0.005900	-3.368842	1.075077

E_{total} = -436.8760813