Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Medium-sized rings: conformational preferences in cyclooctanone driven by transannular repulsive interactions

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Table S1. Spectroscopic parameters of the conformers of cyclooctanone at the M062X/6-311++G(d,p) level of theory.

M062X	**BC1**	**TBC1**	**BC2**	**CR**	**BB1**
A (MHz)	1919	2019.1	2032	1936	1960
B (MHz)	1695	1626.7	1657	1734	1626
C (MHz)	1171	1092.9	1128	1132	1239
$\mu_a/\mu_b/\mu_c$ (D)	-2.2/0.1/2.2	2.7/0.2/1.7	2.3/-0.9/-1.9	-0.6/1.7/2.2	-2.3/0.3/2.2
ΔE_{M062X} (cm^{-1})	0	761	834	836	1209
ΔE_{M062X}+ZPC(cm^{-1})	0	760	890	825	1338
ΔG^{347} (cm^{-1})	0	631	818	756	1215

M062X	**BC3**	**TBC2**	**TBC3**	**BC4**	**BB2**
A (MHz)	1924	2138	2009	2273	2171
B (MHz)	1681	1529	1703	1447	1526
C (MHz)	1229	1109	1121	1014	1134
$\mu_a/\mu_b/\mu_c$ (D)	-1.4/0.0/2.7	-2.2/-0.5/2.1	2.0/-1.1/-1.9	3.4/-0.0/-0.7	3.2/-0.2/1.0
ΔE_{M062X} (cm^{-1})	1221	1233	1389	1677	2018
ΔE_{M062X}+ZPC(cm^{-1})	1232	1248	1449	1748	2213
ΔG^{347} (cm^{-1})	1043	1171	1415	1611	2199

Table S2. Spectroscopic parameters of the conformers of cyclooctanone at the B3LYP-D3BJ/6-311++G(d,p) level of theory

B3LYP-D3BJ	**BC1**	**TBC1**	**BC2**	**CR**	**BB1**
A (MHz)	1911	1992	2034	1869	1946
B (MHz)	1674	1614	1624	1735	1589
C (MHz)	1156	1083	1108	1103	1191
$\mu_a/\mu_b/\mu_c$ (D)	-2.2/0.0/1.8	2.6/0.3/1.8	2.6/-0.6/-1.7	-1.1/1.6/2.2	-2.4/0.0/2.2
$\Delta E_{B3LYP-D3BJ}$ (cm^{-1})	0	671	745	806	1056
$\Delta E_{B3LYP-D3BJ}$+ZPC(cm^{-1})	0	593	816	764	1043
ΔG^{347} (cm^{-1})	0	395	792	548	800

B3LYP-D3BJ	**BC3**	**TBC2**	**TBC3**	**BC4**	**BB2**
A (MHz)	1928	2094	1994	2269	2177
B (MHz)	1638	1529	1670	1429	1487
C (MHz)	1200	1101	1095	1004	1094
$\mu_a/\mu_b/\mu_c$ (D)	1.6/-0.0/2.6	2.3/-0.5/2.2	2.3/-0.8/-1.8	-3.4/0.0/0.7	3.3/-0.2/-0.9
$\Delta E_{B3LYP-D3BJ}$ (cm^{-1})	1187	1254	1427	1519	1056
$\Delta E_{B3LYP-D3BJ}$+ZPC(cm^{-1})	1196	1255	1490	1541	2104
ΔG^{347} (cm^{-1})	1038	1150	1440	1405	1967

Table S3. The Cartesian coordinates of the BC1 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	1.914138	-0.671173	0.247362
2	6	1.363196	0.613407	0.884117
3	6	0.909655	1.692423	-0.123973
4	6	-0.612096	1.839398	-0.258965
5	6	-1.353484	0.613954	-0.825369
6	6	-1.282444	-0.575149	0.121540
7	8	-1.963578	-0.592684	1.136905
8	6	1.004208	-1.338502	-0.788255
9	6	-0.373658	-1.734705	-0.246524
10	1	2.132615	-1.393901	1.044772
11	1	2.872279	-0.439521	-0.236446
12	1	1.501739	-2.242283	-1.159411
13	1	0.887048	-0.683074	-1.658438
14	1	2.152865	1.023607	1.524227
15	1	0.535537	0.372161	1.561368
16	1	-0.911075	-2.302152	-1.020899
17	1	-0.283700	-2.382340	0.632320
18	1	1.350664	1.495921	-1.110898
19	1	1.302365	2.665938	0.191563
20	1	-0.831144	2.696886	-0.906473
21	1	-1.038304	2.065674	0.726461
22	1	-2.414640	0.866111	-0.925785
23	1	-0.964714	0.360523	-1.817206

Table S4. The Cartesian coordinates of the TBC1 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.936974	-0.609817	-0.295601
2	6	-1.776039	0.895290	-0.018096
3	6	-0.539669	1.575635	-0.640141
4	6	0.630595	1.809902	0.322224
5	6	1.122383	0.528336	1.017263
6	6	1.332414	-0.544126	-0.034989
7	8	2.239706	-0.438340	-0.847771
8	6	-1.024924	-1.578523	0.472250
9	6	0.402806	-1.746084	-0.063223
10	1	-1.825338	-0.786467	-1.374736
11	1	-2.971716	-0.877839	-0.047462
12	1	-1.488021	-2.572218	0.434061
13	1	-1.008809	-1.300276	1.533182
14	1	-1.795148	1.069110	1.067441
15	1	-2.672868	1.384846	-0.415353
16	1	0.390014	-2.117473	-1.094162
17	1	0.912586	-2.515077	0.537035
18	1	-0.830531	2.550205	-1.048920
19	1	-0.192248	0.984647	-1.498167
20	1	1.468300	2.237788	-0.239161

21	1	0.338285	2.540855	1.086048
22	1	0.410353	0.203811	1.779888
23	1	2.083949	0.721137	1.504358

Table S5. The Cartesian coordinates of the BC2 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.622623	0.926737	0.476356
2	6	-2.021822	-0.406989	-0.184864
3	6	-0.901502	-1.283734	-0.756777
4	6	0.086369	-1.887084	0.246981
5	6	0.933926	-0.852849	1.014120
6	6	1.443699	0.216797	0.059894
7	8	2.263118	-0.067090	-0.802551
8	6	-0.583248	1.757824	-0.301179
9	6	0.876016	1.617248	0.184984
10	1	-1.268301	0.761742	1.499399
11	1	-2.539796	1.518502	0.579401
12	1	-0.632094	1.519282	-1.371001
13	1	-0.836581	2.820188	-0.214919
14	1	-2.701428	-0.171447	-1.014442
15	1	-2.608108	-0.995445	0.533761
16	1	0.919413	1.918885	1.240054
17	1	1.519992	2.283898	-0.396252
18	1	-0.341712	-0.722027	-1.515208
19	1	-1.374822	-2.112073	-1.298538
20	1	-0.451062	-2.515612	0.967968
21	1	0.771016	-2.539632	-0.305576
22	1	0.366092	-0.404344	1.831741
23	1	1.807559	-1.352898	1.446922

Table S6. The Cartesian coordinates of the CR1 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	0.418147	1.781228	-0.291395
2	6	-0.772816	1.439698	0.645252
3	6	-1.963985	0.720212	-0.012591
4	6	-1.843050	-0.804735	-0.105084
5	6	-0.586049	-1.286459	-0.840640
6	6	0.660088	-1.188314	0.032341
7	8	0.691694	-1.733935	1.126204
8	6	1.741472	1.074243	0.040353
9	6	1.833745	-0.375909	-0.472395
10	1	0.147478	1.573961	-1.335527
11	1	0.597692	2.860887	-0.241958
12	1	1.887892	1.072641	1.127476
13	1	2.576709	1.636216	-0.393779
14	1	-0.420480	0.846218	1.499068
15	1	-1.146153	2.377911	1.070085

16	1	1.848484	-0.373675	-1.568137
17	1	2.754732	-0.837019	-0.102587
18	1	-2.122897	1.137153	-1.016824
19	1	-2.872168	0.944964	0.560260
20	1	-1.834148	-1.238445	0.901769
21	1	-2.729734	-1.197278	-0.616542
22	1	-0.694115	-2.350599	-1.087262
23	1	-0.452151	-0.741232	-1.780730

Table S7. The Cartesian coordinates of the BC3 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-1.226498	1.322404	0.395956
2	6	-2.006792	-0.000048	0.313970
3	6	-1.226436	-1.322464	0.395939
4	6	-0.286949	-1.609215	-0.793445
5	6	1.200490	-1.303362	-0.505047
6	6	1.394069	0.000029	0.241910
7	8	1.651681	0.000065	1.439890
8	6	-0.287038	1.609219	-0.793433
9	6	1.200422	1.303380	-0.505103
10	1	-0.660811	1.360852	1.335534
11	1	-1.970839	2.125230	0.453311
12	1	-0.624726	1.054604	-1.674795
13	1	-0.346423	2.669026	-1.064470
14	1	-2.588453	-0.000054	-0.619180
15	1	-2.739057	-0.000071	1.131479
16	1	1.761512	1.279359	-1.447252
17	1	1.614240	2.092547	0.129676
18	1	-0.660754	-1.360898	1.335520
19	1	-1.970738	-2.125327	0.453279
20	1	-0.624616	-1.054563	-1.674792
21	1	-0.346311	-2.669010	-1.064534
22	1	1.761636	-1.279374	-1.447164
23	1	1.614277	-2.092496	0.129792

Table S8. The Cartesian coordinates of the TBC2 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-0.820598	1.351934	0.650592
2	6	-2.047779	0.448776	0.463833
3	6	-1.820336	-0.846439	-0.333021
4	6	-0.607824	-1.705819	0.064861
5	6	0.722993	-1.351454	-0.644322
6	6	1.503848	-0.243597	0.044154
7	8	2.140412	-0.487233	1.059811
8	6	-0.032406	1.620584	-0.649901
9	6	1.430226	1.155959	-0.533965
10	1	-1.149713	2.295898	1.099332

11	1	-0.155886	0.894348	1.393637
12	1	-0.042349	2.686187	-0.900652
13	1	-0.509896	1.108678	-1.492149
14	1	-2.435877	0.187821	1.456718
15	1	-2.841608	1.016457	-0.039538
16	1	1.911930	1.159551	-1.520884
17	1	1.996298	1.814806	0.131566
18	1	-2.726602	-1.454264	-0.221177
19	1	-1.749968	-0.623619	-1.405184
20	1	-0.835503	-2.745289	-0.195926
21	1	-0.452432	-1.687521	1.151313
22	1	1.374262	-2.231322	-0.615034
23	1	0.525312	-1.103533	-1.693896

Table S9. The Cartesian coordinates of the BB1 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	1.187934	-1.483624	0.400241
2	6	1.338656	-0.100552	1.055104
3	6	1.669909	1.071611	0.118495
4	6	0.548988	1.527840	-0.840057
5	6	-0.854471	1.489826	-0.228183
6	6	-1.406052	0.119502	0.149010
7	8	-2.142605	0.002509	1.118971
8	6	0.352130	-1.531527	-0.883873
9	6	-1.119049	-1.085451	-0.739237
10	1	2.187204	-1.867073	0.155899
11	1	0.761819	-2.174335	1.139877
12	1	0.339638	-2.565526	-1.249256
13	1	0.857927	-0.952633	-1.659500
14	1	2.144120	-0.173501	1.796705
15	1	0.443278	0.144223	1.634911
16	1	-1.712065	-1.902756	-0.317147
17	1	-1.521043	-0.865203	-1.738471
18	1	1.933885	1.926225	0.754580
19	1	2.569509	0.836294	-0.466172
20	1	0.757514	2.560976	-1.142701
21	1	0.555790	0.946851	-1.765305
22	1	-0.915662	2.115017	0.669304
23	1	-1.569348	1.905634	-0.953497

Table S10. The Cartesian coordinates of the TBC3 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	-0.234723	1.543215	-0.689230
2	6	-1.334262	1.210654	0.341714
3	6	-2.157864	-0.041159	0.005061
4	6	-1.343120	-1.300466	-0.337084

5	6	-0.145312	-1.579925	0.598612
6	6	1.114909	-0.860672	0.126605
7	8	1.741995	-1.297226	-0.828682
8	6	1.171463	1.643364	-0.078776
9	6	1.544544	0.429835	0.802624
10	1	-0.214169	0.775941	-1.472124
11	1	-0.463156	2.483574	-1.202753
12	1	1.254466	2.551667	0.530580
13	1	1.904255	1.725102	-0.888738
14	1	-0.885246	1.074647	1.332148
15	1	-2.021183	2.057574	0.450318
16	1	1.086649	0.512077	1.791765
17	1	2.631330	0.398801	0.930754
18	1	-2.809811	-0.263121	0.859857
19	1	-2.820649	0.174933	-0.842978
20	1	-2.021561	-2.160212	-0.303314
21	1	-0.965855	-1.257117	-1.364923
22	1	-0.392981	-1.316190	1.632764
23	1	0.088147	-2.648940	0.558945

Table S11. The Cartesian coordinates of the BC4 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)		
		X	Y	Z
1	6	1.642047	-1.306596	-0.148751
2	6	1.872993	-0.000001	0.615788
3	6	1.642049	1.306595	-0.148750
4	6	0.203200	1.601502	-0.604175
5	6	-0.885502	1.318559	0.463063
6	6	-1.601298	0.000001	0.217177
7	8	-2.735782	0.000002	-0.244183
8	6	0.203197	-1.601503	-0.604174
9	6	-0.885504	-1.318559	0.463063
10	1	1.961680	-2.128295	0.505860
11	1	2.303678	-1.335083	-1.024723
12	1	0.150361	-2.661075	-0.877003
13	1	-0.033819	-1.053029	-1.521208
14	1	2.913792	-0.000002	0.963748
15	1	1.264822	-0.000001	1.528595
16	1	-1.658591	-2.090007	0.421357
17	1	-0.443040	-1.333346	1.466556
18	1	1.961680	2.128293	0.505863
19	1	2.303682	1.335083	-1.024721
20	1	-0.033815	1.053026	-1.521208
21	1	0.150364	2.661073	-0.877005
22	1	-1.658587	2.090009	0.421357
23	1	-0.443037	1.333346	1.466555

Table S12. The Cartesian coordinates of the BB2 conformation of cyclooctanone from MP2/3-611++G(d,p).

Centre Number	Atomic Number	Coordinates (Å)

		X	Y	Z
1	6	-1.719556	0.682518	0.578090
2	6	-1.957751	-0.345485	-0.534528
3	6	-0.799700	-1.321618	-0.826801
4	6	0.025274	-1.782091	0.385854
5	6	0.950615	-0.716524	1.034900
6	6	1.483980	0.252976	-0.000617
7	8	2.597307	0.110740	-0.485733
8	6	-0.663907	1.773604	0.308708
9	6	0.593569	1.395142	-0.487862
10	1	-2.670777	1.191555	0.777663
11	1	-1.488273	0.141336	1.500178
12	1	-1.146768	2.580976	-0.255964
13	1	-0.367116	2.217101	1.267843
14	1	-2.832869	-0.937579	-0.237248
15	1	-2.239991	0.167676	-1.463687
16	1	1.248988	2.270911	-0.565324
17	1	0.319660	1.149689	-1.521132
18	1	-1.226857	-2.217039	-1.294621
19	1	-0.118060	-0.907025	-1.576243
20	1	0.667570	-2.602553	0.046689
21	1	-0.637605	-2.198410	1.154748
22	1	1.810896	-1.214321	1.491033
23	1	0.427603	-0.159371	1.815454

Table S13. Measured frequencies and residuals (in MHz) for the rotational transitions of the parent species of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
4	4	1	4	3	1	2197.7575	0.0010
5	3	2	5	3	3	2199.6797	0.0003
6	5	2	6	4	2	2283.9775	0.0059
2	2	0	2	1	2	2595.0648	0.0194
4	2	2	4	2	3	2628.2886	0.0003
3	3	0	3	2	2	2809.7264	-0.0026
1	0	1	0	0	0	2845.3742	-0.0015
3	1	2	3	1	3	2928.8730	0.0033
1	1	1	0	0	0	3071.9416	0.0031
5	5	1	5	4	1	3149.7381	-0.0013
4	4	0	4	3	2	3206.0952	-0.0034
7	4	3	7	4	4	3289.0077	0.0024
7	6	2	7	5	2	3312.1505	-0.0013
4	3	2	4	1	3	3412.1423	0.0014
1	1	0	0	0	0	3592.5791	-0.0049
5	5	0	5	4	2	3766.7681	-0.0017
6	3	3	6	3	4	3788.8203	0.0006
6	6	1	6	5	1	4115.2158	-0.0024
5	2	3	5	2	4	4118.1711	-0.0008
5	4	1	5	3	3	4175.7158	0.0001

4	1	3	4	1	4	4288.8620	-0.0015
6	5	1	6	4	3	4292.2434	-0.0015
5	3	3	5	1	4	4379.1883	0.0010
8	7	2	8	6	2	4388.7380	0.0010
6	6	0	6	5	2	4445.5722	0.0001
2	0	2	1	1	0	4590.1200	0.0050
7	6	1	7	5	3	4637.1492	-0.0003
8	4	4	8	4	5	5000.3328	-0.0017
7	7	1	7	6	1	5040.7774	0.0032
2	0	2	1	1	1	5110.7477	-0.0128
2	1	2	1	1	1	5170.1082	0.0052
8	7	1	8	6	3	5174.6072	0.0034
7	7	0	7	6	2	5197.9806	-0.0042
7	3	4	7	3	5	5319.8702	0.0006
3	1	3	2	2	1	5333.1963	-0.0054
2	0	2	1	0	1	5337.3236	0.0004
2	1	2	1	0	1	5396.6701	0.0043
9	8	2	9	7	2	5428.9533	-0.0002
6	2	4	6	2	5	5490.0626	-0.0018
6	3	4	6	1	5	5551.2456	0.0010
8	6	2	8	5	4	5568.9579	0.0008
5	1	4	5	1	5	5572.1771	-0.0001
9	7	2	9	6	4	5640.8480	0.0011
7	5	2	7	4	4	5754.0101	-0.0013
9	8	1	9	7	3	5846.0310	-0.0054
8	8	1	8	7	1	5922.5425	-0.0074
8	8	0	8	7	2	5991.1218	0.0000
3	0	3	2	1	1	6002.7627	-0.0033
6	4	2	6	3	4	6122.0547	-0.0040
2	1	1	1	1	0	6211.3935	0.0019
9	4	5	9	4	6	6521.4145	-0.0026
8	3	5	8	3	6	6685.6046	-0.0014
4	1	4	3	2	2	6716.2328	0.0007
9	9	1	9	8	1	6776.1366	0.0076
7	2	5	7	2	6	6776.8091	-0.0036
7	3	5	7	1	6	6788.3516	-0.0008
6	1	5	6	1	6	6828.8018	0.0000
2	2	1	1	1	0	6891.0769	-0.0038
2	1	1	1	0	1	6958.6001	0.0002
4	0	4	3	1	2	6988.8503	-0.0009
2	2	0	1	1	0	7244.5029	0.0001
2	2	1	1	1	1	7411.7277	0.0014
3	0	3	2	1	2	7564.7025	0.0024
3	1	3	2	1	2	7574.8279	0.0029
3	0	3	2	0	2	7624.0441	0.0015
3	1	3	2	0	2	7634.1697	0.0022

10	4	6	10	4	7	7875.4128	0.0059
5	1	5	4	2	3	7890.3753	0.0011
5	0	5	4	1	3	7958.0775	-0.0011

Table S14. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_1$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2814.2090	-0.0062
1	1	0	0	0	0	3566.8421	-0.0008
2	1	2	1	1	1	5116.3318	0.0016
2	0	2	1	0	1	5290.0114	0.0034
2	1	1	1	1	0	6140.5224	0.0004
2	1	1	1	0	1	6893.1520	0.0023
2	2	0	1	1	0	7200.5290	-0.0015
3	1	3	2	1	2	7501.4046	-0.0046
3	0	3	2	0	2	7556.0982	0.0028

Table S15. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_2$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2822.6069	-0.0001
1	1	0	0	0	0	3569.0798	-0.0034
2	1	2	1	1	1	5134.8736	0.0002
2	0	2	1	0	1	5306.1333	-0.0004
2	1	1	1	1	0	6155.5451	-0.0008
2	1	1	1	0	1	6902.0236	0.0016
2	2	0	1	1	0	7203.0375	0.0008
3	1	3	2	1	2	7528.9720	0.0004
3	0	3	2	0	2	7582.1907	-0.0001

Table S16. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_3$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2826.7172	-0.0058
1	1	0	0	0	0	3567.2742	-0.0038
2	1	2	1	1	1	5130.9911	0.0000
2	0	2	1	0	1	5293.8069	-0.0007
2	1	1	1	1	0	6175.8914	-0.0006
2	1	1	1	0	1	6916.4509	0.0039
2	2	0	1	1	0	7189.8336	-0.0013
2	2	1	1	1	1	7352.6555	0.0009
3	1	3	2	1	2	7513.2113	0.0010

3	0	3	2	0	2	7559.3924	0.0007

Table S17. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_4$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2834.5673	-0.0085
1	1	0	0	0	0	3565.1608	-0.0064
2	1	2	1	1	1	5139.4307	0.0013
2	0	2	1	0	1	5293.1576	-0.0005
2	1	1	1	1	0	6198.8651	0.0001
2	1	1	1	0	1	6929.4604	0.0040
2	2	0	1	1	0	7177.4700	-0.0002
2	2	1	1	1	1	7331.2031	0.0010
3	1	3	2	1	2	7518.0276	0.0014
3	0	3	2	0	2	7558.0205	-0.0002

Table S18. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_5$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2827.9108	-0.0092
1	1	0	0	0	0	3570.5360	-0.0018
2	1	2	1	1	1	5141.8547	0.0021
2	0	2	1	0	1	5309.5621	-0.0006
2	1	1	1	1	0	6169.8180	-0.0007
2	1	1	1	0	1	6912.4403	0.0038
2	2	0	1	1	0	7201.9901	-0.0010
2	2	1	1	1	1	7369.7046	0.0002
3	1	3	2	1	2	7535.9815	0.0014
3	0	3	2	0	2	7586.3131	-0.0003

Table S19. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_6$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2831.0670	-0.0020
2	1	2	1	1	1	5146.0876	0.0003
2	0	2	1	0	1	5317.3364	0.0000
2	1	1	1	1	0	6178.1788	-0.0009
3	0	3	2	0	2	7595.4359	-0.0011
3	1	3	2	1	2	7542.9578	0.0015
1	1	0	0	0	0	3582.1519	-0.0071
2	1	1	1	0	1	6929.2728	0.0031
2	2	1	1	1	1	7399.3569	0.0012

2	2	0	1	1	0	7228.1038	0.0003

Table S20. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_8$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2829.5957	-0.0041
1	1	0	0	0	0	3565.4285	-0.0068
2	1	2	1	1	1	5138.7917	-0.0010
2	0	2	1	0	1	5299.9788	0.0015
2	1	1	1	1	0	6179.5981	0.0003
2	1	1	1	0	1	6915.4364	0.0031
2	2	0	1	1	0	7185.1084	-0.0012
2	2	1	1	1	1	7346.2995	0.0020
3	1	3	2	1	2	7525.1693	0.0012
3	0	3	2	0	2	7570.5441	-0.0007

Table S21. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}C_9$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2835.1755	-0.0016
2	1	2	1	1	1	5143.8826	0.0009
2	0	2	1	0	1	5301.9008	-0.0003
2	1	1	1	1	0	6196.8170	-0.0010
2	1	1	1	0	1	6932.1391	0.0012
2	2	0	1	1	0	7191.8170	-0.0003
2	2	1	1	1	1	7349.8398	-0.0001
3	1	3	2	1	2	7528.3191	0.0011
3	0	3	2	0	2	7571.1345	-0.0009

Table S22. Measured frequencies and residuals (in MHz) for the rotational transitions of the $^{13}O_7$ isotopologue of cyclooctanone BC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2767.9788	0.0134
1	1	0	0	0	0	3521.9482	-0.0057
2	1	2	1	1	1	5048.5763	-0.0015
2	0	2	1	0	1	5232.0860	-0.0012
2	1	1	1	1	0	6023.2717	-0.0035
2	1	1	1	0	1	6777.2639	0.0002
2	2	0	1	1	0	7127.0337	0.0046
2	2	1	1	1	1	7310.5400	-0.0017
3	1	3	2	1	2	7416.6214	0.0005
3	0	3	2	0	2	7482.5757	-0.0010

Table S23. Experimental spectroscopic parameters for all singly substituted ^{13}C and ^{18}O isotopic species of the BC1 conformer of cyclooctanone.

Parameter	**$^{13}C_1$**	**$^{13}C_2$**	**$^{13}C_3$**	**$^{13}C_4$**	**$^{13}C_5$**
A (MHz)	1908.60080(73)	1899.58571(93)	1883.0199(10)	1892.69070(73)	1902.61094(53)
B (MHz)	1673.55905(65)	1670.95299(83)	1682.14826(91)	1674.58818(64)	1666.47311(34)
C (MHz)	1157.51096(34)	1156.96807(43)	1152.42858(47)	1152.13583(33)	1156.13498(17)
σ (kHz)	2.6	3.3	3.7	2.6	1.3
N	10	10	10	10	9

Parameter	**$^{13}C_6$**	**$^{13}C_7$**	**$^{13}C_8$**	**^{13}O**
A (MHz)	1903.6868(13)	1890.43352(81)	1889.67383(27)	1894.2963(14)
B (MHz)	1663.15703(81)	1675.00266(71)	1680.82408(24)	1627.6585(13)
C (MHz)	1151.05925(41)	1154.59819(37)	1154.35408(12)	1140.30796(67)
σ (kHz)	3.2	2.9	0.9	5.1
N	9	10	9	10

Table S24. Measured frequencies and residuals (in MHz) for the rotational transitions of cyclooctanone TBC1.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
4	2	2	4	2	3	2594.8198	-0.0065
1	0	1	0	0	0	2724.7589	-0.0063
7	4	3	7	4	4	2792.1636	-0.0064
3	1	2	3	1	3	3105.5121	-0.0006
4	4	1	4	3	1	3328.0771	0.0015
3	3	0	3	2	2	3410.1156	0.0016
1	1	0	0	0	0	3617.1094	-0.0042
6	3	3	6	3	4	3631.1505	-0.0013
4	4	0	4	3	2	4110.4209	-0.0032
4	3	2	4	1	3	4123.5168	-0.0069
2	0	2	1	1	0	4244.2377	-0.0045
5	2	3	5	2	4	4283.3386	-0.0024
4	1	3	4	1	4	4673.0759	0.0020
8	4	4	8	4	5	4726.6660	0.0012
2	0	2	1	1	1	4784.7981	0.0089
2	1	2	1	1	1	4908.9797	0.0000
5	3	3	5	1	4	4974.8132	0.0044
5	5	0	5	4	2	5016.1214	0.0001
2	0	2	1	0	1	5136.5888	-0.0019
2	1	2	1	0	1	5260.7903	0.0091
7	3	4	7	3	5	5478.1190	0.0108
3	0	3	2	1	1	5550.1844	-0.0112
6	2	4	6	2	5	5930.6433	-0.0021
2	1	1	1	1	0	5990.0618	-0.0023
5	1	4	5	1	5	6149.2532	0.0019
6	3	4	6	1	5	6162.8940	0.0046
9	4	5	9	4	6	6688.0565	0.0020
2	1	1	1	0	1	6882.4112	-0.0013
3	0	3	2	1	2	7171.8366	0.0097

8	3	5	8	3	6	7179.6412	-0.0059
3	1	3	2	1	2	7201.3659	0.0068
3	0	3	2	0	2	7296.0254	0.0080
3	1	3	2	0	2	7325.5343	-0.0154
2	2	0	1	1	0	7358.3881	0.0002
7	2	5	7	2	6	7436.6744	-0.0030
6	1	5	6	1	6	7566.6001	-0.0003
2	2	1	1	1	1	7586.0130	0.0002

Table S25. Measured frequencies and residuals (in MHz) for the rotational transitions of cyclooctanone BC2.

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	ν_{obs}	ν_{obs}- ν_{calc}
1	0	1	0	0	0	2753.8306	0.0036
3	1	2	3	1	3	3022.2846	-0.0029
3	2	2	3	0	3	3706.0092	-0.0007
4	2	3	4	0	4	4851.3487	0.0001
2	1	2	1	1	1	4984.7597	-0.0003
2	0	2	1	0	1	5223.2149	-0.0021
2	1	2	1	0	1	5373.1467	-0.0014
2	1	1	1	1	0	6030.5536	0.0007
3	1	3	2	1	2	7328.8701	-0.0138
3	0	3	2	0	2	7439.2517	-0.0137
3	1	3	2	0	2	7478.8012	-0.0137
2	2	0	1	1	0	7480.1497	-0.0068
2	2	1	1	1	1	7718.6153	0.0018

Table S26. Substitution coordinates of the heavy atoms of cyclooctanone BC1.

	a	*b*	*c*
C_1	-1.85974(81)	-0.9109(17)	-0.2614(58)
C_2	-1.4720(10)	0.4191(36)	-0.9043(17)
C_3	-1.1883(13)	1.57034(96)	0.075(20)
C_4	0.2775(54)	1.92021(78)	0.2661(56)
C_5	1.1736(13)	0.8064(19)	0.8824(17)
C_6	1.3014(12)	-0.3715(40)	-0.062(24)
O_7	2.02753(74)	-0.3199(47)	-1.0233(15)
C_8	-0.8901(17)	-1.4608(10)	0.7812(19)
C_9	0.5368(28)	-1.65569(91)	0.2869(53)