The Bisketene Radical Cation and its Formation by Oxidative Ring-Opening of Cyclobutenedione.

Krzysztof Piech and Thomas Bally^{*} Department of Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland Annette D. Allen and Thomas T. Tidwell Department of Chemistry, University of Toronto, Ontario, Canada M5S 3H6

Supporting Information

A. Complete Reference 11	1
B. Table S1: Results of B3LYP and G4 calculations for 1, 2, and their radical cations (cf. Figures 2 and 3)	2
C. Cartesian coordinates of all stationary points listed in Table S1	3

A. Complete Reference to the Gaussian program package (Reference 11)

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

B. Table S1: Results of B3LYP and G4 calculations for 1, 2, and their radical cations (cf. Figures 2 and 3)

				B3LYP	B3LYP	B3LYP	G4	G4	G4
	species:	symm	state:	w/zpve	enthalpy	free energy	energy	ethalpy	free energy
1	CBD	C2v	neutral	-303.951906	-303.946040	-303.979596	-303.880332	-303.879388	-303.912966
2	CBD-BK TS	C2	neutral	-303.906620	-303.900570	-303.935310	-303.830848	-303.829904	-303.863959
	Ea(CBD-BK)		neutral	28.42	28.53	27.79	31.05	31.05	30.75
3	BK (eq)	C2	neutral	-303.949137	-303.942262	-303.978695	-303.876122	-303.875178	-303.911587
	CBD-> BK (eq)		neutral	1.74	2.37	0.57	2.64	2.64	0.87
4	BK (C2h)	C2h	neutral	-303.947717	-303.940576	-303.977741	-303.873413	-303.872468	-303.909127
	BK(C2h-C2)		neutral	0.89	1.06	0.60	1.70	1.70	1.54
5	BK TS (C2h->C2)	C2	neutral	-303.947650	-303.941458	-303.975680	-303.874885	-303.873941	-303.908165
	Ea(BK C2h -BK-eq)			0.04	-0.55	1.29	-0.92	-0.92	0.60
6	BK (C2v, TS)	C2v	neutral	-303.945737	-303.939474	-303.974327	-303.872236	-303.871292	-303.906169
	Ea(BK-C2v)		neutral	2.13	1.75	2.74	2.44	2.44	3.40
7	CBD	C2v	radical cation	-303.624165	-303.617576	-303.653526	-303.543004	-303.542060	-303.577960
	adiabat. IP CBD/eV			8.91	8.93	8.87	9.18	9.18	9.11
8	CBD-BK TS	C2	radical cation	-303.624062	-303.617759	-303.653092	-303.542099	-303.541154	-303.576385
9	BK1	C2h	radical cation	-303.665613	-303.658830	-303.694974	-303.580858	-303.579914	-303.616014
10	BK2	C2v	radical cation	-303.662478	-303.655825	-303.692070	-303.577550	-303.576606	-303.612821
	adiabat. IP BK/eV			7.80	7.79	7.80	8.12	8.12	8.13
	CBD-BK1		radical cation	-26.01	-25.89	-26.01	-23.75	-23.75	-23.88
	CBD-BK2		radical cation	-24.04	-24.00	-24.19	-21.68	-21.68	-21.88
	EA(CBD-BK2)		radical cation	0.06	-0.11	0.27	0.57	0.57	0.99
							B3LYP	CCSD(T)	M42SDTQ
	BK (C2h)	C2h					-304.023379	-303.179696	-303.399713

-304.022970

-303.181103

-303.345287

BK TS1

C2

C. Cartesian coordinates of all stationary points listed in Table S1

Note: The B3LYP geometries that are obtained with the larger basis set used in the G4 method are nearly identical to those obtained with the 6-31G* basis set, so only the latter are listed,

Numbers correspond to entries in Table S1 where absolute and relative energies are listed.

1.	Neutral CBD	(C _{2v} ,	mini	mum)			
6	0.0000	00	0.67	6248	1	.272	2951
6	0.0000	00	-0.67	6248	1	.272	2951
6	0.0000	00	0.79	3677	-0	.236	5743
6	0.0000	00	-0.79	93677	-0	.236	5743
1	0.0000	00	-1.41	4793	2	.062	2705
1	0.0000	00	1.41	4793	2	.062	2705
8	0.0000	00	-1.67	7217	-1	.034	1994
8	0.0000	00	1.67	7217	-1	.034	1994
2.	Transition s	tate	neutr	al CBD	\rightarrow	BK	(C ₂)
6	0.6746	88	1.17	2490	0	.231	L880
6	-0.6746	88	1.17	2490	-0	.231	L880
6	1.0419	90	-0.16	51209	0	.087	7438
6	-1.0419	90	-0.16	51209	-0	.087	7438
1	1.1888	32	1.95	53468	0	.788	3696
1	-1.1888	32	1.95	53468	-0	.788	3696
8	1.8386	33	-1.00	2645	-0	.164	1726
8	-1.8386	33	-1.00	2645	0	.164	1726
3.	Neutral BK (C ₂ , m	inimu	ım)			
3. 6	Neutral BK (0 0.3244	C ₂ , m 49	inimu 0.66	um) 57845	0	.866	5869
3. 6 6	Neutral BK (0 0.3244 -0.3244	C ₂ , m 49 49	inimu 0.66 -0.66	um) 57845 57845	0	.860	5869 5869
3. 6 6 6	Neutral BK (0 0.3244 -0.3244 -0.0212	C ₂ , m 49 49 86	inimu 0.66 -0.66 1.56	m) 57845 57845 59025	0	.860 .860	5869 5869 9856
3. 6 6 6 6	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212	C ₂ , m 49 49 86 86	inimu 0.66 -0.66 1.56 -1.56	m) 57845 57845 59025 59025	0 0 -0 -0	.860 .860 .029	5869 5869 9856 9856
3. 6 6 6 6 1	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788	C ₂ , m 49 49 86 86 74	inimu 0.66 -0.66 1.56 -1.56 0.94	m) 57845 57845 59025 59025 19867	0 0 -0 -0 1	.860 .860 .029 .029	5869 5869 9856 9856 1726
3. 6 6 6 1 1	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788	C ₂ , m 49 49 86 86 74 74	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94	m) 57845 57845 59025 59025 19867 19867	0 0 -0 1 1	.860 .860 .029 .029 .594	5869 5869 9856 9856 1726 1726
3. 6 6 6 1 1 8	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244	C ₂ , m 49 49 86 86 74 74 49	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35	m) 57845 57845 59025 59025 19867 19867 58382	0 -0 -0 1 1 -0	.866 .866 .029 .029 .594 .594	5869 5869 9856 9856 1726 1726 1726 7100
3. 6 6 6 1 1 8 8	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244	C ₂ , m 49 49 86 86 74 74 49 49	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35	m) 57845 57845 59025 59025 19867 19867 58382 58382	0 -0 -0 1 -0 -0 -0 -0	. 866 . 866 . 029 . 029 . 594 . 827 . 827	5869 5869 9856 9856 1726 1726 7100 7100
3. 6 6 6 1 1 8 8 4.	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (0	C ₂ , m 49 49 86 86 74 74 49 49 C _{2h} , 7	0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35	m) 57845 57845 59025 59025 19867 19867 58382 58382 58382 shallow	0 -0 -0 1 -0 -0 -0 -0 -0	.866 .866 .029 .029 .594 .827 .827	5869 5869 9856 9856 1726 1726 7100 7100
 3. 6 6 6 1 8 8 4. 6 	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (0 -0.3262	C ₂ , m 49 49 86 86 74 74 49 49 C _{2h} , 7 45	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35 very 0.65	m) 57845 57845 59025 59025 19867 19867 58382 58382 58382 shallow	0 -0 -0 1 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0	.866 .866 .029 .029 .594 .827 .827	5869 5869 9856 9856 1726 1726 7100 7100 num)
 3. 6 6 1 8 4. 6 6 	Neutral BK (0 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (0 -0.3262 0.3262	C ₂ , m 49 49 86 86 74 74 49 49 C _{2h} , 45 45	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35 very 0.65 -0.65	m) 57845 57845 59025 59025 9867 9867 58382 58382 58382 58382 58382 58382 58382	0 -0 -0 1 -0 -0 -0 -0 -0	.866 .029 .029 .594 .594 .827 .827 .827	5869 5869 9856 9856 1726 1726 1726 7100 7100 7100
3. 6 6 6 1 1 8 8 4. 6 6 6 6 6 6 7 8 8 8 8 8 8 8 8 8 8 8 8 8	Neutral BK (4 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (4 -0.3262 0.3262 -0.3262	C ₂ , m 49 49 86 74 74 49 49 C _{2h} , 7 45 45 45	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35 very 0.65 -0.65 -1.80	m) 57845 57845 59025 99025 9867 9867 58382 58382 shallow 58617 58617 58617	0 -0 -0 1 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0	.860 .860 .029 .594 .827 .827 .827 .827	5869 5869 9856 9856 4726 4726 7100 7100 7100 1000 0000 0000 0000
3. 6 6 6 6 1 1 8 8 4. 6 6 6 6 6 6 6 6 6 6 7 1 8 8 8 4.	Neutral BK (4 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (4 -0.3262 0.3262 0.3262	C ₂ , m 49 49 86 74 74 49 C _{2h} , 7 45 45 45 45	inimu 0.66 -0.66 1.56 0.94 -0.94 2.35 -2.35 very 0.65 -0.65 -1.80 1.80	m) 57845 57845 59025 59025 19867 19867 58382 58382 shallow 58617 58617 58617 58617 58617 58619 58619 58619	0 -0 -0 1 1 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0 -0	.866 .866 .029 .594 .594 .827 .827 .827 .000 .000	5869 5869 9856 9856 1726 1726 7100 7100 7100 0000 0000 0000 0000 000
<pre>3. 6 6 6 6 1 1 8 8 4. 6 6 6 8</pre>	Neutral BK (4 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (4 -0.3262 0.3262 -0.3262 0.3262 -0.8888	C ₂ , m 49 49 86 74 74 49 C _{2h} , 45 45 45 45 45	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35 very 0.65 -1.80 1.80 -2.83	m) 57845 57845 59025 59025 9867 9867 58382 58382 58382 58382 58617 58617 58617 58617 58617 58617 58617 58617 58617 58617 58617	0 0 -0 1 -0 -0 0 0 0 0 0 0 0 0 0 0 0 0 0	.866 .866 .029 .029 .594 .827 .827 .827 .827 .000 .000	5869 5869 9856 9856 4726 7100 7100 7100 0000 0000 0000 0000 000
3. 6 6 6 1 1 8 4. 6 6 6 6 8 8 8 8 4.	Neutral BK (4 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (4 -0.3262 0.3262 -0.3262 0.3262 -0.3262 0.3262 -0.8888 0.8888	C ₂ , m 49 49 86 74 74 49 49 C _{2h} , 7 45 45 45 45 45 45 18 18	inimu 0.66 -0.66 1.56 -1.56 0.94 -0.94 2.35 -2.35 very 0.65 -1.80 1.80 -2.83 2.83	m) 57845 57845 59025 59025 9867 58382 58382 58382 58617	0 -0 -0 1 -0 -0 0 0 0 0 0 0 0 0 0 0 0 0 0	.866 .866 .029 .594 .594 .827 .827 .827 .827 .000 .000 .000	5869 5869 9856 9856 4726 4726 7100 7100 7100 0000 0000 0000 0000 000
3. 6 6 6 6 1 1 8 8 4. 6 6 6 6 8 8 1 1 8 8 4.	Neutral BK (4 0.3244 -0.3244 -0.0212 0.0212 1.0788 -1.0788 -0.3244 0.3244 Neutral BK (4 -0.3262 0.3262 -0.3262 0.3262 -0.3262 0.3262 -0.8888 0.8888 1.4090	C ₂ , m 49 49 86 74 74 49 C _{2h} , 7 45 45 45 45 45 45 18 18 62	inimu 0.66 -0.66 1.56 0.94 -0.94 2.35 -2.35 very 0.65 -1.80 1.80 -2.83 2.83 -0.73	m) 57845 57845 59025 59025 9867 9867 58382 58382 shallow 58617 58621 58617 58621 58621 58621 586217 58621 586217 58621 586217 58621 586217 58621 586217 58621 586217 58621 586217 58621 58621 58621 58621 58621 58621 586217 58621 58621 58621 58621 58621 58621 58621 58621 58621 58621 58621 58621 58621 586217 58621 586217 58675555555555555555555555555555555555	0 0 -0 1 1 -0 -0 0 0 0 0 0 0 0 0 0 0 0 0 0	.866 .866 .029 .594 .594 .827 .827 .827 .000 .000 .000 .000	5869 5869 9856 9856 1726 1726 7100 7100 7100 0000 0000 0000 0000 000

5. Neutral BK, (very flat) saddle point beween the $\text{C}_{2\text{h}}$ and C_2 structures

6	0.421435	0.606133	0.354390
6	-0.421435	-0.606133	0.354390
6	-0.023375	1.783806	-0.031001
6	0.023375	-1.783806	-0.031001
1	1.452954	0.578784	0.688248
1	-1.452954	-0.578784	0.688248
8	-0.421435	2.836667	-0.328572
8	0.421435	-2.836667	-0.328572

6. Neutral BK (C $_{\rm 2v},$ saddle point)

6	0.00000	0.736700	1.003068
6	0.000000	-0.736700	1.003068
6	0.000000	1.540774	-0.045280
6	0.000000	-1.540774	-0.045280
1	0.000000	1.236129	1.966515
1	0.000000	-1.236129	1.966515
8	0.00000	2.271651	-0.964155
8	0.000000	-2.271651	-0.964155

7. CBD radical cation (C_{2v} , minimum)

6	0.00000	0.674114	1.211713
6	0.00000	-0.674114	1.211713
6	0.00000	1.050802	-0.207952
6	0.00000	-1.050802	-0.207952
1	0.000000	-1.385459	2.034059
1	0.00000	1.385459	2.034059
8	0.00000	-1.886609	-1.007078
8	0.00000	1.886609	-1.007078

8. Transition state $CBD^{*+} \rightarrow BK^{*+}$ (C₂)

6	0.038936	0.675510	1.163821
6	-0.038936	-0.675510	1.163821
6	-0.038936	1.154998	-0.201719
6	0.038936	-1.154998	-0.201719
1	0.165786	1.346973	2.011371
1	-0.165786	-1.346973	2.011371
8	-0.273073	1.980068	-0.972999
8	0.273073	-1.980068	-0.972999

9. BK radical cation (planar, $C_{\rm 2h})$

6	-0.337113	0.618591	0.00000
6	0.337113	-0.618591	0.00000
6	-0.337113	-1.807230	0.00000
6	0.337113	1.807230	0.00000
8	-0.876334	-2.816973	0.00000
8	0.876334	2.816973	0.00000
1	1.422403	-0.703283	0.00000
1	-1.422403	0.703283	0.00000

10. BK radical cation (planar, $C_{\rm 2v})$

6	0.00000	0.705700	1.032673
6	0.000000	-0.705700	1.032673
6	0.00000	1.515116	-0.066822
6	0.000000	-1.515116	-0.066822
1	0.00000	1.233580	1.985406
1	0.000000	-1.233580	1.985406
8	0.00000	2.216565	-0.972564
8	0.00000	-2.216565	-0.972564