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

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Supporting Information

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)

	species:	symm	state:	B3LYP w/zpve	B3LYP enthalpy	B3LYP free energy	G4 energy	G4 ethalpy	G4 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
BK TS1	C2	-304.022970	-303.181103	-303.345287

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}, minimum)

6	0.000000	0.676248	1.272951
6	0.000000	-0.676248	1.272951
6	0.000000	0.793677	-0.236743
6	0.000000	-0.793677	-0.236743
1	0.000000	-1.414793	2.062705
1	0.000000	1.414793	2.062705
8	0.000000	-1.677217	-1.034994
8	0.000000	1.677217	-1.034994

2. Transition state neutral **CBD** → **BK** (C_2)

6	0.674688	1.172490	0.231880
6	-0.674688	1.172490	-0.231880
6	1.041990	-0.161209	0.087438
6	-1.041990	-0.161209	-0.087438
1	1.188832	1.953468	0.788696
1	-1.188832	1.953468	-0.788696
8	1.838633	-1.002645	-0.164726
8	-1.838633	-1.002645	0.164726

3. Neutral **BK** (C_2, minimum)

6	0.324449	0.667845	0.866869
6	-0.324449	-0.667845	0.866869
6	-0.021286	1.569025	-0.029856
6	0.021286	-1.569025	-0.029856
1	1.078874	0.949867	1.594726
1	-1.078874	-0.949867	1.594726
8	-0.324449	2.358382	-0.827100
8	0.324449	-2.358382	-0.827100

4. Neutral **BK** (C_{2h}, very shallow minimum)

6	-0.326245	0.658617	0.000000
6	0.326245	-0.658617	0.000000
6	-0.326245	-1.807599	0.000000
6	0.326245	1.807599	0.000000
8	-0.888818	-2.838201	0.000000
8	0.888818	2.838201	0.000000
1	1.409062	-0.734753	0.000000
1	-1.409062	0.734753	0.000000

5. Neutral **BK,** (very flat) saddle point beween the C_{2h} 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_{2v}, saddle point)

6	0.000000	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	0.000000	2.271651	-0.964155
8	0.000000	-2.271651	-0.964155

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

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

8. Transition state **CBD**$^{\bullet+}$ → **BK**$^{\bullet+}$ (C_2)

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_{2h})

6	-0.337113	0.618591	0.000000
6	0.337113	-0.618591	0.000000
6	-0.337113	-1.807230	0.000000
6	0.337113	1.807230	0.000000
8	-0.876334	-2.816973	0.000000
8	0.876334	2.816973	0.000000
1	1.422403	-0.703283	0.000000
1	-1.422403	0.703283	0.000000

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

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