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Photoinduced Electron-Transfer Bicyclopropenyl-benzene Rearrangements of 2,2′,3,3′-Tetraphenylbicyclopropenyls: A New Mechanism via Dewar Benzene

Hiroshi Ikeda,* Yosuke Hoshi, Yuka Kikuchi, Futoshi Tanaka, and Tsutomu Miyashi

Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-8578, Japan

ikeda@org.chem.tohoku.ac.jp

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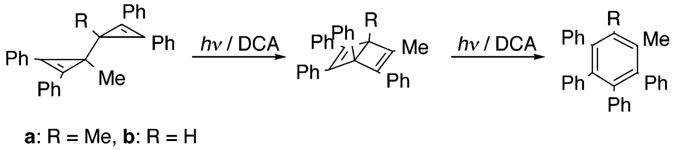
ABSTRACT



The 9,10-dicyanoanthracene-sensitized photoreaction of 1-methyl- and 1,1′-dimethyl-2,2′,3,3′-tetraphenylbicyclopropenyl gives the corresponding benzene and Dewar benzene derivatives, indicating that their photoinduced electron-transfer bicyclopropenyl-benzene rearrangements proceed via Dewar benzenes.

According to theoretical calculations,[1] bicyclopropenyl is the highest in energy among all valence isomers of benzene. Since the pioneering work of Breslow[2a] first demonstrated that, on heating, hexaphenylbicyclopropenyl underwent isomerizatoin to give hexaphenylbenzene, several reaction mechanisms were proposed for the bicyclopropenyl-benzene rearrangements, which were achieved by thermolyses,[2] Ag^+-catalyzed reactions,[3] and photolyses.[4] The rearrangement can be also triggered by photoinduced electron transfer (PET). A CIDNP study[5] of the *p*-chloranil-sensitized photoreaction of 1,1′-dimethylbicyclopropenyl (**1**) revealed that the initially formed tricyclohexane radical cation $\mathbf{2}^{\bullet+}$ rearranges to dimethylbenzvalene radical cations, which, in turn, rearrange to *o*- and *m*-xylenes. The 9,10-dicyanoanthracene (DCA)-sensitized photoreaction of 1,1′-dimethyl-2,2′,3,3′-tetraphenylbicyclopropenyl (**3a**) in acetonitrile was reported[6] to form 1,2-dimethyl-3,4,5,6-tetraphenylbenzene (**4a**) exclusively via a tricyclohexane radical cation intermediate $\mathbf{5a}^{\bullet+}$. To gain further insight into the mechanistic pathway[7] for **3**, we reinvestigated the DCA-sensitized photoreactions of **3a** as well as 1-methyl-2,2′,3,3′-tetraphenylbicyclopropenyl (**3b**).[2c] Here, we report that the intrinsic process is the formation of

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[1] (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 5059−5061. (b) Li, Z.; Rogers, D. W.; McLafferty, F. J.; Mandziuk, M.; Podosenin, A. V. *J. Phys. Chem. A* **1999**, *103*, 426−430.

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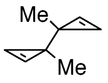
[4] Photolyses: Weiss, R.; Köbl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3222−3224. See also refs 2a,b.

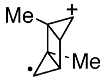
[5] Abelt, C. J.; Roth, H. D. *J. Am. Chem. Soc.* **1985**, *107*, 3840−3843.

[6] Padwa, A.; Goldstein, S. I.; Rosenthal, R. J. *J. Org. Chem.* **1987**, *52*, 3278−3285.

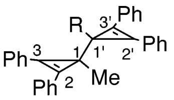
10.1021/ol049917j CCC: $27.50



1

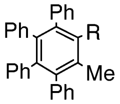


2$^{\bullet+}$



3

a: R = Me, **b**: R = H



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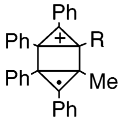
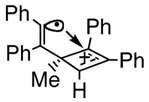
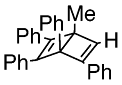


5$^{\bullet+}$



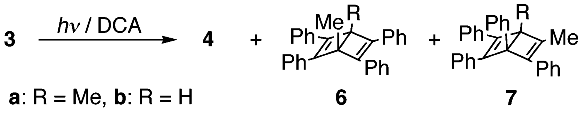
9b$^{\bullet+}$



10b

two types of Dewar benzenes[9] **6** and **7** (Scheme 1), which cannot be accounted for by a tricyclohexane radical cation intermediate like **5**$^{\bullet+}$.

Scheme 1. DCA-Sensitized PET Reaction of **3**



The anodic peak oxidation potentials (E_{pa})[10] of **3a** (+1.24 V vs SCE in dichloromethane) and **3b** (+1.22 V) are low enough to quench the excited singlet state of DCA exergonically, as suggested by their respective calculated free energy changes for electron transfer,[11] $\Delta G_{et} = -1.00$ and -1.02 eV, in dichloromethane. In agreement with the estimate, **3a** and **3b** quench the fluorescence of DCA efficiently with respective rate constants of $k_q = 1.9$ and 1.8×10^{10} M^{-1} s^{-1} in dichloromethane.

The DCA-sensitized photoreactions of **3a** (λ > 410 nm) in degassed dichloromethane-d_2 at 20 °C differ from previously reported results[6] in acetonitrile. As shown in Scheme 1, Dewar benzenes[9] **6a** and **7a** are formed together with **4a** in a product ratio that significantly depends on irradiation time. At 86% conversion (10 h), **4a**, **6a**, and **7a** are formed in 46, 24, and 14% yields, respectively, but prolonged irradiation (30 h) results in the formation of a mixture of **4a** (72%) and **6a** (28%).[14] The fact that the yield of **4a** increases while that of **7a** decreases and that of **6a** does not change suggests that **7a** readily rearranges to **4a**, while **6a** is stable under the conditions employed. Similarly, the DCA-sensitized photoreaction of **3b** in dichloromethane-d_2 at 20 °C gives **4b** (>+2.0 V), **6b**[3b] (+1.48 V), and **7b** (+1.38 V) in 35, 18, and 41% yields, respectively, at 94% conversion of **3b**. Figure 1 shows the time-dependent changes of the product ratios observed during irradiation, suggesting that the immediate precursor of **4b** is Dewar benzene **7b**. Actually, the independent PET reactions of **6b** and **7b** result in the quantitative recovery of **6b** and formation of **4b**, respectively. Note that **7b** rearranges to **4b** slowly, even at 20 °C in the dark. Therefore, the formation of Dewar benzenes **6** and **7** excludes the intermediacy of the tricyclohexane radical cation **5**$^{\bullet+}$.

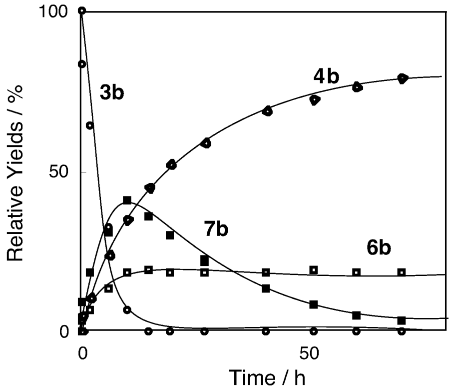
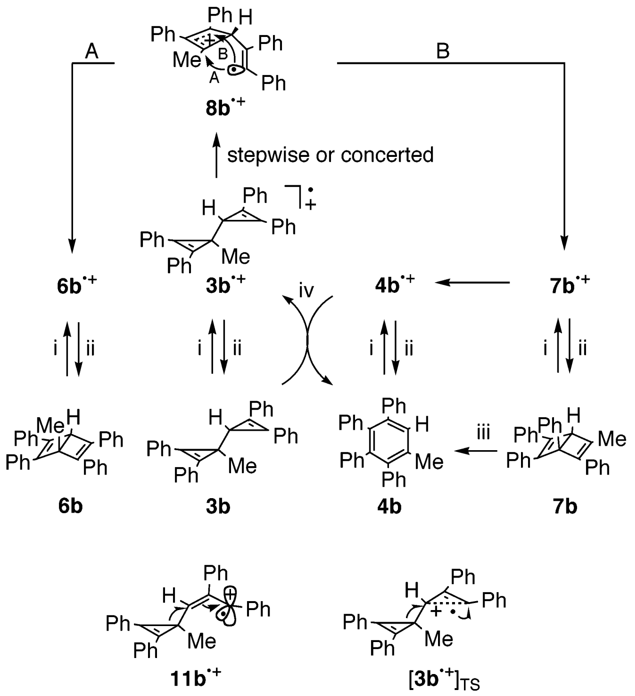


Figure 1. Time-dependent changes in the product ratios in the DCA-sensitized PET reaction of **3b** (0.1 M) in degassed dichloromethane-d_2 at 20 °C. The product yields were determined using ^{1}H NMR. The material balance is 100%.

A plausible mechanism for formation of **3b** via Dewar benzene derivatives is depicted in Scheme 2. The ring cleavage of the cyclopropene $C_{1'}-C_{2'}$ (or $C_{1'}-C_{3'}$) bond

Scheme 2. Plausible Mechanism for the PET Bicyclopropenyl-benzene Rearrangement of **3b**[a]



[a] Conditions: (i) $h\nu$/DCA, (ii) back-electron-transfer from DCA$^{\bullet-}$, (iii) Δ at 20 °C, (iv) hole transfer.

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(7) The real structures of Dewar benzene derivatives and their mechanism of formation in the electron-transfer reactions of bicyclopropenyl or cyclopropenyl cation remain controversial. See ref 8.

(8) Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371−1427.

(9) Weiss and co-workers were the first to isolate Dewar benzene derivatives and demonstrated their contribution in thermal, Ag$^+$-catalyzed, and photolytic bicyclopropenyl-benzene rearrangements. See refs 2c, 3a−c, and 4.

associated with the ring expansion of the other cyclopropene ring of **3b**$^{\bullet+}$ forms a σ radical-allyl cation intermediate **8b**$^{\bullet+}$. Whether this Wagner−Meerwein-type rearrangement occurs stepwise[15] via an intermediate **11b**$^{\bullet+}$ or concertedly via the transition state [**3b**$^{\bullet+}$]$_{TS}$, the two-bond cleavage process to form **8b**$^{\bullet+}$ is essentially the same as those in the Ag$^+$-catalyzed reactions and thermolyses of bicyclopropenyls proposed by Weiss[3b,c,9] and Bergman.[2e,f] Dewar benzene **6b** is formed via the ring closure A in **8b**$^{\bullet+}$ to **6b**$^{\bullet+}$ followed by back electron transfer (BET) from DCA$^{\bullet-}$. Radical cation **7b**$^{\bullet+}$ formed by competitive ring closure B rearranges to **4b**$^{\bullet+}$. Products **7b** and **4b** are formed after BET in **7b**$^{\bullet+}$ and **4b**$^{\bullet+}$, respectively. Dewar benzene **7b** with the phenyl group at the sp^3 carbon rearranges readily to **4b** under the PET conditions employed.

Radical cation **3b**$^{\bullet+}$ can form formally alternative σ radical-allyl cation **9b**$^{\bullet+}$, which would give **6b**, **4b**, and the unobserved Dewar benzene **10b**. Because **10b** with the phenyl and methyl groups at the sp^3 carbons would be probably more unstable than **7b** under the condition employed, the fact that **10b** is not found during the reaction does not necessarily indicate that **9b**$^{\bullet+}$ is not involved with the reaction of **3b**. However, a preferential formation of **8b**$^{\bullet+}$ over **9b**$^{\bullet+}$ is expected from the point of view of thermodynamic stability: **8b**$^{\bullet+}$ with a *tertiary* allylic cation is more stable than **9b**$^{\bullet+}$ containing a *secondary* allylic cation.

The formation of **6b** and **7b** from the unsymmetrical bicyclopropenyl **3b** apparently requires the regiospecific $C_1'-C_2'$ (or $C_1'-C_3'$) cleavage of **3b**$^{\bullet+}$, in which the unpaired electron and positive charge are predominantly localized on the diphenylcyclopropyl (DPC) subunit, the cyclopropene ring without a methyl group (Figure 2). To gain further insight into the electronic structure of **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$, we conducted semiempirical and DFT calculations.[17,22]

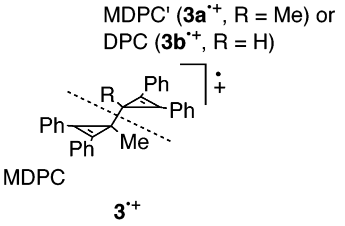

Figure 2. Definition of two subunits in **3**$^{\bullet+}$.

Table 1. Sum of the Calculated Partial Spin (ρ) and Charge (q) Densities of **3a**$^{\bullet+}$ (C_{2h}) and **3b**$^{\bullet+}$ (C_s)

		MDPC		MDPC′ or DPC	
		$\Sigma\rho$	Σq	$\Sigma\rho$	Σq
3a$^{\bullet+}$	AM1/ROHF	+0.50	+0.50	+0.50	+0.50
	AM1/UHF	+0.50	+0.50	+0.50	+0.50
	PM3/UHF	+0.50	+0.50	+0.50	+0.50
	ROB3LYP/6-31G(p)	+0.50	+0.50	+0.50	+0.50
3b$^{\bullet+}$	AM1/ROHF	+0.12	+0.17	+0.88	+0.83
	AM1/UHF	+0.05	+0.12	+0.95	+0.88
	PM3/UHF	+0.05	+0.11	+0.95	+0.89
	ROB3LYP/6-31G(p)	+0.06	+0.17	+0.94	+0.83

Table 1 shows the sum of the calculated partial spin and charge density, $\Sigma\rho$ and Σq, respectively, for two methyldiphenylcyclopropyl (MDPC) subunits of **3a**$^{\bullet+}$ and for the MDPC and DPC subunits in **3b**$^{\bullet+}$. Both $\Sigma\rho$ and Σq values for the MDPC subunit of **3a**$^{\bullet+}$ are +0.50, regardless of the method of calculation. Those for another MDPC subunit (MDPC′) are accordingly +0.50. In sharp contrast, an unsymmetrical electronic structure is suggested for **3b**$^{\bullet+}$. The $\Sigma\rho$ and Σq values for the DPC subunits of **3b**$^{\bullet+}$ are +0.88∼0.95 and +0.83∼0.89, respectively: the residual spin and charge are suggested to locate in the MDPC subunit. Results of the calculation indicate that the unpaired electron and positive charge of **3b**$^{\bullet+}$ are delocalized predominantly on the DPC, the less electron-donating subunit, while they are distributed evenly over two MDPC subunits of **3a**$^{\bullet+}$. Figure 3 represents contrasting SOMOs of **3a**$^{\bullet+}$ and **3b**$^{\bullet+}$ calculated by ROB3LYP/6-31G(p). Thus, the semiempirical and DFT calculations support the characteristic electronic structure of **3b**$^{\bullet+}$. If this estimate is appropriate, the fact that the isomeric Dewar benzene **10b** expected from the alternative radical cation intermediate **9b**$^{\bullet+}$ is not observed during

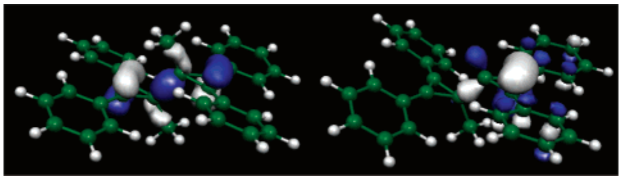

Figure 3. Representation of the SOMOs of **3a**$^{\bullet+}$ (left, C_{2h}) and **3b**$^{\bullet+}$ (right, C_s) calculated by ROB3LYP/6-31G(p).

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(10) Values of E_{pa} were measured by cyclic voltammetry (Pt electrode, scan rate 100 mV/s) in dry dichloromethane with 0.1 M n-$Bu_4N^+BF_4^-$ as a supporting electrolyte. All substrates gave irreversible waves.

(11) Values of ΔG_{et} were estimated by using the Rehm−Weller equation:[12] $\Delta G_{et} = E^{ox}_{1/2}(\mathbf{3}) - E^{red}_{1/2}(\mathrm{DCA}) - E_{0-0}(\mathrm{DCA}) - e^2/\epsilon r$, where $E^{red}_{1/2}(\mathrm{DCA}) = -0.89$ V,[13] $E_{0-0}(\mathrm{DCA}) = 2.87$ eV, and $e^2/\epsilon r = 0.23$ eV in dichloromethane. The halfwave oxidation potentials ($E^{ox}_{1/2}$) were obtained as $E_{pa} - 0.03$ V, assuming a one-electron oxidation process.

(12) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259−271.

(13) Ikeda, H.; Minegishi, T.; Takahashi, Y.; Miyashi, T. *Tetrahedron Lett.* **1996**, *37*, 4377−4380.

(14) We observed also that a similar photoreaction (1.5 h) of **3a** in acetonitrile at 20 °C gave **4a** and **6a** in 83 and 17% yields, respectively.

(15) For the bond cleavage of cyclopropene radical cations, see ref 16.

(16) Padwa, A.; Chou, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555−4564.

(17) Semiempirical and DFT calculation was carried out at C_{2h} (**3a**$^{\bullet+}$) or C_s (**3b**$^{\bullet+}$) symmetry using PC GAMESS ver. 6.3,[18] WinMOPAC2002,[19] and Gaussian98[20] softwares. Figure 3 was drawn using MOLEKEL software.[21]

(18) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(19) *MOPAC2002*; Stewart, J. J. P. Fujitsu, Ltd.: Tokyo, Japan, 2002.

irradiation is not inconsistent with the unique electronic structure of $\mathbf{3b}^{\bullet+}$. According to orbital interaction theory,[24] the characteristic electronic structure of $\mathbf{3b}^{\bullet+}$ is probably due to the electronic coupling of two cyclopropene rings through space and through two C−C σ-bonds ($C_1'-C_1-Me$). Similar electronic couplings were suggested by theoretical calculations for the neutral forms of the parent bicyclopropenyl and related compounds.[25]

The high efficiency of the PET reaction is another feature of **3b**. The corrected quantum efficiency (Φ_c)[26] per ion radical pair [$\mathbf{3b}^{\bullet+}$/DCA$^{\bullet-}$] for the formation of **4b**, **6b**, and **7b** at a 10 mM concentration of **3b** is 1.4, indicating a chain mechanism for the photoreaction of **3b**. The hole transfer (HT) from $\mathbf{4b}^{\bullet+}$ to **3b** with a negative free energy change ($\Delta G_{ht} < -0.81$ eV) is a key process. If the rate of HT (k_{ht}) is close to the diffusion control rate (2.2×10^{10} M^{-1} s^{-1} at 20 °C), the pseudo-first-order rate constant ($k_{ht}[\mathbf{3b}]$) at the initial stage is calculated to be 2.2×10^{8} s^{-1}, which is faster than $k_{bet} < 7.6 \times 10^{7}$ s^{-1} for the BET[27] from DCA$^{\bullet-}$ to $\mathbf{4b}^{\bullet+}$. Thus, $\mathbf{4b}^{\bullet+}$ acts as a carrier and undergoes HT much faster than $\mathbf{6b}^{\bullet+}$ and $\mathbf{7b}^{\bullet+}$, which suffer BET[30] from DCA$^{\bullet-}$ much faster than $\mathbf{4b}^{\bullet+}$. Interestingly, similar thermodynamics and kinetics are expected for $\mathbf{4a}^{\bullet+}$, but the Φ_c of **3a** is as low as 0.13. The remarkable difference in Φ_c between **3a** and **3b** is probably due to the extreme distribution of the unpaired electron and positive charge in $\mathbf{3b}^{\bullet+}$, which facilitates the Wagner−Meerwein-type rearrangement of $\mathbf{3b}^{\bullet+}$ to $\mathbf{8b}^{\bullet+}$.

In conclusion, our experimental results first demonstrate a new mechanism via Dewar benzene for the PET bicyclopropenyl-benzene rearrangements of tetraphenyl-substituted bicyclopropenyl derivatives. This is in line with the mechanisms proposed by Weiss and Bergman for the Ag$^+$-catalyzed reactions and thermolyses. Consequently, this work proposes a topologically common reaction pathway via Dewar benzene that is applicable to thermolyses, Ag$^+$-catalyzed reactions, and PET reactions of tetraphenyl-substituted bicyclopropenyl derivatives.

Acknowledgment. We gratefully acknowledge the financial support of a Grant-in-Aid for Scientific Research on Priority Areas (417) and others (Nos. 12440173 and 14050008) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan.

Supporting Information Available: Experimental details including physical data for **6** and **7** and Cartesian coordinates and $\Sigma\rho$ and Σq values for $\mathbf{3a}^{\bullet+}$ and $\mathbf{3b}^{\bullet+}$ (ROB3LYP/6-31G(p)). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.4; Gaussian, Inc.: Pittsburgh, PA, 1998.

[21] *MOLEKEL 4.3;* Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J.; Swiss Center for Scientific Computing*:* Manno, Switzerland, 2002.

[22] For the ab initio calculation of the related interaction complex between cyclopropenyl cation and cyclopropenenyl radical, see ref 23.

[23] Raghavachari, K.; Roth, H. D. *J. Am. Chem. Soc.* **1989**, *111*, 7132−7136.

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[26] Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87−95.

[27] Rate constant (k_{bet}) for the BET from DCA$^{\bullet-}$ to $\mathbf{4b}^{\bullet+}$ at 20 °C in dichloromethane was calculated using the following equations (1,[28] 2,[28] and 3) and parameters reported by Kikuchi and co-workers:[29]

$$k_{bet} = \left(\frac{4\pi^3}{h^2\lambda_s k_b T}\right)^{1/2} |V|^2 \sum_{w=0}^{\infty} \left(\frac{e^{-s}S^{w}}{W!}\right) \exp\left\{-\frac{(\lambda_s + \Delta G_{bet} + wh\nu)^2}{4\lambda_s k_b T}\right\} \tag{1}$$

$$S = \lambda_v / h\nu \tag{2}$$

$$\Delta G_{bet} = -[E^{ox}{}_{1/2}(\mathbf{4b}) - E^{red}{}_{1/2}(\mathrm{DCA}) - e^2/\epsilon r] \tag{3}$$

where parameters V, λ_s, λ_v, ν, and ΔG_{bet} are, respectively, the electronic coupling matrix element (18 cm^{-1}), solvent reorganization energy (1.0 eV), vibration reorganization energy (0.3 eV), single average frequency (1500 cm^{-1}), and free energy change for electron-transfer process. In addition, h, k_b, and T, are Planck's constant, Boltzmann's constant, and the temperature (293 K), respectively.

[28] (a) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057−5068. (b) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741−747. (c) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 748−752. (d) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183−197. (e) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358−4368.

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[30] Values of k_{bet} for the BET from DCA$^{\bullet-}$ to $\mathbf{6b}^{\bullet+}$ and $\mathbf{7b}^{\bullet+}$ were calculated to be 3.5 and 6.2×10^{9} s^{-1}, respectively.