Kinetics of Bond Shift and Charge Transfer in Dialkynylphenylene-Bridged Dicyclooctatetraenes and Their Dianions

Patrik Boman,[†] Bertil Eliasson,*,[†] Russell A. Grimm,[‡] Gregory S. Martin,[‡] Jeffrey T. Strnad,[‡] and Stuart W. Staley*,[‡]

Contribution from the Department of Organic Chemistry, Umeå University, S-901 87 Umeå, Sweden, and Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

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Abstract: 1,4-Dicyclooctatetraenyl-1,3-butadiyne and *p*-, *m*-, and *o*-di(cyclooctatetraenylethynyl)benzene (**1**−**4**, respectively) and their dipotassium salts ($\mathbf{1^{2-}}$−$\mathbf{4^{2-}}$) in THF-d_8 have been synthesized and studied by dynamic NMR spectroscopy. Rate constants for bond shift (k_{BS}) in the neutral cyclooctatetraene (COT) rings of **1**−**4** and $\mathbf{1^{2-}}$−$\mathbf{4^{2-}}$ and for intramolecular charge (electron and cation) transfer (k_{CT}) between the dianion and the neutral COT rings in $\mathbf{1^{2-}}$−$\mathbf{4^{2-}}$ have been determined. ^{13}C NMR chemical shifts and AM1 π-charges as well as the values of k_{CT} are interpreted on the basis of a stronger through-bond interaction between the COT rings in the order $\mathbf{1^{2-}} \gg \mathbf{2^{2-}} \geq \mathbf{4^{2-}} > \mathbf{3^{2-}}$. Similarly, k_{BS} decreases in the order $\mathbf{1^{2-}} \gg \mathbf{4^{2-}} > \mathbf{2^{2-}} > \mathbf{3^{2-}}$ on going from **1**−**4** to the corresponding dianions. Analysis of the AM1 π-charge densities suggests that these differences are primarily due to a through-bond effect with an additional through-space contribution from the electric field of the dianion ring for bond shift in $\mathbf{4^{2-}}$.

Introduction

Because of the fundamental role of electron transfer (ET) in many branches of chemistry, a large amount of research has been devoted to studies of ET processes.[1] To understand the fundamental mechanisms of ET, studies have commonly been carried out on simplified model compounds for both inter- and intramolecular ET processes. It is well recognized that studies have to be performed on well-defined structures in order to quantitatively evaluate theoretical models.[2] The bridged dicyclooctatetraene dianion system ($COT-X-COT^{2-}$) with alkali metal cations represents one such model system for the investigation of different aspects of thermally induced electron and cation transfer, hereinafter denoted as charge transfer (CT).[3−5]

Our earlier studies revealed that such systems can undergo an unusually slow intramolecular two-electron transfer that can be studied by dynamic ^{1}H and ^{13}C NMR spectroscopy. The main reason for the slow CT is conformational gating,[6] i.e., the need to flatten the neutral ring. In effect, a fast CT process has been "tuned" into the NMR time scale by introducing a large

conformational barrier to CT. This strategy is akin to that of attenuating the rate of ET by bringing the reaction dynamics into the solvent-controlled adiabatic limit through the use of a nematic phase of a liquid crystal.[7]

In this study, intramolecular transfer of electrons and cations for dipotassium salts $\mathbf{1^{2-}}$−$\mathbf{4^{2-}}$ are examined with emphasis on the electronic properties of the spacer that separates the donor and acceptor moieties. These compounds were chosen for
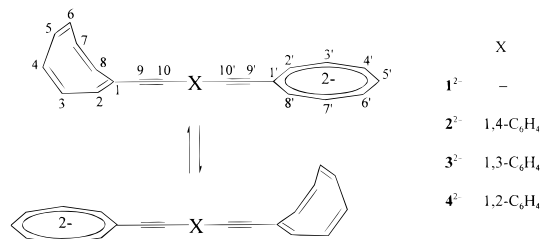
several reasons, including (a) the increasing interest in the phenylethynyl group as a structural unit or building block for various areas of materials chemistry,[8] (b) the well-defined structures of the bridging groups, (c) the opportunity for probing subtle structural and electronic differences by changing the position of substitution on the phenylene ring, and (d) the potential for exploring the energetics of two-electron-transfer processes.[9] The latter represent a class of reactions of great interest to various fields, but for which almost no data are available. In this study, we examine three experimental measures of electronic communication between the two COT rings and

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[†] Umeå University.

[‡] Carnegie Mellon University.

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Table 1. ^{13}C NMR Chemical Shifts for **1**−**4** and Their Dipotassium Salts **1**$^{2-}$−**4**$^{2-}$ in THF-d_8[a]

carbon	**1**$^{2-\,b}$	**2**$^{2-\,c}$	**3**$^{2-\,d}$	**4**$^{2-\,e}$	**1**^{f}	**2**^{g}	**3**^{h}	**4**^{i}
1	128.1	127.0	126.6	127.6	125.2	126.0	126.0	126.4 or 126.5
2	131.2	136.3	138.0	136.6	142.6	139.2	139.2	139.1
3−4, 6−7	131.8−132.4^j	132.2−132.7^k	131.8−133.5^j	132.3−133.6^k	130.5−134.5^k	131.6−133.7^k		
5	132.7	132.6	132.8	132.6	132.5	132.8		
8	133.1	132.2−132.7^k	132.4	132.3−133.6^k	130.5−134.5^k	131.6−133.7^k		
1′	80.0	82.6	81.7	82.8				
2′	94.8	95.4	95.1	95.7				
3′	98.4	97.1	96.1	96.8				
4′	89.0	89.3	89.2	89.1				
5′	99.7	99.3	98.1	99.1				
9	83.6	90.4	89.5	92.8	82.0	92.5	91.2	94.7
9′	110.0	120.7	117.3	120.5				
10	81.2	89.9	88.5	90.1	71.7	87.2	86.6	86.5
10′	68.3	83.7	81.0	82.8				
11		115.0	123.4	122.4		123.7		
11′		130.2	130.5	132.5				
12		131.7	*l*	*m*		132.3		
12′		127.7	*l*	*m*				
13, 13′			*l*	*m*				
$\delta_{av}{}^n$	93.0	93.2	92.6	93.1				

[a] Cyclohexane was used as chemical shift reference (δ = 27.7). [b] −32 °C, 0.5 M. [c] −38 °C, 0.5 M. [d] −42 °C, 0.5 M. [e] −35 °C, 0.1 M. [f] −113 °C, 0.5 M. [g] −50 °C, 0.5 M. [h] −30 °C, 0.1 M. [i] −27 °C, 0.1 M. [j] Four peaks in this region. [k] Five peaks in this region. [l] The proton-bearing phenylene carbons appear at δ 124.7, 128.1, 128.8, and 131.8. [m] The proton-bearing phenylene carbons appear at δ 120.9, 128.2, 128.3, and 132.5. [n] Average δ value for the dianion ring.

analyze them on the basis of semiempirical and ab initio molecular orbital (MO) calculations.

Experimental Section

Synthesis. 1,4-Dicyclooctatetraenyl-1,3-butadiyne (1). Ethynylcyclooctatetraene[10] (0.82 g, 6.4 mmol) and 1.69 g (15.1 mmol) of cupric acetate were dissolved in 6.0 mL of pyridine and 7.0 mL of methanol. This mixture was stirred overnight under a slightly positive pressure of O$_2$ and then taken up in 75 mL of hexane and washed with 3 × 50 mL of 6 M aqueous HCl and 3 × 50 mL of brine. The organic phase was dried (Na$_2$SO$_4$) and filtered, and the solvent was evaporated. The resulting orange solid was chromatographed on silica gel with CH$_2$Cl$_2$ to yield, after recrystallization from 1:1 CH$_2$Cl$_2$/hexane, 0.68 g (84%) of **1**, mp 77−78.5 °C. ^{1}H NMR (THF-d_8, 20 °C): δ 6.00−5.75 (m). ^{13}C NMR: see Table 1. IR (CCl$_4$): 3012, 2964, 2928, 1552, 1223 cm^{-1}. Calcd for C$_{20}$H$_{14}$: C, 94.45; H, 5.55. Found: C, 94.54; H, 5.70.

1,4- and 1,3-di(cyclooctatetraenylethynyl)benzene (**2** and **3**, respectively) were prepared as previously reported.[10]

1,2-Di(cyclooctatetraenylethynyl)benzene (4). To 500 mg (1.85 mmol) of 1,2-di((trimethylsilyl)ethynyl)benzene[11] in 20 mL of dry THF were added 100 mL of 1 M tetrabutylammonium fluoride in THF and 2.0 g (3.4 mmol) of bis(tributyltin) oxide.[12] This solution was stirred at 60 °C for 3 h and cooled to room temperature, and then 0.677 g (3.70 mmol) of bromocyclooctatetraene, 84.7 mg (0.093 mmol) of Pd$_2$-(dba)$_3$, and 48.5 mg (0.185 mmol) of triphenylphosphine were added. After the mixture was stirred for 24 h, 20 mL of H$_2$O was added, and the reaction mixture was extracted with 3 × 30 mL of diethyl ether. The organic fractions were combined, dried over MgSO$_4$, and concentrated. Elution on silica gel with 20% CH$_2$Cl$_2$/pentane afforded 307 mg (50%) of an orange oil (R_f = 0.4). ^{1}H NMR (CDCl$_3$, 25 °C): AA′BB′ multiplets at δ 7.41 (2 H) and 7.22 (2 H), 6.0−6.4 (br, 14 H). ^{13}C NMR (THF-d_8, −27 °C): δ *139.1* (C$_2$), *133.7, 133.3*, 132.8 (C$_5$), *132.6, 132.4*, 132.3, *131.7*, 129.0, 126.5, 126.4, 94.8 (C$_9$), 86.5 (C$_{10}$); the italicized values are those for C$_2$−C$_4$ and C$_6$−C$_8$, which undergo exchange during bond shift. UV (cyclohexane): λ_{max} 212 nm (ϵ 30 000), 254 (20 700), 268 (23 200), 320 (10 800). IR (film): 3058, 3003, 2848, 2195, 1475, 1441 cm^{-1}. Anal. Calcd for C$_{26}$H$_{18}$: C, 94.51; H, 5.49. Found: C, 94.45; H, 5.49.

NMR Samples. Concentrations of the COT compounds of 0.4−0.5 M were typically used, except for **4**$^{2-}$, where a lower concentration (0.1 M) was necessary to obtain a sufficiently long lifetime of the samples for the NMR measurements. Two samples of **1**$^{2-}$/2K$^+$ with concentrations of 0.1 and 0.5 M were prepared in order to study the concentration dependence (see Results section). Attempts to prepare dilithium and disodium salts in the same manner as the dipotassium salts failed. The reactions started in a similar way as the K reactions but stopped at an early stage and left most of the starting material unchanged. The reason for this appeared to be a decomposition at the metal surface, which became deactivated by this process.

NMR samples of the dianions were prepared directly in degassed and sealed NMR tubes by reduction of **1**−**4** in THF-d_8 with a potassium mirror in the upper part of the tube as described elsewhere.[4,5] The reduction was initiated by inverting the NMR tube. The progress of the reduction was followed using ^{1}H NMR spectroscopy and was stopped just before complete consumption of the neutral compound. No intermediates were observed during reduction to the dianion. No indication of the anion radical (**1**$^{\bullet-}$) being present in the completely reduced di-COT samples was found (see Kinetic Measurements section). If present, **1**$^{\bullet-}$ should be in very low concentration since the equilibrium for the disproportionation of **1**$^{\bullet-}$ to **1** and **1**$^{2-}$ is expected to be strongly displaced toward **1** and **1**$^{2-}$.[13]

NMR and Computational Methods. The ^{1}H and ^{13}C NMR spectra were obtained on Bruker AMX-2 or AC-P instruments operating at ^{1}H frequencies of 500 and 250 MHz, respectively, or on a GE GN300 spectrometer operating at 300 MHz. Cyclohexane was used as an internal chemical shift reference (δ ^{1}H = 1.43 and δ ^{13}C = 27.7). The digital resolution in the 1D spectra was generally around 0.2 Hz after zero-filling. At least two samples of each dianion were prepared, and the kinetic experiments were repeated several times at each temperature in order to establish the reproducibility. ^{1}H/^{13}C dual 5-mm probeheads were used on all of the instruments. The temperature was measured before and/or after each kinetic run using methanol.[14] The heating of the sample due to proton decoupling was determined to be a maximum of 0.1 °C for neat methanol, and a similar heating was assumed for the THF-d_8 samples. We estimate a maximum error of ±1 °C in the measured temperatures and a relative error between different NMR experiments of a maximum of ±0.5 °C. Two-dimensional (2D) H−C-correlated[15,16] and H−H−C-relayed coherence transfer[16,17] experiments

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Table 2. Analysis of π Bond Polarization for Dianions $\mathbf{1}^{2-}$–$\mathbf{4}^{2-}$ from AM1 π Charge Densities

bond	compd[a]	$\Delta\rho_\pi^{\mathrm{tot}\,b}$	$\Delta\rho_\pi^{\mathrm{ind}\,c}$	$\Delta\rho_\pi^{\mathrm{TS}\,c}$	$\Delta\rho_\pi^{\mathrm{TB}\,c}$
C_1C_2	$\mathbf{1}^{2-}$	+0.052	−0.063	0	+0.115
	$\mathbf{2}^{2-}$	−0.007	−0.053	0	+0.046
	$\mathbf{3}^{2-}$ (syn)	−0.018	−0.052	0	+0.034
	$\mathbf{3}^{2-}$ (anti)	−0.017	−0.050	+0.001	+0.032
	$\mathbf{4}^{2-}$ (syn)	−0.014	−0.050	−0.013	+0.049
	$\mathbf{4}^{2-}$ (anti)	+0.013	−0.048	+0.014	+0.047
C_9C_{10}	$\mathbf{1}^{2-}$	+0.156	−0.022	d	+0.178
	$\mathbf{2}^{2-}$	+0.062	−0.009	d	+0.071
	$\mathbf{3}^{2-}$ (syn)	+0.039	−0.007	d	+0.046
	$\mathbf{3}^{2-}$ (anti)	+0.040	−0.007	d	+0.047
	$\mathbf{4}^{2-}$ (syn)	+0.061	−0.012	0	+0.073
	$\mathbf{4}^{2-}$ (anti)	+0.063	−0.014	0	+0.077

[a] Dipotassium salts; syn and anti refer to the orientation of the C_1C_2 double bond in the neutral COT ring with respect to the dianion ring. [b] Total effect = inductive + through-space + through-bond effects; $\Delta\rho_\pi(C_2C_1) = \rho_\pi C_2 - \rho_\pi C_1$ and $\Delta\rho_\pi(C_9C_{10}) = \rho_\pi C_9 - \rho_\pi C_{10}$. [c] See text. [d] Not determined; any small contributions are incorporated into the through-bond values.

were employed using standard Bruker software. Delays for three-bond H−H couplings of 10 Hz, one-bond H−C couplings of 125 Hz, and long-range H−C couplings of 15 Hz were selected.

Ab initio MO calculations were performed with Spartan 4.1[18] using the 3-21G(*)[19] or 6-31G*[20] basis sets. Semiempirical AM1[21] calculations were performed with MOPAC 93,[22] where a K^+ ion is simulated by a sphere of diameter 1.4 Å and the charge is delocalized over its surface. Transition structures were verified by analytic frequency analysis.

^{13}C NMR Signal Assignments. In all four dianions, the five signals from the dianion ring appear in the region of 80−100 ppm because of the high π-electron density at these carbons. The eight carbons in the neutral ring have chemical shifts in the sp^2 carbon region of 125−140 ppm, with C_1 appearing at about 126−129 ppm, as expected for an sp^2 carbon bonded to an ethynyl group (Figure 1).[23] Data from dynamic NMR and ^{1}H−^{13}C chemical shift-correlated 2D experiments allowed the assignment of most signals for the K salts of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ (Table 1). The large difference in the chemical shifts for the two alkynyl carbons adjacent to the dianion ring ($C_{9'}$ and $C_{10'}$) is assumed to be an effect of polarization of the triple bond due to the charge in the dianion ring. This assumption and other assignments were supported by AM1 calculations of π-electron density (see Table 2 and Results and Discussion section). The ^{13}C NMR signal assignments of the K salts of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ are based on the dynamic NMR experiments in combination with data from $\mathbf{2}^{2-}/2K^+$ because these three spectra show very similar distributions of signals. The quaternary carbons in $\mathbf{1}$ were assigned by a 1D INADEQUATE experiment, while C_2 in $\mathbf{1}$ and $\mathbf{2}$ was assigned by selective decoupling of the ^{1}H NMR resonance for H_2. The alkynyl carbons of $\mathbf{2}$ were assigned by long-range ($J = 7$ Hz) C−H correlation in a gradient-enhanced HMBC experiment.[24]

Kinetic Measurements. ^{13}C NMR line width (LW) measurements and ^{1}H and ^{13}C spin saturation transfer (SST) experiments were

performed in order to obtain rate constants corresponding to different time scales.[4,5] The former method is appropriate for rate constants in the range of $1-10^2$ s^{-1},[25] i.e., bond shift (BS) dynamics (Figure 3), while the SST method is suitable for smaller values of the rate constants ($1-10^{-2}$ s^{-1}),[26,27] i.e., for studies of CT and, in some cases, BS (see below). The use of ^{1}H resonances other than those from the phenylene hydrogens for kinetic studies was prevented by severe overlap of the signals for the two COT rings.

From spectra acquired at low temperature, where BS exchange broadening of the ^{13}C peaks was absent, the LW of C_5 was found to be very similar to the LWs of the other proton-bearing carbons in the neutral ring. The LW of C_5, which is not affected by BS, was subtracted from the average LW of C_2-C_4 and C_6-C_8 to give the line broadening due to BS exchange.

We were quite concerned about the possibility of radicals in our NMR samples and their effect on LWs. Several experiments that we performed indicate that radicals, if present, do not affect our kinetic measurements. The SST experiment corrects for the influence of radicals by incorporating the value of the apparent relaxation time ($T_{1(\mathrm{app})}$) into the calculation of the rate constant. The insensitivity of k_{CT} to the presence of radicals was demonstrated as follows.

The C−N bond rotation barrier in dimethylformamide, 0.5 M in 1:1 dimethyl sulfoxide/dimethyl sulfoxide-d_6 solution, was determined by SST to be 21.0 kcal/mol at 325 K. When 0.03 M of the paramagnetic compound chromium(III) 2,4-pentanedionate ($Cr(acac)_3$) was added to the same sample, a value of 21.2 kcal/mol for the energy barrier was obtained, even though $T_{1(\mathrm{app})}$ of the observed methyl carbon was reduced from 8.7 to 0.97 s. The similar energy values show that the SST experiment is insensitive to the presence of radicals.

Having established the validity of SST experiments for these samples, we next extended the temperature range for studies of BS in $\mathbf{1}^{2-}-\mathbf{3}^{2-}$ to lower temperatures with five SST experiments that employed the C_2 and C_8 signals. An average difference of less than 10% was found between the extrapolated rate constants from LW data and the five rate constants from SST data. This establishes that LW studies are also valid for these samples. This conclusion is reinforced by the observation that no irregular or unexpected line broadenings of the peaks from COT dianions, solvent, or cyclohexane were observed, as would be expected had radicals been present in the samples. Further, a uniform line broadening of peaks due to radicals would be largely canceled out in the BS data, since a rate constant always is derived from a difference in the line width for a peak involved in BS and a reference peak.

For CT in $\mathbf{1}^{2-}-\mathbf{3}^{2-}$, ^{13}C SST experiments were performed on at least two carbons involved in exchange between the neutral and dianion rings, or between the two triple bonds. For $\mathbf{4}^{2-}$, ^{1}H SST employed the phenylene signals at δ 6.65 and 6.95. In the SST sequence, care was taken to selectively and completely saturate the irradiated proton or carbon. The saturation was maintained for at least $5T_1$ before acquisition and was always gated off during acquisition. ^{1}H NMR spectra were examined for nuclear Overhauser enhancement (NOE) between neighboring protons at temperatures just below the temperature region investigated for exchange, but no NOE was detected. Hence, the intensity reduction at temperatures where exchange took place is assumed to be absent of interfering NOE effects. Other details regarding the SST experiments have been reported elsewhere.[4,5]

The maximum error in the free energies of activation (Table 3) was estimated from the combination of a 10% error in the rate constants obtained from the LW measurements or a 30% error in the rate constants from the SST measurements and a 1-deg temperature error. Average rate constants for all temperatures studied are given in the Supporting Information. We have not reported or analyzed $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ values. This is because of the large uncertainties associated with these quantities owing to the limited temperature ranges over which k_{BS} and k_{CT} were determined.

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Table 3. Kinetic Data for Bond Shift and Charge Transfer in **1**−**4** and Their Dipotassium Salts in THF-d_8

compd[a]	process	temp range (K)	k[b]	T (K)	$\Delta G^{\ddagger}$ [c]
1	BS	176−246	5.6	243	13.3
1^{2-}/2K$^+$	BS	183−209	1370	243	10.6[d]
	CT	250−271	30.7	300	15.5[d]
2	BS	244−266	5.8	243	13.3[d]
2^{2-}/2K$^+$	BS	228−272	16.5	243	12.8
	CT	298−301	0.62	300	17.9
3	BS	238−272	4.2	243	13.4
3^{2-}/2K$^+$	BS	228−270	7.2	243	13.2
	CT	300−301	0.12	300	18.8
4	BS	242−266	5.1	243	13.4
4^{2-}/2K$^+$	BS	238−246	37.7	243	12.4
	CT	286−297	0.41	300	18.1[d]

^{a} Concentrations in M: **1**$^{2-}$/2K$^+$, 0.1−0.5; **2**$^{2-}$/2K$^+$ and **3**$^{2-}$/2K$^+$, 0.4−0.5; **4**$^{2-}$/2K$^+$, 0.1. ^{b} In s^{-1}; see text for uncertainties. ^{c} In kcal/mol; ±0.1 for BS and ±0.2 for CT unless noted otherwise. ^{d} Extrapolated; ±0.2 kcal/mol.
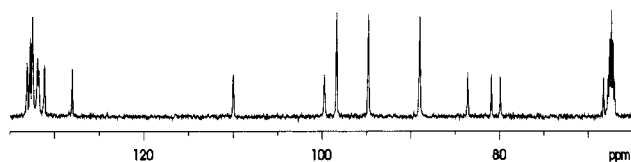
Figure 1. ^{13}C NMR spectrum of the dipotassium salt of **1**$^{2-}$ in THF-d_8 at −74 °C. The multiplet centered at δ 67 is due to THF-d_8, with C$_{10'}$ appearing immediately upfield of these peaks.

Results and Discussion

Structure and ^{13}C NMR Chemical Shifts. An analysis of the structural features of the dianions is essential for an understanding of orbital interactions and the transmission of electronic effects. The number of ^{13}C NMR peaks and the chemical shifts of **1**$^{2-}$−**4**$^{2-}$/2K$^+$ are consistent with a general structure that has a neutral ring and a dianion ring (Table 1, Figure 1). The average chemical shift of 131.7−132.6 ppm for the neutral ring carbons in **1**$^{2-}$−**4**$^{2-}$/2K$^+$ is close to the corresponding value for **1** (132.9 ppm) and **2** (132.6 ppm) and for neutral COT rings in other neutral or dianionic systems, such as COT−COT, COT−COT^{2-}/2K$^+$, and COT−(*p*-C$_6$H$_4$)−COT^{2-}/2K$^+$ (132.8−133.7 ppm).^{3,5} Furthermore, the upfield shifts of the resonances for the COT^{2-} ring are as expected for sp^2-carbons with negative charge in the π system.^{28} The average δ values for the dianion rings in **1**$^{2-}$−**4**$^{2-}$ are in the range of 92.6−93.2 ppm, which is similar to values for other COT dianions, e.g., δ_{av} = 93.3 for COT−COT^{2-}/2K$^+$,^{3b} δ_{av} = 92.2 for COT−Si(Me)$_2$−COT^{2-}/2K$^+$,^{4} and δ_{av} = 94.0 for COT−(*p*-C$_6$H$_4$)−COT^{2-}/2K$^+$.^{5}

Geometry optimizations with the AM1 MO method for dianions **1**$^{2-}$−**4**$^{2-}$ with two K$^+$-like spherical charges show the expected tub shape for the neutral COT ring and a planar 10 π-electron COT^{2-} ring. The optimized geometry of **1**$^{2-}$ also shows coplanarity for the C$_1$C$_2$ double bond in the neutral ring and the plane of the dianion ring. For **2**$^{2-}$−**4**$^{2-}$, the C$_1$C$_2$ bond is coplanar with both the phenylene ring and the dianion ring. For **3**$^{2-}$, the two conformers with the C$_1$C$_2$ double bond either adjacent to or distal from the dianion ring (syn and anti, respectively) have identical energies, while for **4**$^{2-}$ the two conformers differ by only 0.2 kcal/mol (the syn conformer is lower in energy). Generally, the calculations show shallow minima for the preferred conformations. For example, the energy barrier for rotation of the dianion ring relative to the neutral

ring in **1**$^{2-}$ is 0.5 kcal/mol, as obtained from AM1 transition-state calculations. In **2**$^{2-}$, the barriers for rotation of the dianion ring and the neutral COT ring relative to the phenylene ring are 2.6 and 0.3 kcal/mol, respectively.
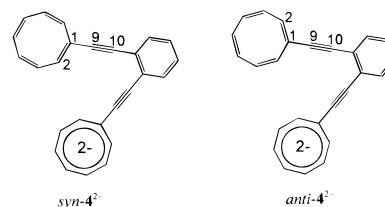
In this study, we are primarily concerned with the transmission of π-electronic effects through the bridging groups connecting the two COT rings when one of the rings is a dianion. One possible measure of this electronic communication is the polarization of the C$_1$C$_2$ double bond in the neutral COT rings of **1**$^{2-}$−**4**$^{2-}$ relative to those in **1**−**4**, respectively. Comparison of the ^{13}C NMR spectrum of **1**$^{2-}$ with that of **1** shows a downfield shift of 2.9 ppm for C$_1$, while C$_2$ is shifted upfield by 11.4 ppm. These values afford a corrected value of the polarization of the C$_1$C$_2$ bond ($\Delta\delta_{1,2}^{corr} = (\delta C_2 - \delta C_1)(\mathbf{1}^{2-}) - (\delta C_2 - \delta C_1)(\mathbf{1})$), which equals the polarization (−14.3 ppm) that occurs in one COT ring on reduction of the other COT ring to a dianion. This compares with the changes in AM1 π-electron density (ρ_π) of −0.04 and +0.07 electrons for C$_1$ and C$_2$, respectively, on going from **1** to **1**$^{2-}$.

For the comparison between **2**−**4** and **2**$^{2-}$−**4**$^{2-}$, respectively, only small changes in δ are found; e.g., the C$_1$ signal in **2**$^{2-}$ shifts downfield by 1.0 ppm whereas C$_2$ displays an upfield shift of 2.9 ppm. The value of $\Delta\delta_{1,2}^{corr}$ for **1**$^{2-}$−**4**$^{2-}$ is −14.3, −3.9, −1.8, and −3.7 or −3.6 ppm, respectively. Hence, the polarization of the C$_1$C$_2$ bond in the dianions as estimated from ^{13}C chemical shifts decreases in the order **1**$^{2-}$ ≫ **2**$^{2-}$ ≈ **4**$^{2-}$ > **3**$^{2-}$.

A similar analysis can be made for the alkynyl carbons distal from the dianion ring. The chemical shifts of C$_9$ and C$_{10}$ in **1**$^{2-}$−**4**$^{2-}$ differ only slightly, although AM1 calculations predict a significantly larger value of ρ_π at C$_9$ ($\Delta\rho_\pi(C_9C_{10}) = \rho_\pi C_9 - \rho_\pi C_{10}$ is calculated to be +0.16, +0.06, +0.04, and +0.06 electrons in **1**$^{2-}$−**4**$^{2-}$, respectively). However, when we compare the values of $\Delta\delta_{9,10}^{corr}$ (−7.9, −4.8, −3.6, and −5.5 ppm, respectively), these chemical shift differences are in much better agreement with $\Delta\rho_\pi(C_9C_{10})$, and the polarization of the C$_9$C$_{10}$ bond (**1**$^{2-}$ > **4**$^{2-}$ > **2**$^{2-}$ > **3**$^{2-}$) follows essentially the same order as that of the C$_1$C$_2$ bond.

A more detailed analysis of the polarization of the C$_1$C$_2$ π bond ($\Delta\rho_\pi(C_2C_1) = \rho_\pi C_2 - \rho_\pi C_1$) in **1**$^{2-}$−**4**$^{2-}$ is based on AM1 π-charge densities (Table 2). An inductive polarization ($\Delta\rho_\pi^{ind}$), which has a negative sign, results from the electron-withdrawing effect of the sp-hybridized C$_9$^{29} and is taken to be equal to $\Delta\rho_\pi(C_2C_1)$ in the corresponding neutral compounds (**1**−**4**). Subtraction of $\Delta\rho_\pi^{ind}(C_2C_1)$ from $\Delta\rho_\pi(C_2C_1)$ in Table 2 gives the sum of the through-space and through-bond π polarization due to the reduction of a neutral COT ring to a COT^{2-} ring.

Note that $\Delta\rho_\pi(C_2C_1)$ has opposite signs in the syn and anti conformers of **4**$^{2-}$. We postulate that this arises from through-

space polarization ($\Delta\rho_\pi^{TS}$) due to an electric field effect of the dianion ring since this ring is closer to C$_2$ in syn-**4**$^{2-}$. This effect is estimated (Table 2) as the difference in $\Delta\rho_\pi(C_2C_1)$ between anti- and syn-**4**$^{2-}$ ($\Delta\Delta\rho_\pi$) as follows. The value of $\Delta\rho_\pi^{TS}$ is

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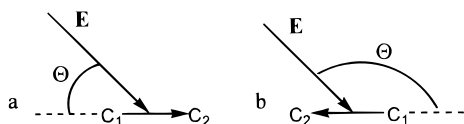
Figure 2. Definition of Θ as in (a) the anti conformers of 3^{2-} and 4^{2-} and (b) the syn conformers.

proportional to the electric field at the C_1C_2 bond (eq 1),

$$\Delta\rho_\pi^{\mathrm{TS}} \propto E_\| / R^2 \tag{1}$$

where $E_\|$ is the component of the electric field vector (**E**) along the C_1C_2 bond and R is the distance between the center of the C_1C_2 bond and the point where a line between the two potassium ions passes through the plane of the COT^{2-} ring. $E_\|$ is given by $\mathbf{E}\cos\Theta$, where Θ is defined as in Figure 2.[30] The values of $\Delta\rho_\pi^{\mathrm{TS}}(\mathrm{anti})$ and $\Delta\rho_\pi^{\mathrm{TS}}(\mathrm{syn})$ are calculated by eqs 2 and 3, respectively, where $A = E_\|/R^2$.

$$\Delta\rho_\pi^{\mathrm{TS}}(\mathrm{anti}) = \Delta\Delta\rho_\pi A(\mathrm{anti})/[A(\mathrm{anti}) - A(\mathrm{syn})] \tag{2}$$

$$\Delta\rho_\pi^{\mathrm{TS}}(\mathrm{syn}) = \Delta\Delta\rho_\pi A(\mathrm{syn})/[A(\mathrm{anti}) - A(\mathrm{syn})] \tag{3}$$

Essentially no through-space effect was noted for syn- and anti-3^{2-}, both because of the greater distance between the C_1C_2 bond and the dianion ring and because the electric field vector is nearly perpendicular to the C_1C_2 bond in the syn conformer. Finally, the through-bond polarization ($\Delta\rho_\pi^{\mathrm{TB}}$) is taken to be the remaining contribution to $\Delta\rho_\pi(C_2C_1)$ (eq 4).

$$\Delta\rho_\pi(C_2C_1) = \Delta\rho_\pi^{\mathrm{ind}} + \Delta\rho_\pi^{\mathrm{TS}} + \Delta\rho_\pi^{\mathrm{TB}} \tag{4}$$

A similar analysis can be made for the polarization of the C_9C_{10} π bond in $1^{2-}-4^{2-}$ (Table 2). No through-space effect is expected in syn- and anti-4^{2-} since **E** is nearly perpendicular to the C_9C_{10} bond. The essentially equal values of $\Delta\rho_\pi(C_9C_{10})$ in 2^{2-} and 4^{2-} indicate that $\Delta\rho_\pi^{\mathrm{TS}}$ is small or nil in 2^{2-}, and presumably in 3^{2-} as well. We note that the calculated through-bond polarization values in Table 2 are internally self-consistent in that the value for 3^{2-} is about two-thirds the values for 2^{2-} and 4^{2-} for both the C_1C_2 and C_9C_{10} π bonds. The same ratio is observed for $\Delta\delta_{9,10}^{\mathrm{corr}}$ but is somewhat smaller (ca. 1/2) for $\Delta\delta_{1,2}^{\mathrm{corr}}$. Unequal populations of the syn and anti conformations in 3^{2-} and/or 4^{2-} may influence the latter value.

Bond Shift in the Neutral Ring. The BS reaction in monosubstituted COTs such as $1-4$ and $1^{2-}-4^{2-}$ affects the pairwise exchange of C_2, C_3, and C_4 with C_8, C_7 and C_6, respectively (Figure 3).[31] The BS rate constants (k_{BS}) were determined from the broadening in the low-temperature region of the NMR signals of the exchanging carbons according to eq 5,[25]

$$k_{\mathrm{BS}} = \pi\Delta\nu_{1/2}(\mathrm{ex}) \tag{5}$$

where $\Delta\nu_{1/2}(\mathrm{ex})$ is the exchange broadening obtained as described in the Experimental Section. The $\Delta G^\ddagger$ values were

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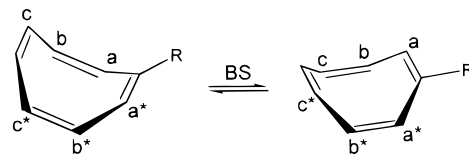
Figure 3. Bond shift in a monosubstituted COT. Atoms a−c undergo mutual exchange with a*−c*, respectively.

calculated from the Eyring equation (eq 6),

$$k = \kappa k_{\mathrm{B}}T/h \exp(-\Delta G^\ddagger/RT) \tag{6}$$

where the transmission coefficient κ is taken as unity, and the other quantities have their usual meaning.

As shown in Table 3, the free energies of activation for BS ($\Delta G^\ddagger_{\mathrm{BS}}$) for the neutral compounds $1-4$ are identical, at 13.4 $\pm$ 0.1 kcal/mol at 243 K. The value of $\Delta G^\ddagger_{\mathrm{BS}}$ decreases in the corresponding dianions in all cases, with the possible exception of the 1,3-phenylene-bridged compound (3^{2-}). The magnitude of the decrease ($\Delta\Delta G^\ddagger_{\mathrm{BS}} = \Delta G^\ddagger_{\mathrm{BS}}(\mathrm{neutral}) - \Delta G^\ddagger_{\mathrm{BS}}(\mathrm{dianion})$) is 2.7, 0.5, 0.2, and 1.0 kcal/mol for $1^{2-}-4^{2-}$, respectively, at 243 K. Note that the influence of the dianion ring on the barrier to BS in the neutral ring changes in essentially the same order ($1^{2-} \gg 4^{2-} \geq 2^{2-} > 3^{2-}$), as does its influence on the degree of π polarization of the C_1C_2 ($\delta_{1,2}^{\mathrm{corr}}$ or $\Delta\rho_\pi^{\mathrm{TS}}(C_2C_1) + \Delta\rho_\pi^{\mathrm{TB}}(C_2C_1)$) and C_9C_{10} bonds.

Recent photoelectron spectroscopic studies[32] and ab initio MO calculations[33] of COT that incorporate configuration interaction have shown that the BS transition-state structure is planar with equal bond lengths (D_{8h} symmetry). π-Electron donation from the dianion ring is enhanced since D_{8h} COT is a better acceptor than a tub-shaped ground-state COT ring by virtue of a low-lying unoccupied π^* MO (at the HF level of theory) in the former. Therefore, the degree of polarization of the C_1C_2 bond in $1^{2-}-4^{2-}$ is taken to be an indication of an even larger stabilizing interaction in the BS transition states.

A simple rationale for less efficient conjugation and larger BS barriers in the phenylene-bridged compounds ($2^{2-}-4^{2-}$) as compared with 1^{2-} is that extended conjugation will make the bonds less equal in the aryl ring, i.e., the gain of extended conjugation is partially offset by a reduced aromaticity of the phenylene ring. Because a resonance effect is expected to be more effective with ortho and para substitution than with meta substitution, the somewhat larger $\Delta\Delta G^\ddagger_{\mathrm{BS}}$ value for 2^{2-} as compared with that for 3^{2-} provides strong support for a through-bond or resonance contribution in the BS transition state.

A more quantitative explanation is based on a perturbation MO (PMO) model. In this model, the stabilization energy (ΔE) resulting from the interaction between a π and a π^* orbital is given by eq 7,
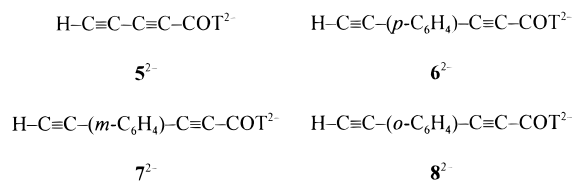
$$\Delta E = \frac{\langle\pi|H|\pi^*\rangle^2}{\epsilon_{\pi^*} - \epsilon_\pi} \tag{7}$$

where ϵ_π and ϵ_{π^*} are the energies of the unperturbed basis orbitals and H is the interaction Hamiltonian. The most important MO interaction between a neutral planar COT ring

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and a bridge−COT dianion is expected to be a bridge−COT^{2-}-(HOMO)−COT(LUMO) interaction, both because COT dianions typically have relatively high HOMO energies and because of a low-energy LUMO in planar COT. The HOMO energies of dianions $5^{2-}/2K^{+}$−$8^{2-}/2K^{+}$ at the HF/3-21G(*) level are nearly identical (-5.04, -4.94, -4.92, and -4.87 eV, respectively), but the π coefficients at the terminal alkynyl carbon vary significantly (0.222, 0.095, 0.014, and 0.071, respectively) and in almost the same order as k_{BS}.

$$H-C\equiv C-C\equiv C-COT^{2-} \qquad H-C\equiv C-(p\text{-}C_6H_4)-C\equiv C-COT^{2-}$$

$$\mathbf{5^{2-}} \qquad\qquad \mathbf{6^{2-}}$$

$$H-C\equiv C-(m\text{-}C_6H_4)-C\equiv C-COT^{2-} \qquad H-C\equiv C-(o\text{-}C_6H_4)-C\equiv C-COT^{2-}$$

$$\mathbf{7^{2-}} \qquad\qquad \mathbf{8^{2-}}$$

In 4^{2-}, the dianion ring is in close proximity to the neutral ring; the C_1 to $C_{1'}$ distance is only 5.6 Å in the AM1-optimized structure, as compared to 6.6, 10.8, and 9.4 Å in 1^{2-}, 2^{2-}, and 3^{2-}, respectively. Because of this, it is possible that the observed difference of 0.5 kcal/mol at 243 K in $\Delta\Delta G^{\ddagger}_{BS}$ for 2^{2-} and 4^{2-} originates from an electric field (through-space) effect due to the dianion ring. This is supported by the value of $\Delta\rho_\pi^{TS}$ for anti-4^{2-} in Table 2.

An alternative explanation for this difference in $\Delta G^{\ddagger}_{BS}$ could be that there is greater through-bond coupling due to there being fewer bonds between C_1 and $C_{1'}$ in 4^{2-} than in 2^{2-}. The value of $\Delta\rho_\pi^{TB}$ in Table 2 is, indeed, larger in 4^{2-} than in 2^{2-}, but the difference is small. Furthermore, CT does not occur faster in 4^{2-}. We therefore favor a through-space electrostatic interaction as the origin of the enhanced rate of BS in 4^{2-} compared to that in 2^{2-}.

Charge Transfer. The rate constants and free energies of activation for CT in $1^{2-}/2K^{+}$−$4^{2-}/2K^{+}$ in THF-d_8 are given in Table 3. We have determined that changing the concentration of $1^{2-}/2K^{+}$ from 0.1 to 0.5 M gives the same CT barrier within experimental uncertainty. This indicates that intermolecular CT does not compete with intramolecular CT in this concentration range, and we assume that the same is also true for 2^{2-}−4^{2-}.

There are three issues that we address with regard to CT in 1^{2-}−4^{2-}: (a) the effect of 1,3- vs 1,4-phenylene substitution, (b) the effect of 1,2- vs 1,4-phenylene substitution, and (c) the effect of the insertion of a 1,4-phenylene group into the diethynyl bridging group.

(a) Meta vs Para Linkage. There are a number of studies that have addressed the issue of the relative rates of electron and energy transfer across bridges containing 1,3- and 1,4-phenylene linkages. In a majority of cases, energy transfer occurs faster in the meta vs the para linkage (typically by a factor of <1.5),[7,34] and through-space mechanisms have generally been proposed. Such mechanisms have been supported by several theoretical analyses.[34b,35]

In one case, charge separation from an excited singlet zinc porphyrin (ZnP) across a 1,3- or 1,4-phenylene link and a free base porphyrin to a quinone group was studied. A through-bond (superexchange) mechanism was proposed, based on a weak dependence of the rate constant on the temperature.[34d] This mechanism is consistent with the greater degree of twist between the porphyrin rings and the phenylene bridge in the para isomer compared with that in the meta isomer, as determined by X-ray diffraction studes of closely related compounds.[36] In a second, structurally almost identical case it was concluded that the rate of photoinduced charge separation from a ZnP to ferric porphyrin chloride across a number of aryl bridges, including the 1,3- and 1,4-phenylene bridges, depends primarily on distance.[34c] This implies a through-space mechanism.

In several other cases of energy (EN) or ET, the para isomers reacted faster than the corresponding meta isomers by factors of 1.3−4.4.[37] A through-bond mechanism was proposed in most cases, based upon molecular orbital analyses.[37b,c,38]

We also obtained a greater value of k_{CT} for the para isomer in comparison with that for the meta isomer ($k_{CT}(2^{2-})/k_{CT}(3^{2-})$ = 5.2). It is interesting to note that this ratio is only slightly greater than the upper limit of the range from previous studies, even though k_{CT} for these dianions at 300 K (Table 3) is 6−10 orders of magnitude smaller than that found in previous studies. However, it should be recognized that most of the activation energy for CT in 1^{2-}−4^{2-} is the energy required to flatten the neutral COT ring. The difference between $\Delta G^{\ddagger}_{CT}$ and $\Delta G^{\ddagger}_{BS}$ ($\Delta\Delta G^{\ddagger}$) in these compounds affords a barrier that can be considered to represent the energy required for CT in hypothetical dianions where both COT rings are planar. The values of $\Delta G^{\ddagger}_{CT}$ and extrapolated values of $\Delta G^{\ddagger}_{BS}$ indicate that CT in such a species would occur with a rate constant of ca. 10^9 s^{-1} at 300 K, which is about the same as most values of k_{EN} and k_{CT} reported in the literature. Thus, CT in 1^{2-}−4^{2-} is actually a rapid step that is gated by slow conformational change in the neutral COT ring.[6] The requirement for transferring two cations suggests that this mechanism may require two ET steps,[39] but this issue is still very much an open question.[9]

A PMO model for ET in 1^{2-}−4^{2-} is based on the interaction between the COT dianion ring as the donor and the bridge as the primary acceptor. This should be the most important step in the ET mechanism. Later steps such as ET from the bridge to the neutral COT ring should occur faster because of an easily accessible LUMO in the planar neutral COT ring. According to eq 7, a decreased energy gap between the donor π and the bridge π^* orbitals and increased MO coefficients at the point of attachment of the donor and bridge are expected to enhance the rate of ET. Accordingly, HF/6-31G*//3-21G(*) MO calculations were performed on the bridge subunits with hydrogens replacing the COT rings. The LUMO energies of HCCCCH, HCC(p-C$_6$H$_4$)CCH, HCC(m-C$_6$H$_4$)CCH, and HCC(o-C$_6$H$_4$)CCH are 3.73, 2.29, 2.66, and 2.55 eV, respectively. This suggests that the bridge in 2^{2-} may be a better electron conductor than that in 1^{2-}, but the larger LUMO coefficient for the 1^{2-} bridge

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(0.827), as compared to 0.468 for the bridge in 2^{2-}, dominates because it contributes to a squared term in eq 7. The LUMO coefficients at the terminal sites of the bridges in 3^{2-} and 4^{2-} are 0.408 and 0.452, respectively. Thus, both a higher LUMO energy and a smaller coefficient provide an explanation for the larger $\Delta G^{\ddagger}_{CT}$ value for 3^{2-} as compared to those for 2^{2-} and 4^{2-}. This parallels the larger BS energy barrier for 3^{2-} and the δ ^{13}C analysis that showed the bridge in 3^{2-} to be the least efficient in transmitting the effect of the charge from the dianion ring.

(b) Ortho vs Para Linkage. All previous studies of energy and charge transfer have found that the ortho isomer reacts faster than the corresponding para isomer.[34a,f−h,37a,d] In the majority of cases, a through-space mechanism was proposed for energy transfer, although a through-bond mechanism was proposed in one study of energy transfer[37b] and one of charge transfer.[37d] In addition, Kawabata et al. proposed a through-space mechanism for an ortho isomer and a through-bond mechanism for the corresponding para isomer.[34f]
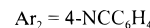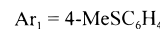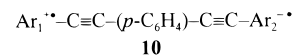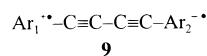
As shown in Table 3, charge transfer in the para isomer (2^{2-}/$2K^+$) occurs at the same rate as (within experimental uncertainty) or possibly at a slightly greater rate than that in the ortho isomer (4^{2-}/$2K^+$). This result is most consistent with a through-bond transfer of electron density in both isomers and appears to exclude the possibility of a through-space "short circuiting" of charge (perhaps via a bridging K^+)[40] between the proximate COT rings.

A PMO analysis (eq 7) supports a slightly greater rate of CT in 2^{2-} than in 4^{2-}, because of both a greater LUMO energy and a smaller coefficient at the terminal bridge carbon (see previous section) in the latter. However, these differences are small and should only be taken as not contradicting the observed rate constants.
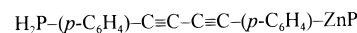
(c) Insertion of a 1,4-Phenylene Group. The rate constants and $\Delta G^{\ddagger}$ values for BS and CT in 2^{2-} compared to those for 1^{2-} give a direct measure of the additional barrier imposed by a 1,4-phenylene group. The value of $\Delta G^{\ddagger}_{BS}$ in 2^{2-} is larger than that in 1^{2-} by 2.2 kcal/mol at 243 K, whereas $\Delta G^{\ddagger}_{CT}$ is increased by 2.4 kcal/mol at 300 K. Interestingly, these values are essentially identical to the increase in $\Delta G^{\ddagger}$ for charge recombination at 293 K recently reported for **10** relative to **9**.[41]

$$Ar_1{}^{\bullet\bullet}{-}C{\equiv}C{-}C{\equiv}C{-}Ar_2{}^{-\bullet}$$
9

$$Ar_1{}^{\bullet\bullet}{-}C{\equiv}C{-}(p{-}C_6H_4){-}C{\equiv}C{-}Ar_2{}^{-\bullet}$$
10

$$Ar_1 = 4\text{-MeSC}_6H_4$$
$$Ar_2 = 4\text{-NCC}_6H_4$$

A related comparison can be made for energy transfer between a zinc porphyrin (ZnP) and a free base porphyrin (H$_2$P) in porphyrin dimers **11**[42,43] and **12**[34f,44] with almost identically

$$H_2P{-}(p{-}C_6H_4){-}C{\equiv}C{-}C{\equiv}C{-}(p{-}C_6H_4){-}ZnP$$
11
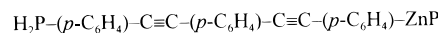
$$H_2P{-}(p{-}C_6H_4){-}C{\equiv}C{-}(p{-}C_6H_4){-}C{\equiv}C{-}(p{-}C_6H_4){-}ZnP$$
12

substituted porphyrin rings. A 3.5-fold decrease in k_{EN} is observed at ambient temperature on going from **11** to **12**, corresponding to an increase in $\Delta G^{\ddagger}_{EN}$ of 0.6 kcal/mol.

Thus, insertion of a 1,4-phenylene group into a 1,3-butadiynyl group appears to increase the barrier to electronic communication between donor and acceptor groups by ca. 2 kcal/mol for three different processes (bond shift, two-electron charge transfer, and charge recombination) at or near room temperature. However, comparison of **11** and **12** indicates that a smaller "1,4-phenylene barrier" is appropriate for singlet energy transfer across a bridge extended by two phenylene groups. Additional data regarding this problem will undoubtedly prove to be interesting.[45]

Supporting Information Available: Tables of rate constants obtained at various temperatures (PDF). This material is available free of charge on the Internet at http://pubs.acs.org.

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(43) The rate constant for **9** in ref 42 was corrected as in footnote 14 of: Strachan, J.-P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191.

(44) See also: Jensen, K. K.; van Berlekom, S. B.; Kajanus, J.; Mårtensson, J.; Albinsson, B. *J. Phys. Chem. A* **1997**, *101*, 2218.

(45) (a) For other examples of the effect of phenylene insertion into an alkynyl bridge, see: Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1884. (b) Arnold, D. P.; James, D. A. *J. Org. Chem.* **1997**, *62*, 3460.