# Effect of Para Substituents on the Rate of Bond Shift in Arylcyclooctatetraenes

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The rate constants for bond shift ($k_{BS}$) in phenylcyclooctatetraene (**1b**) and its *p*-nitro and *p*-methoxy analogues (**1a** and **1c**, respectively) in THF-$d_8$ were determined by dynamic NMR spectrometry to be identical, but $k_{BS}$ is *eight* times greater at 280 K relative to **1b** when the para substituent is cyclooctatetraenyldipotassium (**2**$^{2-}$/2K$^+$). These results are discussed in the context of (a) possible intrinsically small substituent effects (as determined by $^{13}$C chemical shifts in the ground state (GS)) for **1a**−**c** and (b) differences in steric interactions and resonance stabilization between the ground and BS transition state (TS). The latter factor was modeled by employing HF/3-21G$^{(*)}$ ab initio molecular orbital calculations of the GS and ring inversion TS. It is concluded that $k_{BS}$ is unchanged in **1a**−**c** because the potentially greater $\pi$ interaction in the BS TS is counterbalanced by a greater degree of twist between the aryl and COT rings resulting from increased steric hindrance relative to the GS. However, $\pi$ interaction assumes a greater importance in the TS of **2**$^{2-}$/2K$^+$ owing to a decreased HOMO−LUMO energy gap compared to **1a**−**c**, particularly when the counterions are solvated. This causes a decrease in the inter-ring twist angle and, together, these changes are responsible for the observed increase in $k_{BS}$ in **2**$^{2-}$/2K$^+$. The effect of substituents on a possible contribution of heavy atom tunneling to the reaction mechanism is also discussed.

Substituent effects on allowed electrocyclic reactions have received considerable attention in recent years.[1] In contrast, few experimental or theoretical investigations of such effects have been reported on formally symmetry-forbidden pericyclic processes,[2,3] despite the fact that the latter are intrinsically interesting and of practical use synthetically.[4]

Carpenter employed a Hückel molecular orbital (HMO) model to predict that substituent effects on forbidden pericyclic processes will be larger than those on closely related allowed reactions.[5] This model also predicts that *both* $\pi$-electron donors and acceptors accelerate the rate of a forbidden pericyclic process through $\pi$ interactions. However, there is little evidence regarding the validity of these hypotheses.

One relevant study was reported by Spellmeyer et al.,[2] who found that the rate of disrotatory electrocyclization of an *o*-xylylene increases on substitution by both donors and acceptors, in accord with the prediction of Carpenter's model. These authors also modeled this reaction by employing substituted butadienes at the RHF/3-21G// UHF/3-21G level and computed substituent-induced

**Scheme 1.   Ring Inversion (top) and Bond Shift (bottom) in COT**
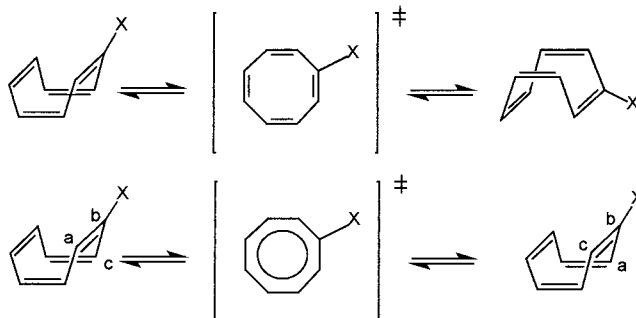


decreases in activation energies that were quantitatively in accord with the measured values. The greater substituent effect expected on the basis of the HMO model for a forbidden reaction compared to a corresponding allowed reaction was confirmed for electron acceptors, but just the opposite was found for electron donors.[2]

The bond shift (BS) reaction in cyclooctatetraenes (COTs) (Scheme 1) is a well-known example of a formally forbidden electrocyclic reaction. Substituted cyclooctatetraenes represent attractive compounds for the investigation of Carpenter's postulate.[5] The formally antiaromatic nature of the BS transition state (TS) implies that (at the HMO level) COTs will possess a high-lying highest occupied MO (HOMO) and a low-lying lowest unoccupied MO (LUMO). As a result, any perturbation in $\pi$-electron density by a substituent would be expected to accelerate the rate of the reaction because the antiaromatic destabilization of the TS can be mitigated either by increasing or decreasing the $\pi$-electron density.[5b]

The TSs of some formally forbidden pericyclic reactions that have been studied theoretically have been shown to

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be partially or almost fully biradicaloid in character with little overlap between the reacting orbitals.[3] An important advantage of COT for the study of pericyclic reactions is that the strong overlap between the reacting orbitals is maintained throughout the BS reaction, the $D_{8h}$ TS of which was calculated to be a singlet at the MCSCF/6-31G*//HF/6-31G* level of theory.[6]

Trindle and Wolfskill performed AM1 semiempirical MO calculations of formyl-, methoxy-, and methylene ion-substituted COTs.[7] These workers predicted that a methoxy substituent decreases the barrier to ring inversion ($\Delta G^{\ddagger}_{RI}$) but that a formyl group increases it (Scheme 1). Their calculations also suggested that strong electron-donor substituents are more effective than strong electron-withdrawing substituents at flattening the tub conformation of COT, thereby reducing $\Delta G^{\ddagger}_{RI}$.

Kinetic studies on substituted COTs have shown substantial steric effects of substituents on the RI and BS energy barrier relative to COT.[8] As the COT ring flattens toward the transition state, steric crowding between a substituent and the hydrogens at the vicinal positions increases, especially across the single bonds. An increase in steric interactions has been shown to increase $\Delta G^{\ddagger}_{BS}$ by several kcal mol$^{-1}$ in homologous compounds.[9] Conversely, destabilization of the ground state has been shown to reduce $\Delta G^{\ddagger}_{BS}$ in sterically crowded COTs.[10]

The substituents calculated by Trindle and Wolfskill ($OCH_3$ and CHO) span a large range of $\pi$-electronic perturbations. However, they also differ in steric effects and, more importantly, electronegativity. It has been our experience that such differences will significantly affect the rate of BS.[8b,c]

To explore the effect of substituents on forbidden electrocyclic processes, we decided to investigate the BS in COTs by employing para donor- and acceptor-substituted phenylCOTs (**1a–c**). These compounds have identical steric and hybridization effects at the position of substitution on the COT ring yet represent a potentially wide range of $\pi$-electronic effects.



| | |
|---|---|
| **1a** | X = $NO_2$ |
| **b** | X = H |
| **c** | X = $OCH_3$ |
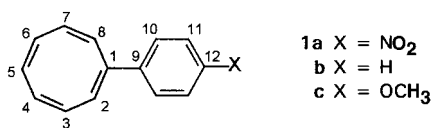
Although steric and hybridization effects often dominate $\Delta\Delta G^{\ddagger}_{BS}$, it is reasonable to expect that $\pi$ delocalization could also play a measurable role. We recently measured a 6-fold increase in $k_{BS}$ on going from 1,4-dicyclooctatetraenylbenzene (**2**) to its dipotassium salt (**2**$^{2-}$/2K$^+$) at 280 K.[10a] This acceleration is undoubtedly due to a $\pi$-electronic effect. The present study was designed to relate this observation to the effects of other common donors and acceptors and has led to the discovery of some unexpected results.
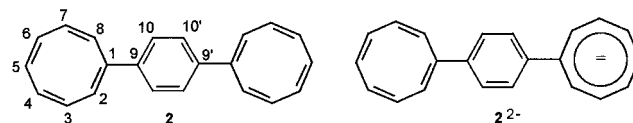


## Results

**Synthesis.** The syntheses of phenylCOT (**1b**) and its *p*-methoxy analogue (**1c**) were straightforward. Compound **1b**, first prepared by Cope[11] in 25% yield, was synthesized by DeKock's modification[12] of Cope's procedure. The first step involves nucleophilic attack of an organolithium reagent on COT to form a cyclooctatatrienyl anion. Subsequent abstraction of a proton with a second equivalent of organolithium affords the substituted COT dianion, which can be cleanly oxidized to the arylCOT with oxygen.
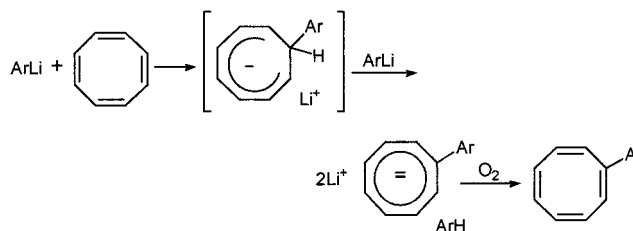


Paquette and co-workers first reported the synthesis of **1c** by the Cope method in <2% yield.[13] A more recent synthesis by Harmon and Streitwieser, which employed the coupling of bromoCOT with the cuprate of anisole,[14] gave a much higher yield (80%) but is less convenient. The Cope/DeKock procedure has the advantage that the synthesis of bromoCOT is not required, and a separation of cyclooctatriene side products is avoided. Consequently, the latter method was employed to afford **1c** in 64% yield.

We were concerned about the stability of phenyllithium substituted in the para position by a strong electron-withdrawing group when subjected to the higher temperatures required for the Cope/DeKock reaction.[15] Conversely, an acceptor in the para position of an aryl halide is known to facilitate the Stille reaction.[16] Thus, Stille coupling of 1-iodo-4-nitrobenzene with tributylstannyl-cyclooctatetraene cleanly afforded *p*-nitrophenylCOT (**1a**) in 70% yield.[17]
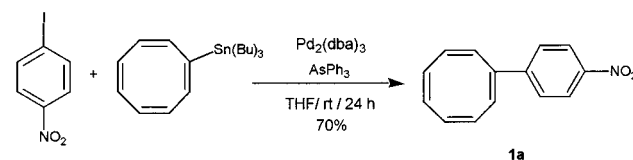
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**Chemical Shift Assignments.** The following general procedure was employed for the assignment of $^1$H and $^{13}$C NMR signals for **1a**−**c**, **2**, and **2**$^{2-}$/2K$^+$. The eight carbons in the neutral ring resonate in the region of $\delta$ 125−150, while the five signals for the $C_{2v}$ dianion ring appear at $\delta$ 83−96 due to the higher electron density at these carbons.[18] The peaks for $C_2$−$C_4$ and $C_6$−$C_8$ were identified on the basis of exchange broadening as a result of BS, although, except for $C_2$, assignments were not made for individual carbons. The most upfield of these signals was assigned to $C_2$ by analogy with similar compounds,[19] while $C_5$ was assigned based on the absence of exchange broadening and an increased peak area relative to $C_1$. The proton signals of the aryl ring were easily assigned and the details are given below. The signals for $C_{10}$ and $C_{11}$ were assigned by heteronuclear correlation spectroscopy (HETCOR) on the basis of coupling to $H_{10}$ and $H_{11}$, respectively. The remaining quaternary signals were identified by C−H long-range correlation or cross-relaxation correlation experiments. Additional assignments for each compound are given below.

The downfield aryl doublet in the $^1$H spectrum of **1a** was assigned to $H_{11}$ due to the electron-withdrawing character of the nitro group, whereas the upfield doublet was assigned to $H_{10}$. Long-range correlation spectroscopy (COLOC) with delays corresponding to a $^3J_{CH(trans)}$ value of approximately 8 Hz led to the correlation of $H_{11}$ and $H_{10}$ with $C_9$ and $C_{12}$, respectively. The latter assignment is supported by the chemical shift of $C_1$ of nitrobenzene ($\delta$ 148.5).[20]

The phenyl proton signals of **1b** ($H_{10}$−$H_{12}$) were assigned on the basis of their integration and apparent multiplicities. They were then correlated with coupled $^{13}$C signals by HETCOR and COLOC in order to assign $C_{10}$−$C_{12}$ and $C_9$, respectively.

The upfield aryl doublet in the $^1$H spectrum of **1c** was assigned to the proton ortho to the methoxy group ($H_{11}$) due to the $\pi$-donor character of the methoxy substituent. Likewise, the downfield aryl doublet was assigned to $H_{10}$. A COLOC experiment with delays corresponding to a $^3J_{CH(trans)}$ value of approximately 8 Hz led to the correlation of $H_{11}$ with $C_9$ and $H_{10}$ with $C_{12}$. The literature value for $\delta$ $C_1$ of anisole ($\delta$ 159.9)[21] supports the assignment of $C_{12}$.

The singlet at $\delta$ 7.31 in the spectrum for **2** was assigned to $H_{10}$ due to its multiplicity and integrated area. A cross-correlation experiment was employed to assign $H_2$ based on a significant NOE with $H_{10}$. The 3.9 Hz coupling constant measured for $H_2$ at −40 °C also supports this assignment. Long-range correlation experiments with delays corresponding to $^3J_{CH(trans)} \approx 8$ Hz correlated $H_{10'}$ with $C_9$ (which is the same as $H_{10}$ with $C_{9'}$), while the same experiment with longer delays (corresponding to $^3J_{CH(cis)} \approx 5$ Hz) led to the correlation of $H_2$ and $H_{10}$ with $C_9$ and $C_1$, respectively.

The doublets in the $^1$H spectrum for **2**$^{2-}$/2K$^+$ at $\delta$ 7.34 and 6.85 were assigned to $H_{10}$ and $H_{11}$ by analogy to **2**.

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**Table 1. Kinetic Data for Bond Shift in ArylCOTs in THF-$d_8$**

| compound | $T$ range (K) | $k_{BS}{}^{a,b}$ | $\Delta G^{\ddagger}{}_{BS}{}^{b,c}$ |
|---|---|---|---|
| C$_6$H$_5$-COT (**1b**) | 262−293 | 5.3 | 15.4 ± 0.1 |
| $p$-CH$_3$O-C$_6$H$_4$-COT (**1c**) | 260−320 | 6.8 | 15.3 ± 0.1 |
| $p$-NO$_2$-C$_6$H$_4$-COT (**1a**) | 262−289 | 6.5 | 15.3 ± 0.1 |
| $p$-COT-C$_6$H$_4$-COT (**2**)$^d$ | 271−298 | 7.5 | 15.2 ± 0.1 |
| $p$-COT-C$_6$H$_4$-COT/2K$^+$ (**2**$^{2-}$/2K$^+$)$^d$ | 248−284 | 43.3 | 14.3 ± 0.1 |

$^a$ In s$^{-1}$. $^b$ At 280 K. $^c$ In kcal mol$^{-1}$; calculated from van't Hoff plot. $^d$ Reference 10a.

A cross-correlation experiment confirmed the assignment of $H_{10}$ based on a significant NOE with $H_2$. $C_9$ and $C_{12}$ were assigned on the basis of long-range correlations (corresponding to $^3J_{CH(trans)} \approx 8$ Hz) with $H_{11}$ and $H_{10}$, respectively, while the same experiment with longer delays (corresponding to $^3J_{CH(cis)} \approx 5$ Hz) led to the correlation $H_{10}$ with $C_1$.

**Kinetics.** Rate constants for bond shift ($k_{BS}$) were obtained at a number of temperatures where line broadening could be measured in the slow exchange region. Kinetic data were obtained for duplicate samples of **1a**−**c** in THF-$d_8$. $^{13}$C line broadening was measured for one nonoverlapped signal ($\delta$ 133.4) in **1a**, for six nonoverlapped signals ($\delta$ 133.7, 133.2, 133.0, 132.4, 132.2, 126.7) in **1b**, and for four nonoverlapped signals ($\delta$ 132.9, 131.4, 130.8, 125.7) in **1c**. Values of $k_{BS}$ were determined over 27, 31, and 60 degree temperature ranges for **1a**−**c**, respectively. The kinetics for BS in **1c** were determined by employing three NMR spectrometers operating at different magnetic field strengths in order to extend the temperature range for line broadening measurements. Although the COT $^{13}$C signals had coalesced and were emerging from the baseline by 50 °C, five distinct signals were not observed. Rate constants and free energies of activation at 280 K are listed in Table 1. Complete tables of kinetic data and the corresponding van't Hoff plots are given in the Supporting Information.

## Discussion

A perturbation of the $\pi$-electron density within the COT ring might be expected to affect the energy required for BS due to the antiaromatic nature of the transition state. Surprisingly, none of the neutral substituted COTs (**1a**−**c**, **2**) show an experimentally significant variation in $k_{BS}$ (Table 1). In contrast, the dianion ring in **2**$^{2-}$/2K$^+$ causes an 8-fold enhancement of the rate of BS in the neutral COT ring at 280 K relative to **1b**.

We have considered three possible explanations for these interesting but unexpected results. (1) Resonance effects in **1a**−**c** and **2** might be intrinsically too small to be detected in either the ground state (GS) or the BS TS while **2**$^{2-}$/2K$^+$, being a charged species, is a markedly superior donor. (2) Resonance effects (in the Hartree−Fock (HF) model) in the GS of **1a**−**c** and **2** might be substantial but of similar magnitude to those in the TS and therefore their effects on $\Delta G^{\ddagger}{}_{BS}$ cancel. (3) The absence of any effect in **1a**−**c** and **2** might be related to heavy-atom tunneling or configuration interaction (CI). Each of these possibilities is discussed and a reasonable explanation is offered.

**Intrinsically Small Substituent Effects.** NMR chemical shifts have long been one of the principal probes of substituent electronic effects. Among the nuclei most widely employed are the para $^{13}$C in monosubstituted

**Table 2. ¹³C Chemical Shifts for ArylCOTs in THF-$d_8$ and Derived $\sigma$ Constants**

| compound | substituent | $\delta$ C$_2$ | $\delta$ C$_9$ | $\sigma_p{}^a$ | $\sigma_p{}^{+\ a}$ | $\sigma^{13\ a}$ |
|---|---|---|---|---|---|---|
| **1a** | NO$_2$ | 132.8 | 147.9 | 0.78 | 0.74 | 1.01 |
| **1b** | H | 126.7 | 141.0 | 0 | 0 | 0 |
| **2** | COT | 128.7 | 140.0 | 0.15$^b$ | 0.1$^b$ | 0.1$^b$ |
| **1c** | OCH$_3$ | 125.7 | 132.5 | −0.27 | −0.65 | −0.74 |
| **2²⁻/2K⁺** | COT$^{2-}$/2K⁺ | 122.2 | 129.4 | −0.7$^b$ | −1.0$^b$ | −1.1$^b$ |

$^a$ Reference 27d unless indicated otherwise. $^b$ This work; ±0.1.

benzenes,[22] ¹⁹F in para-disubstituted benzenes,[23] and ¹³C at the $\beta$ position in substituted styrenes.[24] To address the possibility that some substituent effects are too small to exert an influence on bond shift, the ¹³C NMR spectra for **1a–c**, **2**, and **2²⁻/2K⁺** were fully assigned in order to compare the relative magnetic and electronic environments of the $\beta$ and para carbons (C$_2$ and C$_9$, respectively) in these compounds.

Due to the distance of C$_9$ and C$_2$ from the position of substitution, the chemical shifts of these carbons (especially C$_2$) should primarily reflect resonance ($\pi$ delocalization) effects of the substituents on these carbons, as opposed to inductive and/or electric field effects. This qualitative interpretation of ¹³C chemical shifts in aromatic systems follows interpretations by previous authors who have concluded that ¹³C chemical shifts are useful probes of $\pi$-electron density.[24]

The change in chemical shift for C$_9$ ($\Delta\delta$C$_9$) on going from **1a** to **1c** is 15.4 ppm (Table 2). This corresponds to a difference in charge density that *does not* manifest itself in a measurable difference in $k_{BS}$ (Table 1). Conversely, $\Delta\delta$C$_9$ on going from **1c** to **2²⁻/2K⁺** is only 3.1 ppm, yet the rate constant for bond shift increases *by over 6-fold*. Similarly, $\Delta\delta$C$_2$ on going from **1a** to **1c** is 7.1 ppm while $\delta$C$_2$(**1c**) − $\delta$C$_2$(**2²⁻/2K⁺**) is only 3.5 ppm, yet the rate constant for bond shift is appreciably increased relative to **1b** only in the dianion. This analysis *appears* to preclude the explanation that the rate of bond shift in **1a–c** and **2** is unchanged because electronic effects are intrinsically too small while the COT$^{2-}$ ring in **2²⁻/2K⁺** is a much superior donor. Note that these measurements reflect electronic effects in the GS, and it is not known whether a similar trend applies to the TS.

A more quantitative measure of the substituent effect of $p$-COT and $p$-COT$^{2-}$/2K⁺can be obtained by plotting the chemical shifts in Table 2 against appropriate Hammett-type substituent constants. Previous workers have reported excellent correlations of $\sigma$ constants, particularly $\sigma_p{}^+$,[25] with ¹³C chemical shifts for the para carbon of substituted benzenes[21,24b,26] and the $\beta$ carbon of substituted styrenes.[27]
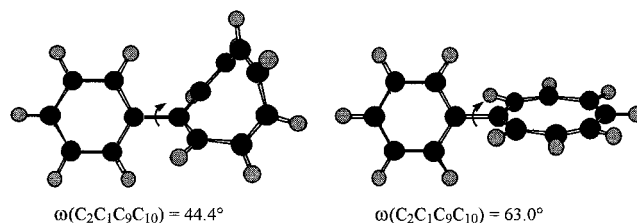
Dual substituent parameter (DSP) treatments have also been employed for these nuclei with good success.[23,28] However, in view of the minimal number of substituents



$\omega$(C$_2$C$_1$C$_9$C$_{10}$) = 44.4°          $\omega$(C$_2$C$_1$C$_9$C$_{10}$) = 63.0°

**Figure 1.** HF/3-21G-optimized GS (left) and RI TS (right) of **1b**.

included in the present study, one cannot expect to get more than an approximate correlation with even a single-parameter, let alone a DSP, treatment. Average values of $\sigma_p$, $\sigma_p{}^+$, and $\sigma^{13}$ for $p$-COT and $p$-COT$^{2-}$/2K⁺ obtained by interpolation or extrapolation of the correlation lines for plots of $\delta$C$_2$ and $\delta$C$_9$ against the corresponding $\sigma$ values for the $p$-phenyl substituents in **1a–c** are given in Table 2. The values derived using $\delta$C$_2$ do not vary by more than 0.15 from those using $\delta$C$_9$ and the correlations involving $\sigma_p$ and $\sigma_p{}^+$ are comparable. The NMR-derived parameter $\sigma^{13}$ has only been defined for the $\beta$ carbon of styrenes.[27d]

The derived $\sigma$ values indicate that COT$^{2-}$/2K⁺ in THF-$d_8$ is only a moderately stronger donor than methoxy in the GS. However, substituent constants for COT$^{2-}$ are undoubtedly dependent on the cation and the solvent, i.e., on the degree and type of ion pairing.

**Compensating Effects in the Ground and Transition States.** To assess both steric and electronic factors, HF/3-21G$^{(*)29}$ geometry optimizations and harmonic frequency analyses[30] were performed on the GS and RI TS of **1a–c**, **2**, and **2²⁻/2K⁺** (Figure 1 and Table 3). The RI TS (Scheme) is a reasonable model for steric interactions in the BS TS, which was not calculated owing to the large multiconfigurational wave function necessary to represent it accurately.[6,31,32]

Two models were investigated for **2²⁻/2K⁺**, the first of which involved a complete geometry optimization of the

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**Table 3. Relative Energies and Torsional Angles for the HF/3-21G$^{(*)}$-Optimized Ground State and Ring Inversion Transition State of ArylCOTs**

| compound | substituent | state | $\Delta(E+\text{ZPE})_{RI}{}^a$ | $\omega_1{}^b$ | $\Delta\omega_1{}^{c,d}$ | $\omega_2{}^e$ | $\cos^2\omega_1$ |
|---|---|---|---|---|---|---|---|
| **1a** | NO$_2$ | GS | | 43.3 | 1.1 | | 0.53 |
| | | TS | 19.17 | 62.9 | 0.1 | | 0.21 |
| **1b** | H | GS | | 44.4 | (0) | | 0.51 |
| | | TS | 18.93 | 63.0 | (0) | | 0.21 |
| **1c** | OCH$_3$ | GS | | 42.4 | 2.0 | | 0.55 |
| | | TS | 19.14 | 61.4 | 1.6 | | 0.23 |
| **2**$^f$ | COT | GS | | 43.1 | 1.3 | 43.1 | 0.53 |
| | | TS | 18.99 | 61.7 | 1.3 | 43.2 | 0.22 |
| **2**$^{2-}$/2K$^+$ $^{f,g}$ | COT$^{2-}$/2K$^+$ | GS | | 42.8 | 1.6 | 45.5 | 0.54 |
| | | TS | 18.91 | 58.8 | 4.2 | 45.4 | 0.27 |
| **2**$^{2-}$/2K$^+$ $^{f,h}$ | COT$^{2-}$/2K$^+$ | GS | | 40.1 | 4.3 | 44.7 | 0.59 |
| | | TS | 18.61 | 57.2 | 5.8 | 45.7 | 0.29 |

$^a$ In kcal mol$^{-1}$ relative to the ground state. $^b$ $\omega$(C$_2$C$_1$C$_9$C$_{10}$); in degrees. $^c$ $\Delta\omega_{1,GS} = \omega_{GS}(\mathbf{1b}) - \omega_{GS}$. $^d$ $\Delta\omega_{1,TS} = \omega_{TS}(\mathbf{1b}) - \omega_{TS}$. $^e$ $\omega$(C$_{2'}$C$_1$C$_{9'}$C$_{10'}$), the twist of the second COT ring in **2** or the COT$^{2-}$ ring in **2**$^{2-}$/2K$^+$; in degrees. $^f$ The COT$^{2-}$ ring and the neutral COT ring (or its C$_1$C$_2$ double bond) are nearly coplanar in the minimum energy conformation. $^g$ Fully optimized. $^h$ Solvated K$^+$; the potassium ions were fixed 2.400 Å above and below the center of the ring (approximately as found by X-ray diffraction [refs 33, 34]), and all other parameters were optimized.

ion triplet. In the second, the potassium ions were fixed above the center of the COT$^{2-}$ ring at a distance (2.400 Å) similar to that found by X-ray diffraction (2.32–2.46 Å) for contact ion pairs of COT$^{2-}$ $^{33}$ or substituted COT$^{2-}$ $^{34}$ and K$^+$ solvated with glyme or diglyme and all other parameters were optimized. The counterions are located 2.312 and 2.400 Å from the plane of the ring in these two structures, which we designate as **2**$^{2-}$/2K$^+$ and **2**$^{2-}$/2K$^+$ (solvated K$^+$), respectively.

The value of $\omega$(C$_2$C$_1$C$_9$C$_{10}$) ($\omega_1$) in **1a–c** and **2** is about 19° greater in the RI TS than in the GS (Table 3). This is due primarily to increased steric interactions between the ortho aryl hydrogens and the COT hydrogens at C$_2$ and C$_8$ as $\angle$CCC in the COT ring increases from ca. 126°$^{35}$ in the ground state to ca. 135° in the RI TS.

As a working hypothesis, we assume that the twist angle between the aryl and COT or COT$^{2-}$ ring ($\omega_1$ and $\omega_2$, respectively [Table 3]) primarily reflects $\pi$ resonance interactions between the two rings *if steric effects remain constant*. Thus, the fact that the COT$^{2-}$ ring is more twisted with respect to the phenylene ring in the RI TS of **2**$^{2-}$/2K$^+$ than in the GS ($\omega_2$ in Table 3) is taken to indicate that there is more $\pi$ resonance with the neutral COT ring in the GS. Further, the reduction in twist for the neutral compounds (**1a**, **1c**, and **2**) relative to **1b** ($\Delta\omega_1$) is the same or slightly less in the TS than in the GS, suggesting that resonance due to the substituent either increases less in the TS (consistent with the small increase in $\Delta(E+\text{ZPE})_{RI}$ for **1a** and **1c** relative to **1b**) or remains relatively constant (as in **2**) in these two states. *Thus, the absence of a substituent effect on $\Delta G^{\ddagger}_{BS}$ in these compounds can be attributed to a fortuitous cancellation of two effects*: (a) an *increase* in $\pi$ delocalization in the RI TS relative to the GS assuming no change in $\omega_1$ and (b) a *decrease* in $\pi$ delocalization in the TS owing to a

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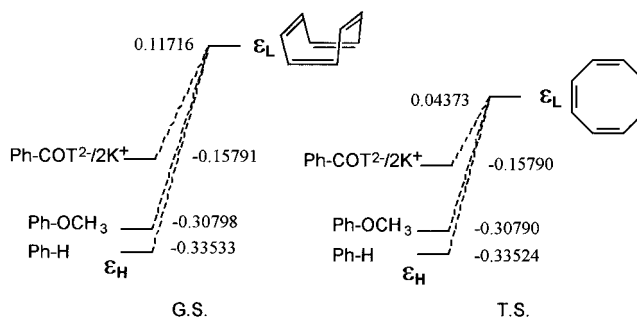


**Figure 2.** Diagram showing interaction (in hartrees) between the HF/3-21G$^{(*)}$ frontier molecular orbitals of the COT and aryl rings in the GS and RI TS of **1b**, **1c**, and **2**$^{2-}$/2K$^+$ (solvated K$^+$). These calculations employed the aryl and COT or COT$^{2-}$/2K$^+$ substructures from the corresponding GS or RI TS.

greater degree of sterically induced inter-ring twist relative to the GS.

In contrast, $\Delta\omega_1$ for **2**$^{2-}$/2K$^+$ (solvated K$^+$) is 1.5° larger in the TS than in the GS. In accord with this result, $\Delta(E+\text{ZPE})_{RI}$ is calculated to be 0.32 kcal mol$^{-1}$ *smaller* than for **1b**. Why does the COT$^{2-}$ substituent increase $k_{BS}$ while the methoxy group, which is only a moderately weaker donor in the GS, has no effect? An insight can be gained by employing second-order perturbation theory.

In eq 1, the interaction energy ($\Delta E$) between the COT and COT$^{2-}$ ($\pi$) HOMO and the aryl ($\pi^*$) LUMO in *weakly coupled* aryl and COT or COT$^{2-}$ rings is inversely proportional to the LUMO–HOMO energy gap ($\epsilon_L$-$\epsilon_H$) and directly proportional to the square of the resonance integral ($\langle\pi|\mathcal{H}'|\pi^*\rangle^2$) as well as to $\cos^2\omega$. Although it is likely that these two rings are more strongly coupled than is appropriate for the *quantitative* application of a second-order perturbation model, the *relative values* of $\Delta E$ that are predicted by eq 1 should nevertheless be valid.

$$\Delta E = \frac{\langle\pi|\mathcal{H}'|\pi^*\rangle^2}{\epsilon_1 - \epsilon_2} \tag{1}$$

If the resonance integral remains unchanged, $\Delta E$ is calculated to increase by 136% on going from the GS to the TS in **2**$^{2-}$/2K$^+$ (solvated K$^+$) (Figure 2) due to the decrease in $\epsilon_L - \epsilon_H$. In contrast, the stabilization of **1b** and **1c** increases by only 119 and 121%, respectively. This is due to the fact that, since the decrease in $\epsilon_L$ is essentially the same for all of the substituents, the change in $\epsilon_L - \epsilon_H$ is *proportionately* much greater for the donor with the highest-lying HOMO (C$_6$H$_4$COT$^{2-}$).

This type of perturbation argument has, for example, been employed previously to explain the effects of substituents on the rates of 1,3-dipolar cycloaddition$^{36}$ and Diels–Alder$^{37}$ reactions. Sustmann and Schubert concluded that "introducing a substituent into a diene has a greater effect on the rates of [Diels–Alder] reactions of TCNE [tetracyanoethene] than on those of MA [maleic anhydride]" due to a smaller HOMO–LUMO separation in the TS of TCNE.$^{37}$ The Diels–Alder TSs for MA and TCNE in their comparison are analogous to the GS and BS TS, respectively, in our study.

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This analysis can be extended to the numerator of eq 1. Thus, if $\epsilon_L - \epsilon_H$ remains unchanged, $\Delta E$ is calculated to decrease by only 50% due to the decrease in $\cos^2 \omega$ on going from the GS to the TS in $\mathbf{2}^{2-}/2K^+$ (solvated $K^+$) (Table 3), whereas decreases of 60 and 58% are calculated for $\mathbf{1b}$ and $\mathbf{1c}$, respectively. Although this model employs only the HOMO and LUMO, it illustrates how a strong $\pi$-orbital interaction in $\mathbf{2}^{2-}/2K^+$ (solvated $K^+$) can cause a decrease in inter-ring twist that reinforces this interaction and increases $k_{RI}$ or $k_{BS}$ while a weaker donor ($C_6H_4$-$OCH_3$ in $\mathbf{1c}$) has no observable effect.

The TS for BS should be stabilized even more by resonance than that for RI owing to its higher HOMO and lower LUMO. Furthermore, ion pairing for $COT^{2-}/2K^+$ might be even looser in THF solution than in the crystal structures that we employed as a model.[33,34] Both factors would decrease the calculated barriers reported in Table 3 and tend to bring their relative values more into line with the relative values for $\Delta G^{\ddagger}_{BS}$ in Table 1. However, this conclusion is dependent on whether BS occurs by passage over a classical barrier. A complete analysis requires that tunneling through the barrier also be considered.

**Heavy Atom Tunneling.** Carpenter was the first to propose that heavy-atom tunneling (HAT) contributes to the mechanism of bond shift in COT.[38] HAT can occur only if the atomic positions of the interconverting species are nearly the same, thereby causing the barrier separating them to be narrow. The distance carbon atoms in $D_{4h}$ COT have to move in the bond shift process ($\Delta r_{BS}$) is about half the difference in length between a CC double bond and a CC single bond (1.32 and 1.48 Å, respectively),[39] or ca. 0.08 Å. Since $\Delta r_{BS}$ is less than the de Broglie wavelength of 0.1 Å calculated for a CH particle with a kinetic energy of 15.0 kcal mol$^{-1}$,[40] the postulation of HAT is reasonable.

HAT in processes such as BS in COT has been termed vibrationally assisted tunneling (VAT) by Dewar et al.[41] in order to describe tunneling that originates from a vibrationally excited state. In COT, the unfolding of the tub conformation to a planar or nearly planar RI TS can be viewed as a large amplitude vibration that must take place before tunneling can occur. The tunneling step would then involve the movement of CH groups concomitant with $\pi$-bond shift.

Because the tunneling rate constant is temperature independent, a significant contribution from a tunneling mechanism can cause a curved Arrhenius plot.[40] Tunneling might also manifest itself in an unusually small, commonly negative, entropy of activation ($\Delta S^{\ddagger}_{BS}$).[40] To determine a reasonably reliable value for $\Delta S^{\ddagger}_{BS}$, we measured the rate of bond shift for $\mathbf{1c}$ over a 50 degree temperature range and calculated $\Delta S^{\ddagger}_{BS}$ to be $-10 \pm 5$ cal mol$^{-1}$ K$^{-1}$ from a van't Hoff plot (Supporting Information). This is in good agreement with the value of $-9.7$ cal mol$^{-1}$ K$^{-1}$ determined by Naor and Luz[42] for COT in liquid crystalline solvents measured over a temperature range of 195 degrees, as well as with expectations based on a tunneling contribution to the mechanism of BS.[38,40]
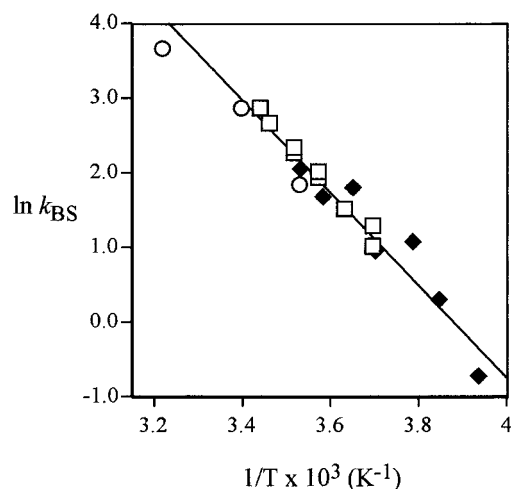


**Figure 3.** Arrhenius plot for bond shift in $\mathbf{1c}$; $r = 0.942$. The symbols represent measurements on 200 (○), 300 (□), and 500 MHz (◆) NMR spectrometers.

An Arrhenius plot for BS in $\mathbf{1c}$ gives a straight line (Figure 3). However, this does not exclude a contribution from tunneling for at least two reasons. First, the kinetics were measured only down to 271 K; second, theoretical treatments of quantum tunneling reactions (such as proton transfer) by Borgis and Hynes[43] and by Kim and co-workers[44] have shown that the appearance of classical Arrhenius behavior can result primarily from the classical bath contribution to the rate constant.

The energetics of BS in COTs are dominated by the ring-flattening step,[6] which we assume to be the origin of the observed Arrhenius behavior of $k_{BS}$. This is in accord with the calculations of Andrés et al., who employed CASSCF imaginary frequencies and MP2–CASSCF barrier heights (including vibrational zero point energy corrections) to compute tunneling corrections for COT of 1.04 and 15.2 for RI and BS, respectively, at 200 K.[31d] These authors concluded that "the experimental rate constants [for BS] mainly provide information about the RI process."

The question of the electronic effect of substituents on the rate of tunneling has been addressed recently by Mackenzie and co-workers,[45] who studied the intramolecular $4\sigma + 2\pi$ dyotropic reaction (2H transfer) of $N,N$-diarylpyrazolines. These authors found that rearrangement occurs over twice as fast when aryl = $p$-MeC$_6$H$_4$ than when aryl = $p$-ClC$_6$H$_4$. They also found strong evidence for H-atom tunneling in the latter compound but not for the former.

The contribution of tunneling is dependent on both the height and width of the barrier,[40,46] as well as on the symmetry of the potential energy wells for the initial and final states.[47] Simply stated, the probability of tunneling at a given temperature is greater through a high, thin

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**Table 4. Bond Lengths for COT in the HF/3-21G$^{(*)}$-Optimized Ring Inversion Transition States for ArylCOTs$^a$**

| compd | $r_{12}$ | $r_{23}$ | $r_{34}$ | $r_{45}$ | $r_{56}$ | $r_{67}$ | $r_{78}$ | $r_{18}$ | $r_{18} - r_{12}$ | $\Delta r_{BS}$$^b$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | 1.3271 | 1.4760 | 1.3226 | 1.4745 | 1.3217 | 1.4759 | 1.3228 | 1.4881 | 0.1610 | 0.07754 |
| **1b** | 1.3230 | 1.4758 | 1.3218 | 1.4742 | 1.3228 | 1.4765 | 1.3270 | 1.4893 | 0.1663 | 0.07765 |
| **1c** | 1.3276 | 1.4764 | 1.3229 | 1.4740 | 1.3218 | 1.4758 | 1.3232 | 1.4901 | 0.1625 | 0.07760 |
| **2** | 1.3274 | 1.4764 | 1.3229 | 1.4741 | 1.3218 | 1.4758 | 1.3230 | 1.4895 | 0.1621 | 0.07765 |
| **2**$^{2-}$/2K$^{+}$ $^c$ | 1.3283 | 1.4762 | 1.3233 | 1.4735 | 1.3219 | 1.4758 | 1.3233 | 1.4912 | 0.1631 | 0.07747 |
| **2**$^{2-}$/2K$^{+}$ $^d$ | 1.3289 | 1.4757 | 1.3252 | 1.4738 | 1.3221 | 1.4759 | 1.3235 | 1.4914 | 0.1625 | 0.07715 |

$^a$ In angstroms. $^b$ Average single bond length − average double bond length. $^c$ Fully optimized. $^d$ Solvated K$^+$; see footnote $g$ in Table 3.

barrier separating isoenergetic potential energy wells than through a short, broad barrier between minima of different energies. We expect that the heights of the classical BS barriers in arylCOTs will parallel those of the RI barriers in Table 3. However, differences between substituents might be enhanced owing to greater $\pi$ interaction between the substituent and the COT ring in the classical BS TS as a result of its higher HOMO and lower LUMO.

The width of the barrier is dependent on the distance the CH groups move during interconversion between planar bond-alternant structures. In arylCOTs, the position of $C_1$ is essentially fixed by the mass of the aryl group. Consequently, $\Delta r_{BS}$ for $C_2$ and $C_8$ will be about twice as large as in COT with smaller differences for $C_3$–$C_7$, significantly decreasing the contribution of tunneling to $k_{BS}$.

Table 4 gives the CC bond lengths for the RI TS of arylCOTs optimized at HF/3-21G$^{(*)}$. Note that there is little variation in $\Delta r_{BS}$ (±0.0001 Å) within the series **1a**–**c**, **2**, and **2**$^{2-}$/2K$^+$ whereas $\Delta r_{BS}$ for **2**$^{2-}$/2K$^+$ (solvated K$^+$) is 0.0003−0.0005 Å less than for the above compounds. This is probably a result of "leakage" of $\pi$ electron density from the dianion ring to the neutral COT ring in the RI TS of **2**$^{2-}$/2K$^+$ (solvated K$^+$) and might contribute to the larger value of $k_{BS}$ in the latter. On the other hand, $r_{18} - r_{12}$ in **2**$^{2-}$/2K$^+$ (solvated K$^+$) is as large as or larger than for the other arylCOTs. Since $C_2$ and $C_8$ would have to tunnel the greatest distance, there is no clear evidence that the BS barrier is narrower in **2**$^{2-}$/2K$^+$ (solvated K$^+$) at the HF/3-21G$^{(*)}$ level of theory.

We do not expect symmetry to play a major role in determining the value of $k_{BS}$ in arylCOTs. This is because BS changes the RI TS of **1b** into an identical structure, so the classical potential energy surface (PES) is symmetrical for all angles of twist between the phenyl and planar COT rings. The $C_2$ symmetry of the RI TS of **1b** is broken when *p*-phenyl substituents with various degrees of twist are introduced, but the *local* symmetry at $C_1$ of the COT ring, and therefore the PES, should not be greatly affected. Further, torsional vibrations of the phenylene−substituent bond occur on a much shorter time scale than HAT.[48]

## Summary

The *p*-NO$_2$, *p*-OCH$_3$, and *p*-COT substituents in **1a**, **1c**, and **2**, respectively, in THF-$d_8$ have no effect within

experimental error on the rate of BS relative to the parent phenylCOT (**1b**). In contrast, $k_{BS}$ for **2**$^{2-}$/2K$^+$ is eight times greater than that for **1b** at 280 K. These results are unexpected on the basis of classical ground-state substituent effects, as exemplified by NMR-derived values of $\sigma_p$ and $\sigma_p^+$ for *p*-NO$_2$, *p*-OCH$_3$, and *p*-COT$^{2-}$/2K$^+$. The values of $\sigma_p$ and $\sigma_p^+$ for *p*-COT$^{2-}$/2K$^+$ (determined to be −0.7 and −1.0, respectively, from ^{13}C NMR chemical shifts) indicates that it is a significantly stronger donor than *p*-OCH$_3$. However, these values are undoubtedly highly dependent on the degree and type of ion pairing involved.

Geometry optimization of the GS and RI TS at HF/3-21G$^{(*)}$ suggests that the absence of a substituent effect on $k_{BS}$ in **1a**−**c** and **2** results from the fortuitious cancellation of (a) an *increase* in $\pi$ delocalization in the RI TS relative to the GS assuming no change in the COT−aryl dihedral angle and (b) a *decrease* in $\pi$ delocalization in the TS relative to the GS due to increased sterically induced twisting in the former. In contrast, *p*-COT$^{2-}$/2K$^+$ is a strong enough donor that the effect of increased $\pi$ delocalization in the TS outweighs the rate-retarding effect of increased sterically induced twisting.

Heavy-atom tunneling is expected to be less important for BS in arylCOTs than in COT itself. We were unable to assess the effect of configuration interaction (CI) on $k_{BS}$ owing to the size of the multiconfigurational wave functions required. Since CI is known to be important in calculating the BS TS of COT,[6,31,32] the above conclusions need to be tested at the CI level when this is computationally feasible.

## Experimental Section

**General.** Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl. Preparative column chromatography was performed on 40 μM silica gel. NMR spectra (CDCl$_3$ solutions) were obtained at 300 and 75 MHz for ^{1}H and ^{13}C, respectively, unless otherwise noted. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, IN.

**Synthesis. Phenylcyclooctatetraene** (**1b**) was prepared by the method of DeKock and co-workers.[12] Final purification was achieved by HPLC on a C$_{18}$ column on elution with 95/5 acetonitrile/water. ^{1}H NMR (THF-$d_8$, 25 °C): $\delta$ 7.0−7.2 (5 H, m), 5.8−6.1 (7 H, m). ^{13}C NMR (THF-$d_8$, 25 °C): $\delta$ 142.7 (C$_1$), 141.1 (C$_9$), *133.7, 133.2, 133.0*, 132.9 (C$_5$), *132.4, 132.2*, 128.9 (C$_{11}$), 128.2 (C$_{12}$), 126.8 (C$_{10}$), 126.7 (C$_2$). The italicized values are those for C$_3$, C$_4$, and C$_6$−C$_8$, which undergo exchange due to bond shift.

***p*-(Methoxyphenyl)cyclooctatetraene (1c).** One-centimeter pieces of clean lithium wire (1.39 g, 0.20 mol) were added to a dry three-necked round-bottomed flask equipped with an addition funnel and a reflux condenser and charged with 100 mL of ether under argon. 4-Bromoanisole (0.598 g, 32.0 mmol) in 60 mL of diethyl ether was added dropwise over 1 h at a rate sufficient to maintain reflux. The mixture was heated to reflux for an additional 1 h and transferred via a cannula to

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a vigorously stirred solution of COT (0.111 g, 10.6 mmol) in 50 mL of ether under argon. The resulting dark-orange solution was stirred for 24 h in order to complete the formation of the dianion. Oxygen was then passed over the reaction mixture for 2 h. Saturated aq $NH_4Cl$ was added, and the organic layer was separated and washed with 2 × 50 mL of water. After extraction of the combined aqueous layers with 2 × 50 mL of ether, the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with 10% $CH_2Cl_2$/hexane to afford 350 mg (64%) of **1c**, mp 64.5−65 °C (lit.[13] 64−65 °C). Final purification was achieved by HPLC on a $C_{18}$ column by eluting with acetonitrile. ^{1}H NMR (THF-$d_8$, 25 °C): δ 7.05 (2 H, d, $J$ = 9.0 Hz), 6.59 (2 H, d, $J$ = 9.0 Hz), 5.8−6.2 (7 H, br m) and 3.6 (3 H, s); ^{13}C NMR (THF-$d_8$, 25 °C): δ 160.0 ($C_{12}$), 141.0 ($C_1$), 132.5 ($C_9$), *132.9, 132.2,* 131.9 ($C_5$), *131.8, 131.4, 130.8,* 127.9 ($C_{10}$), 125.7 ($C_2$), 114.1 ($C_{11}$), 55.0 ($C_{13}$). The italicized values are those for $C_3$, $C_4$, and $C_6$–$C_8$, which undergo exchange due to bond shift.

**Tributylstannylcyclooctatetraene (3)** was prepared by the method employed for the synthesis of trimethylstannylCOT by Stone and co-workers.[49] *n*-Butyllithium (15.0 mL, 2.0 M in hexane) was added over 2 min to a stirred solution of bromocyclooctatetraene (5.00 g, 27.3 mmol) in ether (15 mL) at −80 °C. The reaction mixture was stirred for an additional 1.5 h at −80 °C, 8.14 g (25.0 mmol) of tributylchlorostannane was added, and the mixture was allowed to warm to room temperature over 30 min. The mixture was hydrolyzed with 20 mL of satd aq $NH_4Cl$ and washed with 2 × 20 mL of satd aq $NH_4Cl$. After extraction of the aqueous layers with 2 × 50 mL of ether, the combined organic layers were dried ($MgSO_4$) and distilled to afford a yellow oil, bp 80 °C (0.1 mm) in 68% yield. ^{1}H NMR ($CDCl_3$): δ 5.8−6.2 (7 H, broad m), 1.47 (6 H, m), 1.36 (6 H, m), 0.91 (15 H, m). Calcd for $C_{20}H_{34}Sn$: C 61.10%, H 8.72%. Found: C 61.14%, H 8.90%.

***p*-(Nitrophenyl)cyclooctatetraene (1a).** To a stirred solution of 1-iodo-4-nitrobenzene (0.249 g, 10.0 mmol), tris-(dibenzylideneacetone)palladium(0) (23 mg, 0.025 mmol Pd), and triphenylarsine (31 mg, 0.10 mmol) in 10 mL of THF at room temperature was added 3.26 g (10 mmol) of tributyl-stannylcyclooctatetraene in 10 mL of THF. After 24 h, the reaction mixture was diluted with 10 mL of EtOAc, and 10 mL of 50% satd aq KF was added. The reaction mixture was stirred for 15 min and filtered, and the organic layer was washed with 20 mL of $H_2O$ and 20 mL of brine. The combined aqueous layers were extracted with 20 mL of EtOAc, and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel with 10% $CH_2$-$Cl_2$/hexane to afford a yellow solid, mp 33−34 °C, in 70% yield. Final purification was achieved by HPLC on a $C_{18}$ column by elution with acetonitrile. ^{1}H NMR (THF-$d_8$, 25 °C): δ 8.15 (2 H, d, $J$ = 9.0 Hz), 7.58 (2 H, d, $J$ = 9.0 Hz), 5.8 (7 H, br m); ^{13}C NMR (THF-$d_8$, 25 °C): δ 147.9 ($C_9$), 147.2 ($C_{12}$), 140.9 ($C_1$), *134.4, 133.0,* 132.9 ($C_5$), 132.8 ($C_2$), *132.6, 132.4, 132.3,* 127.6 ($C_{10}$), 124.2 ($C_{11}$). The italicized values are those for $C_3$, $C_4$ and $C_6$–$C_8$, which undergo exchange due to bond shift. IR (KBr): 3078, 3002, 1286, 1540 cm$^{-1}$. Calcd for $C_{14}H_{11}NO_2$: C 74.65%, H 4.91%, N 6.22%. Found: C 74.44%, H 4.96%, N 6.32%.

**1,4-Dicyclooctatetraenylbenzene**[10a] **(2).** ^{1}H NMR (THF-$d_8$, 25 °C): δ 7.31 (4 H, s), 5.8 (14 H, br m); ^{13}C NMR (THF-$d_8$, 25 °C): δ 142.2 ($C_9$), 140.2 ($C_9$), *133.6, 133.3, 133.1,* 132.9 ($C_5$), *132.6, 132.5,* 128.7 ($C_2$), 126.7 ($C_{10}$). The italicized values are those for $C_3$, $C_4$, and $C_6$–$C_8$, which undergo exchange due to bond shift.

**1,4-Dicyclooctatetraenylbenzenedipotassium ($2^{2-}$/2K$^+$).** The synthesis and NMR chemical shifts for this compound have been reported previously.[10a]

**Kinetic Methods: General.** All kinetics were measured for at least two independent samples that had been sealed under argon in 5 mm NMR tubes after five freeze−pump−thaw cycles. The temperature of the sample was determined from the difference in the proton chemical shifts of methanol for temperatures <295 K according to the method of Van Geet.[50] The temperature accuracy is estimated to be ±1 °C due to improvements made to the variable temperature system as recommended by Allerhand.[51] The free induction signals were sampled with 32K data points. After zero filling and Fourier transformation, the spectral resolution was typically in the range of 0.3−0.5 Hz/point.

**Line Broadening.** Bond shift rate constants ($k_{BS}$) were calculated at a number of temperatures from ^{13}C signals where line broadening could be determined. Line widths for the pairwise exchanging carbons ($C_2$ and $C_8$, $C_3$ and $C_7$, $C_4$ and $C_6$) could each, in principle, be measured, but $k_{BS}$ was determined only from nonoverlapped signals. Rate constants for bond shift were calculated by eq 5,[52] where $\Delta\nu_{exch}$ is the exchange broadening (in Hz) of a signal in the slow exchange

$$k_{BS} = \pi\Delta\nu_{exch} \tag{5}$$

region, i.e., the observed line width at half-height ($\Delta\nu_{1/2}$) corrected for the intrinsic line width at half-height. This correction was determined as follows. From spectra at low temperature, where bond shift exchange broadening was absent, it was found that the line width of $C_5$ was very similar to those of the other proton-bearing carbons in the neutral COT ring. At higher temperatures, the line width of $C_5$, which does not undergo exchange, was subtracted from that of the exchange-broadened signals to give $\Delta\nu_{exch}$. All line widths were determined by a least-squares fit of the peak to a Lorentzian line shape.

Uncertainties in the rate constants were estimated from replicate measurements because differential error analysis yielded unreasonably small uncertainties in the rate constants. The error in $\Delta G^{\ddagger}_{BS}$ was determined by propagation of the errors from the rate constants. The maximum error was found to be ±10% when $k_{BS}$ was obtained from line width measurements.

**Computational Methods.** Ab initio molecular orbital calculations and geometry optimizations were performed using the GAUSSIAN 92 series of programs[30] at the Hartree−Fock (HF) level of theory with the 3-21G$^{(*)}$ basis set.[29] Fully optimized geometries of the GSs and RI TSs were shown to have zero and one imaginary frequency, respectively, by analytical frequency analysis.

**Supporting Information Available:** Rate constants and temperatures for bond shift in **1a**−**c**, **2**, and $2^{2-}$/2K$^+$ (Tables S1-S5) and the corresponding van't Hoff plots (Figures S1−S5); HF/3-21G$^{(*)}$ energies and Z-matrixes for **1a**−**c**, **2**, $2^{2-}$/2K$^+$, and $2^{2-}$/2K$^+$ (solvated K$^+$) (Tables S6−S17). This material is available free of charge via the Internet at http://pubs.acs.org.

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