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Mechanism of a Novel Exchange Process in Alkali Metal Salts of 1,5-Dicyclooctatetraenylnaphthalene Dianion

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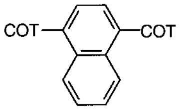
Abstract: A novel low-temperature intramolecular exchange was detected by ^{13}C NMR spectrometry in the Na^+ and K^+ salts of the title compound. The process causes the pairwise exchange in the dianion ring of $C_{2''}$, $C_{3''}$, and $C_{4''}$ with $C_{8''}$, $C_{7''}$, and $C_{6''}$, respectively. The free energy of activation ($\Delta G^{\ddagger}_{exch}$) for the dipotassium salt ($\mathbf{2}^{2-}/2K^+$) in THF-d_8 at 230 K is 12.6 kcal mol^{-1}. Two key questions are addressed: (1) Why are these carbons anisochronous and (2) what is the mechanism of exchange? NMR data for 1-cyclooctatetraenylnaphthalenedipotassium ($\mathbf{3}^{2-}/2K^+$) as well as ab initio HF/3-21G$^{(*)}$ calculations for **3**, $\mathbf{3}^{2-}$, and $\mathbf{3}^{2-}/2K^+$ indicate that the nonequivalence is due to both slow rotation across a barrier at which the naphthalene and COT^{2-} rings are approximately coplanar and slow inversion of the neutral COT ring. This results in the noteworthy circumstance of diastereotopic carbons being observed in a molecule that does not possess either a stereogenic or a prostereogenic center. Comparison of $\Delta G^{\ddagger}_{exch}$ and $\Delta G^{\ddagger}_{BS}$ for $\mathbf{2}^{2-}/2K^+$ with the corresponding values for $\mathbf{2}^{2-}/2Na^+$ and $\mathbf{2}^{2-}/2Li^+$ and of $\Delta G^{\ddagger}_{exch}$ with $\Delta G^{\ddagger}$ for ring inversion in 1,4-dicyclooctatetraenylnaphthalene leads to the conclusion that COT^{2-} ring rotation and COT ring inversion both contribute to exchange in $\mathbf{2}^{2-}/2K^+$ in a 3:1 ratio, but that exchange occurs exclusively by ring rotation in $\mathbf{2}^{2-}/2Li^+$. The latter result is attributed to looser ion pairing in the dilithium (and disodium) salts.

We have been interested in the process of “gated” charge transfer in bridged dicyclooctatetraene dianions.[1−3] The gating step in this system involves both ring flattening and bond equalization in the neutral COT ring, changes that necessarily precede electron transfer and cation migration. As a consequence, gating is closely related to the well-known processes of ring inversion (RI) and bond shift (BS) (Scheme 1). The dipotassium salt of 1,4-dicyclooctatetraenylnaphthalene ($\mathbf{1}^{2-}/2K^+$) undergoes one or more additional dynamic process below 233 K.[1] Analogous behavior was also seen for $\mathbf{2}^{2-}/2K^+$. The observations that motivated the present study are presented in Figure 1.



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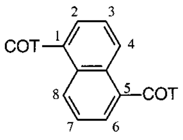

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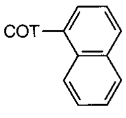
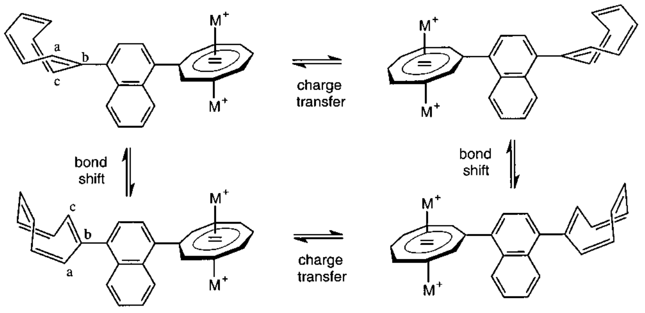
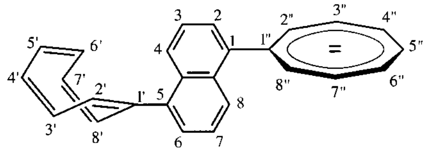


3

Four of the seven ^{13}C signals of the dianion ring of $\mathbf{2}^{2-}/2K^+$ at 225 K coalesce to afford a total of five signals at 255 K. If one makes the reasonable assumption that the most remote carbons ($C_{4''}$ and $C_{6''}$) are accidentally isochronous (magnetically equivalent), then this behavior is fully consistent with a pairwise exchange of $C_{2''}$, $C_{3''}$, and $C_{4''}$ with $C_{8''}$, $C_{7''}$, and $C_{6''}$, respectively. This led us to address two key questions: (1) Why are the exchanging carbons anisochronous and (2) what is the mechanism of exchange? The answers to these questions, which involve some unexpectedly complex results, are detailed below.

Scheme 1





$\mathbf{2}^{2-}$

Results

Synthesis. 1,5-Dicyclooctatetraenylnaphthalene (**2**) was prepared in 35% yield by the Pd-catalyzed (Stille) coupling of 1,5-diiodonaphthalene with (trimethylstannyl)cyclooctatetraene[4] (Me_3SnCOT). Analogously, 1-cyclooctatetraenylnaphthalene (**3**) was prepared in 67% yield by the coupling of 1-bromonaphthalene

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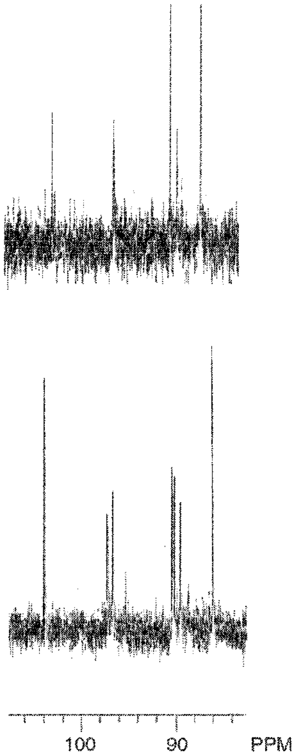
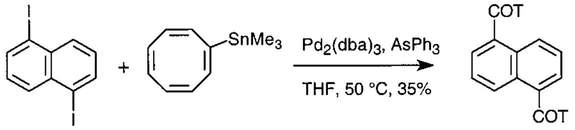


Figure 1. ^{13}C NMR spectra for the dianion ring of 1,5-dicyclooctatetraenylnaphthalenedipotassium ($\mathbf{2}^{2-}$/2K$^+$) in THF-d_8 at 225 (bottom) and 255 K (top).

with Me$_3$SnCOT. This compound had been synthesized previously by the Cope−DeKock method[5] in 11% yield.[6]



2

Kinetic Studies. The alkali metal salts $\mathbf{2}^{2-}$/2M$^+$ (M = Li, Na, K) and $\mathbf{3}^{2-}$/2K$^+$ were generated by carefully contacting a solution of **2** or **3** in THF-d_8 with the alkali metal in a sealed NMR tube. In addition to the expected exchanges of ^{13}C due to BS in the neutral ring (broadening and pairwise exchange of C$_{2'}$, C$_{3'}$ and C$_{4'}$ with C$_{8'}$, C$_{7'}$ and C$_{6'}$, respectively) (see structure $\mathbf{2}^{2-}$) and intramolecular transfer of charge between the COT rings (exchange of ^{1}H and ^{13}C in COT with those in COT^{2-}),[1-3] we observed another, lower energy exchange process affecting the ^{13}C signals in the COT^{2-} ring of $\mathbf{2}^{2-}$/2K$^+$ (Figure 1) and $\mathbf{2}^{2-}$/2Na$^+$.

As seen in Figure 1, this process causes the "doublets" at ca. δ 97 and 90 at 225 K to collapse to singlets at 255 K. We assume that the difference in chemical shifts at 225 K between C$_{2''}$ and C$_{8''}$, C$_{3''}$ and C$_{7''}$, and C$_{4''}$ and C$_{6''}$ decreases with increasing distance from the naphthalene ring, i.e., $\Delta\delta C_{2'',8''} > \Delta\delta C_{3'',7''} > \Delta\delta C_{4'',6''}$. Assuming that the singlet at δ 88 is due to C$_{4''}$ and C$_{6''}$ being accidentally isochronous, then the NMR temperature dependence is fully consistent with pairwise exchange of these carbons.

Table 1. Kinetic Data for Bond Shift in **2** and $\mathbf{2}^{2-}$/2M$^+$ in THF-d_8 at 280 K

compound	T range (K)	k_{BS}[a]	$\Delta G^{\ddagger}_{BS}$[b]
2	260−280	16.9	14.8
$\mathbf{2}^{2-}$/2K$^+$	255−280	17.2	14.8
$\mathbf{2}^{2-}$/2Na$^+$	260−280	22.5	14.6
$\mathbf{2}^{2-}$/2Li$^+$	260−275	29.7[c]	14.5

[a] In s^{-1}; ±10%. Calculated from the van't Hoff plot. [b] In kcal mol^{-1}; ±0.1. [c] Extrapolated.

Table 2. Rate Constants and Free Energies of Activation for Exchange in the COT^{2-} Ring of Alkali Metal Salts of 1,5-Dicyclooctatetraenylnaphthalene Dianion

compound	T (K)	k_{exch}[a]	$\Delta G^{\ddagger}_{exch}$[b]
$\mathbf{2}^{2-}$/2K$^+$	230	5.05	12.6
$\mathbf{2}^{2-}$/2Na$^+$	210	2.5	11.8
$\mathbf{2}^{2-}$/2Li$^+$	180	>2.7	<10[c]

[a] In s^{-1}; ±15%. [b] In kcal mol^{-1}; ±0.2. [c] Maximum estimated from undetectable line broadening (<0.7 Hz) at 180 K.

BS rate constants (k_{BS}) were calculated for duplicate samples and averaged for a number of temperatures where NMR line broadening could be measured in the slow exchange region (Table 1). ^{13}C line broadening for **2** was measured for two nonoverlapped signals (δ 135.9 and 131.9) over a 20 degree temperature range. Although the COT signals coalesced on increasing the temperature from 273 to 298 K, five distinct COT signals had not emerged from the baseline by 323 K, as is expected for the fast exchange region for BS.

The rate constants for BS in $\mathbf{2}^{2-}$/2M$^+$ were determined for two samples of each salt (M = Li, Na, K). ^{13}C line broadening was measured for five nonoverlapped signals [(δ 137.2, 133.8, 132.6, 131.8, 131.6), (δ 136.7, 133.2, 132.2, 131.6, 131.0), and (δ 136.7, 133.2, 132.2, 131.4, 131.1)] over 25, 20, and 15 degree temperature ranges for the K, Na, and Li salts, respectively.

The rate constant for the new exchange process (k_{exch}) was calculated for duplicate samples at a single temperature where line broadening could be measured in the low-temperature region (Table 2). ^{13}C line broadening was measured for four nonoverlapped signals (δ 97.1, 96.6, 90.3, 90.1) at 230 K for $\mathbf{2}^{2-}$/2K$^+$ and for two nonoverlapped signals (δ 93.0. 92.8) at 210 K for $\mathbf{2}^{2-}$/2Na$^+$. No line broadening (<0.7 Hz) was detected for the ^{13}C NMR spectrum of $\mathbf{2}^{2-}$/2Li$^+$ down to 180 K or for that of $\mathbf{3}^{2-}$/2K$^+$ down to 173 K.

Discussion

Nonequivalence of Carbons in the Dianion Ring. There are at least three possible dynamic processes that can occur in $\mathbf{2}^{2-}$/2K$^+$: (1) rotation around the COT^{2-}−naphthalene bond, (2) inversion of the COT ring, and (3) rotation around the COT−naphthalene bond. Fast rotation around the COT^{2-}−naphthalene bond on the NMR time scale would cause rapid exchange, so the observed exchange necessarily requires slow rotation around this bond.

In Table 3, we list the four possible scenarios for the observation of exchange. For slow COT^{2-}−naphthalene rotation with an ω = 90° barrier (where $\omega = \omega(C_{2''}C_{1''}C_1C_2)$ as numbered in $\mathbf{2}^{2-}$) (scenario 1), one side of the COT^{2-} ring would be restricted to the "inside" (i.e., toward the second ring of naphthalene) while the other would be "outside", thereby causing the two sets of carbons to be anisochronous. This result would be obtained regardless of whether dynamic processes of the neutral COT ring are fast or slow. Alternatively, if the overall barrier occurs at 0° one set of COT^{2-} carbons would be

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Table 3. Scenarios for the Observation of Exchange of Carbons in the COT^{2-} Ring of **2**$^{2-}$/2K$^+$

scenario	rotation of COT^{2-a}	inversion of COT	rotation of COT
1	slow (90° barrier)	fast or slow	fast or slow
2	slow	fast	slow [b]
3	slow	slow	slow
4	slow	slow	fast

[a] The naphthalene and COT^{2-} rings are coplanar in the transition structure (0° barrier) unless indicated otherwise. [b] The naphthalene ring and the $C_{1'}C_{2'}$ bond of COT must not be coplanar in the minimum energy conformation.

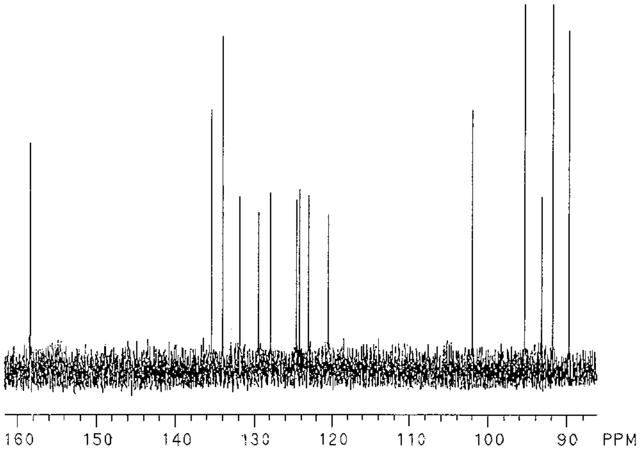

Figure 2. ^{13}C NMR spectrum of 1-cyclooctatetraenylnaphthalenedipotassium (**3**$^{2-}$/2K$^+$) in THF-d_8 at 193 K.

Table 4. Relative Energies and Torsional Angles for HF/3-21G$^{(*)}$ Geometry-Optimized Ground States and 0° and 90° Conformers of **3**$^{2-}$ and **3**$^{2-}$/2K$^+$ (solvated K$^+$)

compound	state	ω^a	E^b	ΔE^c
3^{2-}	GS	35.2	−685.39759	0
		0^d	−685.39173	3.68
		90^d	−685.38649	6.97
3^{2-}/2K$^+$ (solvated K$^+$)^e	GS	57.7	−1878.24290	0
		0^d	−1878.21467	17.72
		90^d	−1878.24001	1.81

[a] $\omega(C_{2''}C_{1''}C_1C_2)$, in deg; twist of COT^{2-} relative to the naphthalene ring. [b] In hartrees. [c] In kcal mol^{-1} relative to the ground state. [d] Value of ω fixed to approximate the transition structure. [e] The potassium ions were fixed 2.400 Å above and below the center of the ring (approximately as found by X-ray diffraction [refs 7, 8]) and all other parameters were optimized.

restricted to the “top” of the naphthalene ring and the other to the “bottom”. This renders them isochronous provided that both rotation and inversion of the neutral COT ring are fast on the NMR time scale.

The question of whether the barrier for rotation of COT^{2-} occurs at 0 or 90° was addressed both experimentally and theoretically. The dipotassium salt of 1-cyclooctatetraenylnaphthalene (**3**$^{2-}$/2K$^+$) was studied to determine whether an analogous exchange could be observed in the absence of a proximate COT ring. No broadening of the ^{13}C signals of the dianion ring was observed down to 173 K (see 193 K spectrum in Figure 2). This indicates that any restricted rotation about the COT^{2-}−naphthalene bond must have $\omega \approx 0°$ as the transition structure (TS). The same conclusion necessarily also applies to **2**$^{2-}$/2K$^+$ since, as discussed below, a proximate COT ring has almost no *electronic* influence on the COT^{2-} ring.

This conclusion is supported by geometry optimizations at the ab initio HF/3-21G$^{(*)}$ level using two models for **3**$^{2-}$/2K$^+$. The first, which we designate **3**$^{2-}$, does not include the counterions and is a model for a fully solvent-separated ion pair. In the second, termed **2**$^{2-}$/2K$^+$ (solvated K$^+$), the potassium ions were fixed above and below 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 between COT$^{2-7}$ or substituted COT$^{2-8}$ and glyme- or diglyme-solvated K$^+$ and all other parameters were optimized. Minima in the inter-ring torsional angles of 35.2 and 57.7°, respectively, were calculated for these two models (Table 4). As expected, there is a smaller twist in **3**$^{2-}$ because of the stronger π donor ability of the uncomplexed dianion ring.

The barrier for rotation in **3**$^{2-}$ is calculated to occur at or near $\omega = 90°$ with an energy of ≥ 7.0 kcal mol^{-1}. In contrast, the contact ion-paired dianion [**3**$^{2-}$/2K$^+$ (solvated K$^+$)] is calculated to have a significantly larger barrier (≥ 17.7 kcal mol^{-1}) at or near $\omega = 0°$. The uncomplexed dianion has a smaller barrier at 0° than at 90° despite greater steric interactions at 0° owing to a greater π delocalization in the latter. Conversely, **3**$^{2-}$/2K$^+$ (solvated K$^+$), which is a weaker π donor, is stabilized much more by reduced steric interactions than it is destabilized by loss of π conjugation on twisting from 0 to 90°. The aforementioned NMR evidence for a 0° rotational barrier for **3**$^{2-}$/2K$^+$ is in accord with these molecular orbital calculations since previous studies showed that the COT^{2-} ring is strongly contact ion paired with K$^+$ in THF both at room temperature[9] and at −60 °C.[10]

These results require that the neutral COT ring play an important role in the nonequivalence of the exchanging carbons in **2**$^{2-}$ (scenarios 2−4 in Table 3). Slow rotation of the neutral COT ring (scenarios 2 and 3) would cause $C_{2''}$ and $C_{8''}$ of the COT^{2-} ring to be anisochronous owing to their different relationship to the single and double bonds of the neutral COT ring. Note that for scenario 2, this requires that $C_{1'}C_{2'}$ of the COT ring be twisted relative to the naphthalene ring in the minimum energy conformation. (If $\omega = 0°$ on the NMR time scale in the latter, then the COT and naphthalene rings would effectively be coplanar due to fast COT ring inversion and the regions above and below the naphthalene ring would be magnetically equivalent.)

Slow inversion of the neutral COT ring (scenarios 3 and 4) results in the circumstance that $C_{2''}$ and $C_{8''}$ are anisochronous because they are *diastereotopic*. This is a consequence of the presence of both a chiral moiety (the monosubstituted COT ring) and a prochiral[11] axis (the COT^{2-}−naphthalene bond), a situation that is obtained even if there is rapid rotation of the neutral COT ring (scenario 4). We are aware of only one other example of diastereotopic atoms in molecules (the highly sterically hindered 1-(4-X-phenyl)-8-(2-methylphenyl)naphthalenes)[12] that do not possess either a stereogenic or a prostereogenic[11] center. The diastereomers of 3,6-di(2,4-dimethylphenyl)-2,5-dibromohydroquinone, which can be interconverted at >200 °C, represent a similar relationship.[13]

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Table 5. Torsional Angles and Energies for Rotation and Inversion of the COT Ring of **3**

state	$\omega(C_{2'}C_{1'}C_5C_6)$[a,b]	$(E_{HF} + ZPE)_{rel}$[b,c]
GS	282.9	(0)
rotational minimum	89.3	0.4
rotational TS	0.0	12.4
rotational TS	180.0	13.3
ring inversion TS	75.9	17.8

[a] Torsional angle in degrees; the numbering is the same as in structure **2**$^{2-}$. [b] Calculated at HF/3-21G. [c] Energy relative to the GS; in kcal mol^{-1}.

To investigate scenarios 2−4, the energetics of rotation and inversion of the neutral COT ring in **3** were calculated at HF/3-21G (Table 5). The energy difference between the rotational minimum at $\omega = 282.9°$ and the maximum at 0° was calculated to be 12.4 kcal mol^{-1} whereas that for RI was calculated to be 17.8 kcal mol^{-1}. These values suggest that RI is slow on the NMR time scale, a conclusion that is supported by k_{RI} for **1** (vide infra). Since TS energies are typically overestimated at the HF/3-21G level,[14] rotation of the neutral COT ring is probably fast and scenario 4 is the most likely.

In support of this conclusion, we observed that the sharp 8.7 Hz doublet for $H_{4,8}$ of **2** at 263 K changed to a broad singlet at 203 K. In contrast, the other two naphthalene ^1H resonances remained relatively sharp at the lower temperature, although a slight broadening was also apparent for $H_{2,6}$. These results are consistent with rapid rotation on the ^1H NMR time scale of the COT ring at 263 K and slow rotation at 203 K. The two rotational conformers given in Table 5 probably have different chemical shifts for the hydrogens proximate to the COT rings ($H_{4,8}$ and, to a lesser extent, $H_{2,6}$). These are averaged at 263 K but are broadened at 203 K as the slow exchange region (where they have different chemical shifts) is approached.

Mechanism of Exchange. Having established that the observation of anisochronous carbons is a consequence of *both* slow rotation about the COT^{2-}−naphthalene bond and slow inversion of the neutral COT ring, we next addressed the question of the mechanism of exchange. We reasoned from the effect of ion pairing on the calculated rotational energy barriers in Table 4 that the counterion probably exerts a strong influence on the rate of rotation of the COT^{2-} ring. The dependence of k_{RI} on the counterion was less clear. We chose to investigate this question experimentally by an indirect approach rather than directly but less definitively by computation.

Ring inversion cannot be observed in **2**$^{2-}$/2M$^+$ without an additional prochiral or chiral reporter group. (The diastereotopic carbons in the dianion ring must be discounted because it is their mechanism of exchange that is under investigation.) However, the rate of BS in the neutral COT ring can be determined through the pairwise exchange of $C_{2'}$, $C_{3'}$, and $C_{4'}$ with $C_{8'}$, $C_{7'}$, and $C_{6'}$, respectively. Kinetic data for BS in **2** and **2**$^{2-}$/2M$^+$ (M = Li, Na, K) are given in Table 1.

Note that $\Delta G^{\ddagger}_{BS}$ decreases by only 0.3 kcal mol^{-1} at 280 K on going from **2**$^{2-}$/2K$^+$ to **2**$^{2-}$/2Li$^+$ (Table 1). Consequently, we expect little dependence of the rate of RI on the counterion. Since the TS for RI is less delocalized than that for BS, the former should be even less sensitive to π electronic effects and the small counterion effect observed for BS should apply for RI as well.

As seen in Table 2, *the rate of the new exchange process is strongly dependent on the counterion.* The value of $\Delta G^{\ddagger}_{exch}$ decreases from 12.6 kcal mol^{-1} at 230 K for the K$^+$ salt to <10 kcal mol^{-1} at 180 K for the Li$^+$ salt. This clearly establishes ring rotation as the dominant pathway for exchange, especially for the Na$^+$ and Li$^+$ salts.

A more quantitative dissection of this mechanism was achieved as follows. We were not able to measure k_{RI} in **2** directly due to insufficient differences in the chemical shifts of the two diastereomers. However, k_{BS} in **1** (18.2 s^{-1} at 280 K)[1] is identical within experimental error to k_{BS} in **2** (Table 1). This indicates that the COT ring has essentially identical steric environments in the two isomers.

The value of k_{RI} for *each* COT ring in **1** at 230 K (interpolated from data obtained over the range 226−242 K) is 1.2 s^{-1}.[1,15] This value provides a very good estimate of k_{RI} in **2**$^{2-}$/2M$^+$. Comparison with the value of k_{exch} for **2**$^{2-}$/2K$^+$ (5.05 s^{-1} at 230 K) (Table 5) indicates that *approximately 1/4 of the exchange occurs by COT ring inversion and 3/4 by COT*$^{2-}$ *ring rotation*. The mechanism of exchange changes on going to the Na$^+$ and Li$^+$ salts where it occurs solely or almost solely by ring rotation.

The ^1H and ^{13}C chemical shifts of alkali metal salts of COT dianions in THF have previously been interpreted in terms of the larger cations existing solely or predominantly as contact ion pairs.[9,10] In contrast, the chemical shifts of the Li$^+$ salts indicate a small but significant proportion of solvent-separated ion pairs and/or more highly solvated contact ion pairs. Strong evidence for increased solvation of COT^{2-} ion pairs in the order K < Na < Li is also seen in the UV−visible spectra of alkali metal salts of *p,p′*-dicyclooctatetraenylbiphenyl dianions in THF at 175 K.[16] The above rate constants can therefore be explained by the COT^{2-} ring being a better donor in the more strongly solvated Li$^+$ salts. That is, cation solvation facilitates ring rotation because it preferentially stabilizes the 0° rotational barrier by promoting greater π-electron delocalization.

Conclusions

The dianion ring carbons of **2**$^{2-}$/2K$^+$ ($C_{2''}$ and $C_{8''}$, $C_{3''}$ and $C_{7''}$, $C_{4''}$ and $C_{6''}$) are anisochronous on the ^{13}C NMR time scale at 230 K. This inequivalence is due to the pairs of carbons being diastereotopic as a result of both slow inversion of the chiral monosubstituted COT ring and slow rotation about the COT^{2-}−naphthalene bond, which is coincident with a prochiral axis. Thus, **2**$^{2-}$ is a rare example of a molecule with diastereotopic atoms that does not possess either a stereogenic or a prostereogenic[11] center.

^{13}C exchange in **2**$^{2-}$/2K$^+$ occurs with a rate constant of 5.05 s^{-1} at 230 K. Two lines of analysis indicate that exchange in this salt occurs by a mixed mechanism involving both rotation of COT^{2-} and inversion of COT. First, inversion of the sterically identical COT ring in **1** is $^1/_4$ as fast ($k_{RI} = 1.2$ s^{-1} at 230 K) as exchange in **2**$^{2-}$/2K$^+$. Second, changing the counterion from M = K to Li has almost no effect on $\Delta G^{\ddagger}_{BS}$ in **2**$^{2-}$/2M$^+$ but causes $\Delta G^{\ddagger}_{exch}$ to decrease by over 2 kcal mol^{-1}. This is consistent with the mechanism of exchange changing from rotation/inversion in **2**$^{2-}$/2K$^+$ to pure rotation in **2**$^{2-}$/2Li$^+$. This change is a reasonable consequence of a corresponding shift to looser ion pairs, which facilitate ring rotation through greater π delocalization from the dianion ring.

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(14) (a) Spellmeyer, D. C.; Houk, K, N. *J. Am. Chem. Soc.* **1988**, *110*, 3412. (b) Spellmeyer, D. C.; Houk, K. N.; Rondan, N. G.; Miller, R. D.; Franz, L.; Fickes, G. N. *J. Am. Chem. Soc.* **1989**, *111*, 5356.

(15) Since there are two COT rings in **1** the value of k_{RI} for **1** in ref 1 (reported on a *per molecule* basis) must be divided by 2 for comparison with **2**$^{2-}$/2K$^+$ on a *per ring* basis.

(16) Peterson, M. L., Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, 1999.

Experimental Section

General. Diethyl ether and tetrahydrofuran were distilled from sodium metal/benzophenone ketyl. TLC was performed on silica gel 60 F_{254} and preparative flash column chromatography was performed on 40 μM silica gel. NMR spectra were obtained at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. The variable-temperature unit was calibrated by the chemical shift difference of the ^{1}H peaks of methanol as a function of temperature according to the method of Van Geet.[17] The temperature accuracy is estimated to be ±1 °C. The free induction decay signals were sampled with 32K data points. After zero filling and Fourier transformation, the spectral resolution was typically in the range of 0.2−0.5 Hz/point. Italicized ^{13}C chemical shifts are those for $C_{2'}$-$C_{4'}$ and $C_{6'}$-$C_{8'}$, which undergo pairwise exchange during bond shift. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana.

Synthesis: **1-Cyclooctatetraenylnaphthalene** (**3**). To a solution of 1-bromonaphthalene (1.035 g, 5.00 mmol), $Pd_2(dba)_3$ (0.114 g, 0.125 mmol), and $AsPh_3$ (0.306 g, 1.00 mmol) in 25 mL of anhydrous THF at 50 °C under nitrogen was added Me_3SnCOT[4] (1.339 g, 5.00 mmol) in 5 mL of dry THF. After 24 h the reaction mixture was diluted with 50 mL of Et_2O and 50 mL of 50% saturated aqueous KF was added. The mixture was stirred for 15 min and filtered, and the organic layer was washed with 1 × 50 mL of 50% saturated aqueous KF, 2 × 50 mL of H_2O, and 1 × 50 mL of brine. The combined aqueous layers were extracted with 25 mL of Et_2O and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was dissolved in 200 mL of CH_2Cl_2/hexane and 4 g of SG was added. The solvent was then removed by rotary evaporation and the residue was chromatographed on 50 g of SG with 10% CH_2Cl_2/hexane to afford 772 mg (67%) of a yellow oil: ^{1}H NMR (THF-d_8, 25 °C) δ 8.30 (m, 1H), 7.80 (m, 1H), 7.74 (d, 1H, J = 8.4 Hz), 7.35−7.45 (m, 3H), 7.27 (dd, 1H, J = 1.2, 6.0 Hz), 5.7−6.2 (m, 5H).

1,5-Dicyclooctatetraenylnaphthalene (**2**). To a stirred solution of 1,5-diiodonaphthalene (0.946 g, 2.50 mmol), $Pd_2(dba)_3$ (0.114 g, 0.125 mmol), and $AsPh_3$ (0.306 g, 1.00 mmol) in 25 mL of anhydrous THF at 50 °C under nitrogen was added a solution of 1.339 g (5.00 mmol) of Me_3SnCOT[4] in 5 mL of dry THF. After 24 h 50 mL of Et_2O was added followed by 50 mL of 50% saturated aqueous KF. The reaction mixture was stirred for 15 min and filtered, and the organic layer was washed with 1 × 50 mL of 50% saturated aqueous KF, 2 × 50 mL of H_2O, and 1 × 50 mL of brine. The combined aqueous layers were extracted with 25 mL of Et_2O and the combined organic layers were dried ($MgSO_4$) and concentrated. The residue was dissolved in 200 mL of CH_2Cl_2/hexane and 4 g of SG was added. The solvent was then removed by rotary evaporation and the residue was chromatographed on 50 g of SG with 5% CH_2Cl_2/hexane to afford 285 mg (35%) of a light yellow solid: TLC (10% CH_2Cl_2/hexane) $R_f = 0.2$; mp 120.0−120.5 °C; IR 3558, 3480, 3400, 3072, 3043, 3008, 1642, 1504, 1370, 808, 764, 680, 620 cm^{-1}; UV λ_{max} (cyclohexane) = 300 nm (ϵ 12 500); ^{1}H NMR (THF-d_8, 25 °C) δ 8.28 (d, 2H, J = 8.7 Hz, H_4), 7.40 (dd, 2H, J = 8.7, 6.9 Hz, H_3), 7.27 (d, 2H, J = 6.9 Hz, H_2), 5.8−6.2 (br m, 14H); ^{13}C NMR (THF-d_8 , −15 °C) δ 144.4, 141.6, *135.9*, 133.9, *132.9*, *132.8*, *132.7*, *132.6*, 132.3 ($C_{5'}$ of COT), *131.9*, 126.5 ($C_{2,4}$), 126.0 (C_3). (HETCOR was employed to locate the overlapped signals at δ 126.5.) Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.68; H, 6.29.

Preparation of NMR Samples of Dianions. Samples of $\mathbf{2}^{2-}/2M^+$ and $\mathbf{3}^{2-}/2K^+$ were prepared directly in custom-lengthened Wilmad Ultra-Imperial 5 mm NMR tubes by reduction of **2** or **3** with an alkali metal. A small glass wool plug was inserted into the upper part of an NMR tube containing **2** or **3**, THF-d_8, and approximately 5 μL of cyclohexane. An excess of alkali metal was placed on top of the glass wool and the sample was degassed with 5 freeze−pump−thaw cycles and sealed under an atmosphere of argon. For the potassium and sodium samples, a mirror of metal was formed by freezing the solution in liquid nitrogen and heating the tube above the metal with a gentle flame. Agitation of the tube to bring the metal into contact with the heated glass produced a mirror. After cooling, reduction was initiated by inverting the tube to allow the solution to filter through the glass wool plug and come into contact with the mirror. In the case of the lithium samples, the solution was allowed to come into contact with cleaned pieces of lithium wire and reduction was initiated with sonication. The tube was inverted repeatedly until the proper reduction stage was reached, as judged from the ^{1}H NMR spectrum. NMR spectra of dianion samples stored in a freezer typically showed no decomposition over a period of several months.

Dipotassium Salt of 1-Cyclooctatetraenylnaphthalene ($\mathbf{3}^{2-}/2K^+$). ^{1}H NMR (THF-d_8, 25 °C) δ 8.64 (d, 1H, J = 8.4 Hz), 7.68 (d, 1H, J = 8.1 Hz), 7.51 (d, 1H, J = 6.9 Hz), 7.32 (d, 1H, J = 7.8 Hz), 7.2−7.1 (m, 3H), 6.13 (d, 1H, J = 11.4 Hz), 5.7−6.0 (m, 5H); ^{13}C NMR (THF-d_8 , −60 °C) δ 158.4, 135.4, 134.1, 131.8, 129.4, 127.8, 124.6, 124.1, 123.0, 120.5, 101.9, 95.3, 93.2, 91.8, 89.8.

Dipotassium Salt of 1,5-Dicyclooctatetraenylbenzene ($\mathbf{2}^{2-}/2K^+$). ^{1}H NMR (THF-d_8, 25 °C) δ 8.34 (d, 1H, J = 7.8 Hz, H_8), 7.60 (d, 1H, J = 8.4 Hz, H_4), 7.36 (d, 1H, J = 7.2 Hz, H_2), 6.96 (dd, 1H, J = 8.4, 7.2 Hz, H_3), 6.8−6.9 (m, 2H, H_6, H_7), 5.4−6.1 (m, 14H); ^{13}C NMR (THF-d_8, −40 °C) δ 159.4, 146.1, 140.0, *137.2*, *134.7*, 133.6, *133.8*, 133.1 ($C_{5'}$ of COT), *132.6*, *131.8*, *131.6*, 129.1, 124.9, 124.7, 122.2, 118.8, 103.3, 96.0, 94.3, 92.5, 89.0.

Disodium Salt of 1,5-Dicyclooctatetraenylbenzene ($\mathbf{2}^{2-}/2Na^+$). ^{1}H NMR (THF-d_8, 24 °C) δ 8.46 (d, 1H, J = 7.8 Hz, H_8), 7.85 (d, 1H, J = 8.4 Hz, H_4), 7.51 (d, 1H, J = 7.2 Hz, H_2), 7.23 (dd, 1H, J = 8.4, 7.2 Hz, H_3), 6.9−7.1 (m, 2H, H_6, H_7), 5.4−6.1 (m, 14H); ^{13}C NMR (THF-d_8, −5 °C) δ 158.5, 146.1, 140.1, *136.7*, *134.6*, 133.5, *133.2*, 133.1 ($C_{5'}$ of COT), *132.2*, *131.6*, *131.0*, 129.1, 124.2, 124.5, 122.2, 119.0, 99.5, 92.7, 89.5, 88.5, 86.2.

Dilithium Salt of 1,5-Dicyclooctatetraenylbenzene ($\mathbf{2}^{2-}/2Li^+$). ^{1}H NMR (THF-d_8, 25 °C) δ 8.34 (d, 1H, J = 7.8 Hz, H_8), 7.65 (d, 1H, J = 8.4 Hz, H_4), 7.33 (d, 1H, J = 6.9 Hz, H_2), 7.05 (dd, 1H, J = 8.4, 6.9 Hz, H_3), 6.8−6.9 (br s, 2H, H_6, H_7), 5.4−6.1 (m, 14H); ^{13}C NMR (THF-d_8, −20 °C) δ 159.1, 146.2, 140.1, *136.7*, *134.7*, 133.6, *133.2*, 133.1 ($C_{5'}$ of COT), *132.2*, *131.4*, *131.1*, 128.1, 124.7, 124.5, 122.0, 118.7, 103.2, 96.0, 89.5, 88.7, 86.0.

Kinetic Methods and Error Analysis. All kinetic studies were performed with duplicate samples and the results were averaged. Rate constants were calculated with the equation $k = \pi\Delta W_{exch}$, where ΔW_{exch} is the exchange broadening (in Hz) in the slow exchange region.[18] In each case the line width of $C_{5'}$ (for BS) or $C_{5''}$ (for the new exchange process) was employed as a reference. The protocol for determining W_{exch} has been given previously.[1] Free energies of activation were calculated from the rate constants by using the Eyring equation.[18]

The uncertainties in the rate constants were estimated from replicate measurements because differential error analysis yielded unreasonably small uncertainties in the rate constants. For the line width studies, the replicate measurements gave errors in the rate constants of ±15% for dianion samples, which propagate as ±0.1 kcal/mol in $\Delta G^{\ddagger}$. The maximum error in these measurements is most likely due to temperature uncertainties (estimated to be ±1 °C), although unknown chemical differences between ostensibly identical samples, magnetic field instabilities, and variations in spectrometer electronics may also contribute.

Computational Methods. Ab initio molecular orbital calculations and geometry optimizations were performed using the GAUSSIAN98W[19] series of programs at the HF/3-21G$^{(*)}$[20] level of theory. The eigenfollower routine was employed to determine the critical points given

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in Table 5. Fully optimized geometries of the ground states and COT ring inversion and bond rotation TSs were shown to have zero and one imaginary frequency, respectively, by analytical frequency analysis.

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Supporting Information Available: Rate constants and temperatures for bond shift in **2** and $\mathbf{2}^{2-}/2M^+$, M = Li, Na, and K (Tables S1−S4), and the corresponding van't Hoff plots (Figures S1−S4) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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