

# Intramolecular Electron Transfer and Cation Migration in the Dianion of Dicyclooctatetraenyldimethylsilane Studied by Dynamic $^{13}\text{C}$ NMR Spectroscopy

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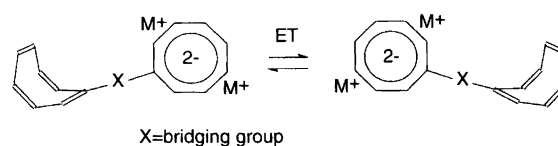
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The thermally activated two-electron and cation transfer from the charged to the neutral cyclooctatetraenyl ring in the title dianion ( $1^{2-}$ ) with alkali-metal cations in  $[\text{}^2\text{H}_8]$ tetrahydrofuran solutions has been studied by  $^{13}\text{C}$  NMR spin saturation transfer. The free energy of activation for this process at  $47^\circ\text{C}$  decreases in the order  $1^{2-}/\text{Na}^+ > \text{K}^+ > \text{Li}^+$ . This is explained by the existence of tight ion pair structures for the Na and K salts, while the Li system has a certain number of loose ion pairs coexisting with tight ion pairs. A stronger interaction between the dianion ring and  $\text{Na}^+$ , as compared with  $\text{K}^+$ , is supported by  $^{13}\text{C}$  NMR chemical shifts of the dianion ring. The activation barrier decreases further for the Li salt when the temperature is lowered, which is accounted for by a shift in the tight/loose ion pair equilibrium. However, the Li system is predominantly a tight ion pair at  $-3^\circ\text{C}$  or lower temperatures as shown by  $^7\text{Li}$  NMR chemical shifts, but it is concluded that the looser ion pairs undergo exchange considerably faster than the tight ion pairs. Rate constants have also been obtained for the bond shift in the neutral ring. The free enthalpy of activation for the bond shift decreases in the cation order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  and the polarization of the double bonds in the neutral ring increases in the same order as probed by  $^{13}\text{C}$  NMR chemical shifts. Concentration studies and  $^{13}\text{C}$  NMR  $T_1$  values of the Li and K salts show that the exchange of electrons and cations is intramolecular and that the aggregation state is the same for the Li and K salts of  $1^{2-}$ . The NMR chemical shifts and gross charges from HF/6–31G\*/3–21G(\*) *ab initio* MO calculations are in accord with a ground state structure that has the two extra charges localized at one of the cyclooctatetraenyl rings.

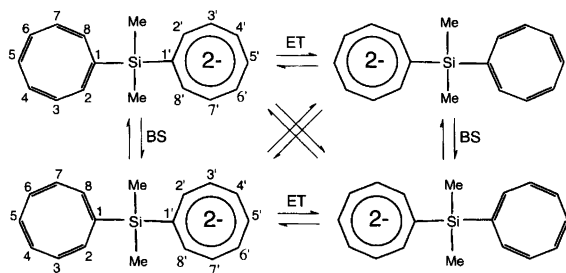
Mechanisms of electron transfer (ET) in condensed media are among some of the most actively pursued research topics in both fundamental and applied chemistry today.<sup>1</sup> A large fraction of the contemporary work on ET in solution deals with intramolecular charge shifts in organic systems where the electron moves without an associated cation. This ET process is generally photo-induced but several reports involve ET induced by pulse radiolysis. It is appropriate to say that these types of study have provided much insight into ET mechanisms during the last two decades. Considerably less work has been done on systems where the intramolecular ET occurs with an accompanying transfer of a counterion.<sup>2–6</sup> One reason is that such systems should be inferior for yielding information about the various factors that influence the rate and mechanism of ET, since the transport of the much heavier counterions should dominate the

energetics. Nevertheless, we believe that studies of suitable ion-pair systems can add to our knowledge about common ET issues, such as the effects of distance and number of bonds between the donor and the acceptor, the geometry and flexibility of the bridging group and of the electroactive parts, and properties of the medium. In addition to these factors, one may investigate to what extent the counterion can be utilized to control the rate and mechanism of ET. The dicyclooctatetraenyl (di-COT) dianions with cations of alkali metals constitute one type of such ion pairs (Scheme 1). In earlier studies of di-COT dianions it has been pointed out that this



Scheme 1.

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Scheme 2.

type of compound can undergo an unusually slow intramolecular two-electron transfer which may be investigated by  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectroscopy.<sup>7-10</sup> The main reason for the slow ET/cation transfer is the need for a conformational change of the neutral ring from a non-planar form in the ground state to a more planar conformation in the transition state for the ET. In the present study, we address the conformation and counterion effects on the thermal ET process in the dicyclooctatetraenyldimethylsilane dianion ( $1^{2-}$ , Scheme 2), with Li, Na and K counterions in  $[\text{}^2\text{H}_8]$ tetrahydrofuran solution.<sup>†</sup> Rate constants for the bond shift (BS) and the ET (Scheme 2) are obtained using dynamic  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  chemical shifts are interpreted in terms of charge distribution and ion pair structure of  $1^{2-}$ , and interactions between the neutral and the dianion ring.  $^{13}\text{C}$  NMR relaxation times ( $T_1$ ), nuclear Overhauser enhancements (NOE),  $^7\text{Li}$  and  $^{29}\text{Si}$  NMR chemical shifts are reported. Some natural atomic gross charges for optimized geometries from *ab initio* MO calculations with the 3-21G(\*) basis set are also given.

## Experimental

**Chemicals and preparation of dianion samples.**  $(\text{COT})_2\text{Si}(\text{Me})_2$  (**1**) was synthesized by reaction of  $(\text{COT})\text{Li}$  with dichlorodimethylsilane according to an earlier procedure.<sup>11</sup> The product was purified by liquid chromatography on silica gel before distillation at low pressure.  $^1\text{H}$  NMR (THF- $d_8$ ; 0.49 M; 27 °C):  $\delta$  6.04 (br s, 1 H), 5.92 (d, 1 H,  $J=11.4$  Hz), 5.85 (dd, 1 H,  $J=2.6, 11.0$  Hz), 5.77–5.63 (m, 4 H), 0.14 (s, 3 H, methyl). All the  $^1\text{H}$  NMR resonances appear at approximately 0.7 ppm higher field than earlier reported for **1**,<sup>11</sup> but our data are consistent with  $^1\text{H}$  NMR spectra of other monosubstituted cyclooctatetraene compounds, where the resonances generally are centered in the region of 5.7–6.0 ppm.  $^{13}\text{C}$  NMR (THF- $d_8$ ; 0.49 M; 27 °C):  $\delta$  147.31 (C-1), 141.37, 135.51, 133.92, 132.70, 132.17, 132.13, 129.97, –3.34 (methyl).  $^{29}\text{Si}$  NMR (THF; 0.1 M;

27 °C):  $\delta$  –11.00. MS (CI),  $m/z$  (% rel. int.): 265 (30,  $M+1$ ), 161 (100,  $M+1-\text{C}_8\text{H}_7$ ).

$[\text{}^2\text{H}_8]$ Tetrahydrofuran (THF- $d_8$ ) was purchased from Glaser AG Basel, and used without further purification. THF that was used for the bond-shift NMR analysis of **1** was refluxed over K metal and distilled prior to use.

The NMR samples of  $1^{2-}$  were prepared directly in the NMR tubes by reduction of **1** with the alkali metal. A small glasswool plug was inserted into the upper part of a lengthened 5 mm tube containing **1**, the solvent, and a small amount of cyclohexane for reference purposes. Typically 2.2–2.5 equiv. of alkali metal cut into pieces were then placed on top of the glasswool. All work was done under an argon atmosphere. The sample was degassed by at least three freeze–pump–thaw cycles and subsequently sealed off from the vacuum line. The reaction was initiated by turning the tube upside-down in a sonication bath. The course of the reduction was followed by  $^1\text{H}$  and sometimes also by  $^{13}\text{C}$  NMR spectroscopy. The upper part of the tube containing the glasswool and the metal was sealed off when the correct reduction stage was established. Because of the disproportionation of  $1^-$  to **1** and  $1^{2-}$  (see Results and Discussion) the reduction does not have to proceed until exactly 2 equiv. of alkali metal have been consumed. A reduction with slightly less than 2 equiv. of the metal gives signals from **1** in the dianion spectra but the same rate constants as more complete reactions. The same seems to be true for a small excess of alkali metal that gives  $1^{4-}$  together with  $1^{2-}$ . NMR spectra show no decomposition of the dianions even after one year of storage of these samples in a refrigerator.  $^1\text{H}$  NMR (K salt; THF- $d_8$ ; 0.40 M; –10 °C):  $\delta$  6.11 (d, 1 H,  $J=11.4$  Hz, H-8), 5.97 (d, 1 H,  $J=3$  Hz, H-2), 5.96–5.90 (m, 4 H, H-2', H-3', H-7', H-8'), 5.83 (d, 1 H, H-3), 5.82 (t, 1 H, H-5'), 5.7 (m, 3 H, H-6, H-4', H-6'), 5.59 (dd, 1 H, H-5), 5.57 (dd, 1 H, H-4), 5.37 (dd, 1 H,  $J=3.4, 11.3$ , H-7), 0.34 (s, 3 H, methyl), 0.32 (s, 3 H, methyl). The  $^{13}\text{C}$  NMR chemical shifts are given in Table 1. An attempt to generate a loose ion pair system of  $1^{2-}/\text{K}^+$  by the addition of Kryptofix<sup>®</sup> 222, purchased from Aldrich, to a cold THF solution of the salt under an argon atmosphere resulted in much precipitate and unidentifiable signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**General methods.** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were usually obtained on a Bruker AM 500 instrument, but many experiments were also done on a Bruker ACP 250 instrument. The  $^7\text{Li}$  and  $^{29}\text{Si}$  NMR spectra were obtained on the ACP 250. Bruker Aspect 3000 computers with DISNMR software was used. Cyclohexane was employed as an internal chemical shift standard with  $\delta$   $^1\text{H}$  1.43 and  $\delta$   $^{13}\text{C}$  27.70. External 1.0 M LiCl in  $\text{H}_2\text{O}$  and 0.25 M LiCl in THF were used as  $^7\text{Li}$  NMR references, while external neat TMS was used for the  $^{29}\text{Si}$  NMR, all with  $\delta=0$ . The digital resolution in the 1D spectra was generally around 0.2 Hz after zero filling. All experiments were done at least twice for a specific sample and most experiments were repeated with new samples until

<sup>†</sup> These studies have recently been extended to a collaborative project with Stuart Staley's group at Carnegie Mellon University, Pittsburgh, to elucidate many aspects on cation and electron transfer and orbital interactions for di-COT dianions with various rigid spacers between the COT rings.

Table 1.  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR chemical shifts,  $^{13}\text{C}$   $T_1$  values and NOE factors for Li, Na and K salts of  $(\text{COT})_2\text{Si}(\text{Me})_2$  dianion in THF- $d_6$ .

Atom	Li <sup>a</sup>			Na <sup>b</sup>		K <sup>c</sup>	
	$\delta$	$T_1/\text{s}$	$\eta/\eta_{\text{max}}$	$\delta$	$\delta$	$T_1/\text{s}$	$\eta/\eta_{\text{max}}$
C-1	155.72	9.5	0.46	156.00	156.34	14.8	0.43
C-2	137.25	1.36	0.76	136.75	136.39	1.54	0.77
C-3	135.26	1.62	0.95	135.32	135.43	1.50	0.83
C-4	130.84	1.18	1.05	130.75	130.59	1.13	0.74
C-5	131.70	1.29	0.97	131.69	131.75	1.41	0.96
C-6	133.13	1.13	1.00	133.04	132.92	1.21	0.81
C-7	126.92	1.53	0.87	126.78	126.57	1.42	0.83
C-8	138.95	1.29	0.72	138.91	139.22	1.45	0.75
C-1'	84.30	7.2	0.42	81.68	85.68	6.9	0.45
C-2',8'	93.48	0.70	0.75	91.40	94.82	0.64	0.80
C-3',7'	91.24	0.89	0.87	90.77	94.10	0.72	0.90
C-4',6'	86.05	0.68	0.76	86.34	90.06	0.61	0.74
C-5'	89.68	0.76	1.00	90.00	93.72	0.64	0.89
Methyl	0.41	2.7	0.94	0.35	0.53	2.6	0.96
Average	136.22			136.16	136.15		
C-1-C-8							
Average	89.44			88.59	92.17		
C-1'-C-8'							
Si	-6.43			-6.74	-6.95		
c-hexane <sup>d</sup>		20.0	0.6			19.2	0.64

<sup>a</sup> 24 °C, 0.43 M. <sup>b</sup> 27 °C, 0.55 M. <sup>c</sup> 24 °C, 0.52 M. <sup>d</sup> c-Hexane is used as an internal chemical shift reference.

reproducibility was obtained.  $^1\text{H}/^{13}\text{C}$  dual 5 mm probeheads were used on both instruments. The temperature was controlled with a Bruker B-VT 1000 unit and was measured with a methanol sample before or after each measurement.<sup>12</sup> A standard composite pulse sequence using low power was used for the  $^1\text{H}$  decoupling in the  $^{13}\text{C}$  experiments. The heating of the sample due to the decoupling was measured with the methanol sample and a pulse sequence that applied  $^1\text{H}$  decoupling for 5 min followed by a  $^1\text{H}$  measuring hard pulse. This heating was typically found to be 0.1 °C. With the assumption of a similar heating in the THF samples, we estimate a maximum error of  $\pm 1$  °C in the measured temperatures, and a relative error between different NMR experiments of maximum  $\pm 0.5$  °C. EPR spectra were obtained on the 5 mm NMR samples on a Bruker ESP 300E instrument at 25 °C. MO calculations were done on a Silicon Graphics Iris Indigo workstation using Spartan 3.1 software.<sup>13</sup> The mass spectrum was obtained on a Finnigan Incos 500 mass spectrometer using chemical ionization.

**NMR signal assignments.** Data from the dynamic NMR experiments and H-C chemical shift correlated 2D experiments gave fully consistent  $^1\text{H}$  and  $^{13}\text{C}$  peak assignments for the K salt of  $1^{2-}$ . The five  $^{13}\text{C}$  signals from the  $C_{2v}$ -symmetric charged ring appear in the region 84–95 ppm because of the high electron density at these carbons. The eight carbons in the neutral ring resonate in the region 126–157 ppm. The C-1 and C-5 peaks could be identified due to the absence of bond-shift exchange

broadening, and C-1 was easily assigned since it lacks directly bonded protons. Homodecoupling of C-1 and C-5 confirmed the assignments of C-1' and C-5'. The doublet at 6.11 with  $J=11.4$  Hz was assigned to H-8, and then the remaining  $^1\text{H}$  and  $^{13}\text{C}$  peaks were assigned by H-C correlated<sup>14</sup> and H-H-C relayed coherence transfer<sup>15,16</sup> 2D experiments. These were performed using the Bruker standard software, and delays were optimized for three-bond H-H coupling constants of 10 Hz and one-bond C-H couplings of 125 Hz. The  $^{13}\text{C}$  signals of the Li and Na salts of  $1^{2-}$  were assigned on the basis of the chemical shift similarities with the K salt.

**NMR  $T_1$  and NOE measurements.** The inversion-recovery method with 12–14 different  $\tau$  values and a  $5 \times T_1$  relaxation delay was used for the  $^{13}\text{C}$   $T_1$  measurements. When  $T_1$  was measured at temperatures that cause exchange, most  $\tau$  values were kept extra short (up to  $0.5 \times T_1$ ) and only 1–2 long ( $5 \times T_1$ )  $\tau$  values were used. This was required in order to avoid  $T_1$  values that are averaged to some extent because of the exchange.<sup>17</sup> The static NOE measurements were done with a pulse program that acquired FIDs with and without NOE in alternating scans to minimize effects from instabilities in instrument electronics. Delays of  $6 \times T_1$  and  $9 \times T_1$  were used for the NOE build-up and disappearance, respectively. The error in the  $T_1$  and NOE values is estimated to be 5%.

**$^{13}\text{C}$  NMR linewidth (LW) measurements and spin saturation transfer (SST) experiments.** The LWs were obtained using the Lorentzian line-fit routine in the DISNMR software. From spectra acquired at low temperature, where BS exchange broadening of the  $^{13}\text{C}$  peaks was absent, it was found that the LW of C-5 was very similar to those of the other proton-bearing carbons in the neutral ring in  $1^{2-}/\text{Li}^+/\text{Na}^+/\text{K}^+$  and in 1. At higher temperature, the LW of C-5 was therefore subtracted from the LWs of C-2 to C-4 and C-6 to C-8 to give the BS exchange broadenings. The BS rate constants were calculated from the average of the exchange broadenings of the six peaks. In the cases where a small difference was noticed between the LW of C-5 and the other carbons at temperatures without BS exchange, the exchange broadenings at higher temperature were corrected for this difference.

The desired power of the  $^{13}\text{C}$  homodecoupling output signal in the SST experiments was set with a Bruker BFX-5 amplifier. The DANTE technique was used for the selective excitation,<sup>18</sup> typically with 100  $\mu\text{s}$  square pulses and 150  $\mu\text{s}$  delays between these pulses. This sequence was looped for the required duration of the homodecoupling. In the experiment without homodecoupling, the DANTE pulsing was not switched off, but positioned at the other frequency side of the observed carbon, with the same offset as the difference between the two exchanging carbons. The  $T_1$  measurements in the SST experiments were done with the inversion-

recovery method. The homodecoupling was gated off during acquisition. All timing of pulses and delays in the experiments was controlled by the software. For  $1^{2-}/K^+$ , the SST measurements were performed on C-1 and C-1', since these carbons were the only ones that had long enough  $T_1$ s to show appreciable intensity changes due to the homodecoupling. For  $1^{2-}/Li^+$ , the SST experiments were undertaken with observation of the carbons C-1, C-5, C-1' and C-5'. For  $1^{2-}/Na^+$ , homodecoupling gave no intensity reductions of either C-1 or C-1' in the temperature region 38–48 °C. The maximum error in the free energies of activation (Table 2) is estimated from the combination of a 10% error in the rate constants obtained from LW measurements or a 20% error in the rate constants from the SST measurements, and a 1 °C temperature error.

## Results and discussion

**Structure of  $1^{2-}$  and dynamic NMR methods.** The number of  $^{13}C$  NMR peaks and the chemical shifts of  $1^{2-}$  (Table 1) are consistent with a structure where one ring resembles a neutral COT ring and the other ring carries the extra charges and attains a planar form with  $C_{2v}$  group symmetry. The average  $^{13}C$  chemical shift of the neutral ring in the  $1^{2-}$  salts (Table 1) is close to that of **1** in THF- $d_8$  at 27 °C (135.63 ppm). The dianion ring in the  $1^{2-}$  systems has an average  $^{13}C$  chemical shift similar to other COT-dianion rings such as the Li salt-THF adduct of 1,4-(SiMe<sub>3</sub>)<sub>2</sub>COT dianion in [2H<sub>6</sub>]benzene (91.8 ppm),<sup>19</sup> the Na salt of the COT-COT tetraanion in THF- $d_8$  at -53 °C (91.2 ppm)<sup>9</sup> and the COT-COT tetraanion K salt in ND<sub>3</sub> at -55 °C (93.1 ppm).<sup>20</sup> The  $^1H$  NMR data (see Experimental) are also as expected for a neutral and a dinegative COT ring. The anticipated high field shift for the dianion ring hydrogens upon reduction of **1** to  $1^{2-}$  is compensated for by the 'ring current' magnetic anisotropy deshielding due to the 10

$\pi$ -electron system. Geometry optimization with *ab initio* HF/3-21G(\*) MO calculations shows  $1^{2-}/Na^+$  to have a tub-shaped neutral ring and a planar dianion ring similar to what is well known for cyclooctatetraene and its dianion, respectively. Although the solvent coordination is clearly important for ion pair systems no attempts were made to include solvation in these calculations. The reason is that geometry optimizations including solvent molecules would be computationally too demanding even at the Hartree-Fock level with as relatively small a basis set as 3-21G(\*). The calculated ground state structure will therefore represent a very tight ion pair. Hence, the value of calculations such as these must not be overestimated, but comparisons between related structures should be informative. The natural atomic population analysis for  $1^{2-}/Na^+$ , using the larger 6-31G\* basis set with the 3-21G(\*) optimized geometry, reveals a difference in the gross charge between the planar ring and the folded ring ( $\Delta\rho$ ) of -1.84 for carbons + hydrogens, and a total  $\rho$  of +1.90 at the Na ions. HF/6-31G\*\*/3-21G(\*) calculations were also done on the COT-COT<sup>2-</sup>/Na<sup>+</sup> system, where  $\Delta\rho$  and  $\rho$  were found to be -1.85 and +1.95, respectively. Further, the same type of calculation on COT<sup>2-</sup>/Na<sup>+</sup> gave  $\rho$  of +1.95 at the Na ions. These results imply that the  $1^{2-}/Na^+$  ion pair has essentially a true dianionic character of one COT ring.

Both the C-1-Si-C-1' angle of 104.5° and the C-1-C-1' distance of 2.99 Å in  $1^{2-}/Na^+$  are similar to the values found for **1** with the same type of calculation, i.e., 109° and 3.04 Å, respectively. The Si  $\rho$  in  $1^{2-}/Na^+$  was found to be +2.03, which is even slightly more positive than the Si  $\rho$  of +1.99 in **1**. We conclude that the Si atom does not carry any of the negative charge in  $1^{2-}/Na^+$  in the ground state. This statement is not contradicted by the fact that the  $^{29}Si$  chemical shifts are very similar for the Li, Na and K salts (Table 1) and does not differ much from that of **1** (see Experimental). Still, ET most likely occurs through the Si bridge since the C-1-C-1'

**Table 2.** Activation parameters for bond shift (BS) and electron transfer (ET) in Li, Na and K salts of (COT)<sub>2</sub>Si(Me)<sub>2</sub> dianion ( $1^{2-}$ ) in THF- $d_8$ , and for BS in neutral (COT)<sub>2</sub>Si(Me)<sub>2</sub> (**1**) in THF.

Activation parameter <sup>a-c</sup>	T/°C	$1^{2-}$			
		<b>1</b>	Li	Na	K
$\Delta G^\ddagger$ BS	39	16.6 ± 0.1	16.1 ± 0.1	16.2 ± 0.1	16.0 ± 0.1
	-3		15.8 ± 0.1		
$\Delta H^\ddagger$ BS			13.9 ± 0.5	13.5 ± 0.5	11.8 ± 0.5
$\Delta S^\ddagger$ BS			-7.1 ± 2	-8.5 ± 2	-13.4 ± 2
$\Delta G^\ddagger$ ET	47		19.0 ± 0.2 <sup>d</sup>	> 22	21.2 ± 0.2
	-3		16.7 ± 0.2		
$\Delta\Delta G^{\ddagger e}$	47		2.8 ± 0.2 <sup>f</sup>	> 5.8	5.2 ± 0.2
	-3		0.9 ± 0.2		
$k^g$	47		8 × 10 <sup>10</sup>	< 7 × 10 <sup>8</sup>	2 × 10 <sup>9</sup>
	-3		1 × 10 <sup>12</sup>		

<sup>a</sup>  $\Delta G^\ddagger$  and  $\Delta H^\ddagger$  in kcal mol<sup>-1</sup>,  $\Delta S^\ddagger$  in cal mol<sup>-1</sup> K<sup>-1</sup>. <sup>b</sup> Experimental temperature regions in °C: **1**, 27-39;  $1^{2-}/Li$ : BS -3 to +42, ET -10 to +42;  $1^{2-}/Na$ : BS 27-49;  $1^{2-}/K$ : BS 22-47. <sup>c</sup> Concentrations in M: **1**, 0.4;  $1^{2-}/Li$ , 0.2-0.4;  $1^{2-}/Na$ , 0.55;  $1^{2-}/K$ , 0.4-0.5. <sup>d</sup> Extrapolated from values in the region 39-42 °C. <sup>e</sup> Difference between  $\Delta G^\ddagger$  BS and  $\Delta G^\ddagger$  ET. <sup>f</sup> Obtained with an extrapolated value for the BS barrier of 16.2 kcal mol<sup>-1</sup> at 47 °C. <sup>g</sup> Rate constant calculated from  $\Delta\Delta G^\ddagger$ , in s<sup>-1</sup>.

distance is large enough to make through-space interactions unlikely.

The BS rate constants ( $k_{BS}$ ) of **1** and  $1^{2-}/Li^+/Na^+/K^+$  were determined from the exchange broadening of the C-2 to C-4 and C-6 to C-8 NMR peaks according to eqn. (1),

$$k_{BS} = \pi \Delta v_{1/2}(ex) \quad (1)$$

where  $\Delta v_{1/2}(ex)$  is the exchange broadening obtained as described in the Experimental section. This relationship is valid in the slow exchange region, when the exchanging peaks are well separated from each other.<sup>21</sup> Lineshape analysis of the  $^1H$  NMR spectra can in principle also be used, but the complication due to signal overlap makes analysis of the  $^{13}C$  spectra preferable. The  $k_{BS}$  values from the linewidth analyses in this study were in the range  $5\text{--}100\text{ s}^{-1}$ , with the most reliable  $k$  values being in the region  $10\text{--}50\text{ s}^{-1}$ . The lower limit is set by the uncertainty in the estimate of small line-broadenings and the upper level by a low signal-to-noise of broad peaks. For  $1^{2-}/Li^+$ ,  $k_{BS}$  was also measured with SST experiments at one lower temperature in order to evaluate better the temperature dependence of  $k_{BS}$ . All ET rate constants ( $k_{ET}$ ) were obtained by SST experiments. Generally, the  $k_{BS}$  and  $k_{ET}$  from the SST measurements were in the range  $0.01\text{--}1\text{ s}^{-1}$ . The SST method is useful when the timescale for exchange is comparable to the longitudinal relaxation times of the carbons under study and extends the region of the rate constants to significantly lower values than can be obtained with lineshape methods.<sup>22,23</sup> In this type of experiment, carbon A in a two-site exchange is homodecoupled while a spectrum is recorded and the intensity ( $I_\infty$ ) of the carbon B signal is measured. Secondly, the same experiment is done without the homodecoupling. In practice, the irradiation is positioned in another part of the spectrum, and the intensity ( $I_0$ ) of B is measured. Finally, the apparent relaxation time ( $T_{1app}$ ) of B during homodecoupling of A is measured by an inversion-recovery experiment. The rate constant is then given by eqn. (2),

$$k = (I_0 - I_\infty) / (I_0 T_{1app}) \quad (2)$$

which allows for different  $T_1$  values of carbons A and B.<sup>23</sup>

The rate data were analyzed using the Eyring equation,

$$k = \kappa k_B T / h \exp(\Delta S^\ddagger / R) \exp(-\Delta H^\ddagger / RT) \\ = \kappa k_B T / h \exp(-\Delta G^\ddagger / RT) \quad (3)$$

where  $\kappa$  is the transmission coefficient, taken as  $\kappa = 1$ , and the other quantities have their usual meaning.

*Bond shift and polarization of the neutral COT ring in  $1^{2-}$ .* The structure of the transition state (TS) for the BS in COT systems has been debated for a considerable time, and is not yet settled. Earlier MO calculations on COT gave support for a planar TS structure with equalized bond lengths,<sup>24</sup> but other structures have also been suggested, such as a flattened saddle shape.<sup>25,26</sup> However, recent *ab initio* MO calculations, that used the 6-31G\*

basis set with complete active space configuration interaction, again showed the planar structure with  $D_{8h}$  symmetry to be the preferred one.<sup>27</sup> In view of this, the somewhat smaller value of  $\Delta G^\ddagger$  BS in the  $1^{2-}$  salts compared with **1** (Table 2) can be rationalized as a result of a slightly less folded neutral COT ring in the ground state of  $1^{2-}$ . As referred to earlier, the average  $\delta^{13}C$  for the neutral ring in the  $1^{2-}$  systems is similar to that of **1**. This argues against delocalization of the negative charge to the neutral ring, where an upfield shift compared with **1** would be expected. The  $\delta^{13}C$  region for the neutral ring in the  $1^{2-}$  salts is also larger than for **1** (Table 1 and Experimental). This can be explained by an interaction between the neutral ring and the charged one, where the latter causes a polarization of the bonds in the neutral ring. The polarization is evident in the double bonds C-7-C-8, C-3-C-4, and C-5-C-6, as probed by the  $^{13}C$  chemical shifts, i.e., C-3, C-6 and C-8 resonate at lower field than the other carbon in each particular double bond (Table 1). As expected for a polarization effect, the chemical shift difference for the carbon pairs in the double bonds is larger when the  $\pi$  bond is closer to the dianion ring. Also the C-1-C-2 bond in  $1^{2-}$  seems to be polarized, where the chemical shift difference is 18.5 ppm for the Li salt and 20 ppm for the K salt. Here, a comparison should be made with the corresponding bond in **1** since the quaternary carbon is involved. Although the C-1-C-2 chemical shift difference for **1** is not available because the signals other than C-1 were not assigned, it is clear from the chemical shift range (147.3–130.0 ppm) that this difference must be smaller in **1** than in the  $1^{2-}$  systems. The  $^{13}C$  chemical shifts also indicate that the polarization of the bonds in the neutral ring of  $1^{2-}$  increases in the order Li, Na, K, although the differences are small. This suggests that an increased interaction between the neutral and the charged ring follows the same order. The  $\Delta G^\ddagger$  BS (Table 2) does not vary significantly between the Li, Na and K salts of  $1^{2-}$ , but the  $\Delta H^\ddagger$  BS values become smaller in that order, which provides support for the idea of a stronger polarization and interaction between the rings with a larger cation in  $1^{2-}$ . The  $\Delta S^\ddagger$  BS values are negative as reported for BS in other COT systems<sup>9,28,29</sup> and seem to become more negative with an increasing size of the cation. This accounts for the similarity between the  $\Delta G^\ddagger$  BS values. Too much emphasis should however not be put on the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  BS values since the error limits are rather large and difficult to estimate.

*Electron transfer and ion pair structure.* As in our studies of the COT-COT dianion,<sup>8,9</sup> the  $\Delta G^\ddagger$  values of  $1^{2-}$  are larger for ET than for BS. This is explained by the requirement of a conformational change, similar to that involved in the BS, to take place together with other changes during the advance to the TS for ET, which is further discussed below. The ET barriers for the three salts differ considerably, ranging from  $16.6\text{ kcal mol}^{-1}$  for the Li system at  $-10^\circ\text{C}$  to such a high barrier for

the Na salt that made it inaccessible by SST experiments even at 49 °C. The lower limit of the ET barrier for the Na<sup>+</sup> case was estimated to be 22 kcal mol<sup>-1</sup>. For 1<sup>2-</sup>/K<sup>+</sup>, SST measurements were undertaken at several temperatures in the region 27–41 °C, but only the homodecoupling experiments at 46.9 °C gave significant intensity changes and thus reliable ET rate constants. The explanation for the variation in  $\Delta G^\ddagger$  ET is related to the structure of the ion pair. Typically, delocalized carbanions with alkali-metal counterions exist to a large extent (Li, Na) or exclusively (Na, K) as contact ion pairs (CIPs) in THF solution at room temperature.<sup>30–32</sup> The anion–cation interaction and the ratio between CIPs and solvent separated ion pairs (SSIPs) has been found to be even larger for dianion systems, including the COT dianion.<sup>32–34</sup> The higher ET barrier for 1<sup>2-</sup>/Na<sup>+</sup> compared with the K salt is best explained by a stronger Coulombic interaction between the dianion ring and the Na cation in the GS, which has to be overcome to the TS where the cations can no longer have the same sites close to the dianion ring as in the GS. The most likely GS structure has one of the cations positioned above the charged ring and the other one below it,<sup>19,32,35,36</sup> as also verified by our *ab initio* MO calculations. The TS may have one of several possible symmetric structures ranging from situations with both cations in close contact with the 1<sup>2-</sup> moiety to a case with negligible anion–cation interactions. However, a TS with some degree of ion pairing seems likely.

The smaller radius for Na<sup>+</sup> and thus a shorter distance to the dianion ring should be the reason why Na<sup>+</sup> interacts more strongly than K<sup>+</sup> with the ring. A change to a smaller cation has been found to give blue shifts of the long wavelength band in absorption studies of carbanions with alkali-metal cations under CIP conditions.<sup>30,31,33,37</sup> The explanation is a shortened anion–cation distance with a smaller cation, which results in a greater stabilization of the anion HOMO than of the first excited state. We believe that an increased interaction between a carbanion and a cation also may show up in the <sup>13</sup>C NMR chemical shifts in a somewhat related way. This would be through the average excitation energy term ( $\Delta E$ ) in the Karplus–Pople equation of paramagnetic shielding,<sup>38</sup> where a larger  $\Delta E$  and an NMR-signal shift to higher field results from a stabilization of occupied MOs relative to virtual orbitals. Although magnetic field induced  $\pi$ – $\pi^*$  transitions do not contribute,<sup>38</sup> many other orbitals are believed to be involved in the  $\Delta E$  term and therefore the stabilization due to a cationic field would indeed influence the  $\Delta E$ . The average NMR chemical shift for the carbons in the dianion ring of 1<sup>2-</sup>/Na<sup>+</sup> is 88.6 ppm while that of the K salt is 92.2 ppm (Table 2). This is in agreement with the reasoning above and a stronger interaction with 1<sup>2-</sup> and the Na ion.

The  $\Delta G^\ddagger$  ET of 1<sup>2-</sup>/Li<sup>+</sup> is not consistent with the same CIP structure as for Na<sup>+</sup> and K<sup>+</sup> since a stronger anion–cation interaction and a higher barrier than for the Na salt would then be expected, and since the average

$\delta^{13}\text{C}$  for the dianion ring has a value in between that of the Na and K salts. Instead, it seems likely that this system exists in a CIP–SSIP equilibrium or has more solvation of the CIP. A situation with one or both cations being more solvated in the GS should most likely facilitate the electron and cation transfer, i.e., result in a lower ET barrier. Studies of intermolecular ET between the anion radical and the neutral parent of unsaturated hydrocarbons have indeed shown faster rates for SSIPs than for CIPs.<sup>39,40</sup> The  $\Delta G^\ddagger$  ET vs. temperature plot for 1<sup>2-</sup>/Li<sup>+</sup> shows a weak curvature with a slightly larger slope, i.e., more negative  $\Delta S^\ddagger$ , at higher temperature (Fig. 1). This can be interpreted as an increased solvent coordination in the TS at higher temperature. Since carbanion systems generally undergo a shift of the ion pair equilibrium from SSIPs to CIPs at increased temperature because of a positive  $\Delta S$ ,<sup>30,31,41</sup> it occurs most likely also for 1<sup>2-</sup>/Li<sup>+</sup>. Hence, a larger CIP/SSIP ratio at higher temperature explains the need for increased solvent coordination to reach the TS. In other words, the curvature in the plot indicates that a change of the ion pair equilibrium is superimposed on the ET dynamics, i.e., a ‘loosening’ of the tight ion pair is part of the nuclear changes attendant on going to the TS for the electron and cation transfer process.

An important method for probing the degree of ion pairing for Li salts of carbanions with cyclic  $\pi$ -systems is <sup>7</sup>Li NMR spectroscopy, where a chemical shift at rather high field is found when the Li ion is located above an ‘aromatic’  $\pi$ -system which displays ‘ring current’ magnetic anisotropy in <sup>1</sup>H NMR.<sup>32,42</sup> In a <sup>1</sup>H and <sup>7</sup>Li NMR study of the COT dianion in THF, it was concluded that the Na and K salts exist as CIPs while Li gives a small fraction of SSIPs.<sup>32</sup> A  $\delta^{7}\text{Li}$  of –8.55 relative to external 1.0 M aqueous LiCl was found in THF. In diethyl ether, which usually gives only tight ion pair structures, the  $\delta^{7}\text{Li}$  was –10.07 and all three salts were found to exist as CIPs.<sup>32</sup> For 1<sup>2-</sup>/Li<sup>+</sup>, we found a  $\delta^{7}\text{Li}$  of –7.92 at 22 °C in accord with a high degree of a CIP structure. An attempt to reduce **1** with Li in diethyl ether-*d*<sub>10</sub> failed to give 1<sup>2-</sup>/Li<sup>+</sup>. To increase our understanding of the ion pair structure we obtained the <sup>7</sup>Li chemical shift in five-degree intervals from –10 to +42 °C. A linear relationship was found ( $r=0.999$ ), with  $\delta = -7.80$  and

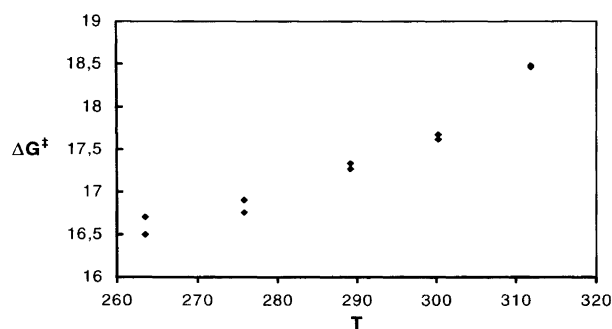


Fig. 1.  $\Delta G^\ddagger$  (kcal mol<sup>-1</sup>) vs. temperature (K) for electron transfer in 0.43 M 1<sup>2-</sup>/Li<sup>+</sup> in THF-*d*<sub>6</sub>.

−8.00 at −10 and +42 °C, respectively. This small but significant difference is in agreement with a slightly larger CIP/SSIP ratio at higher temperature. With external 0.25 M LiCl in THF as the reference instead of aqueous LiCl, the chemical shift was measured at −74, −20 and +42 °C and was found to be −7.05, −7.89 and −8.31 ppm, respectively. No  $^7\text{Li}$  NMR chemical shifts of SSIPs of  $\text{COT}^{2-}/\text{Li}^+$  or other COT dianions have been reported, but depending on the solvent, etc., one would expect values in the region of 0 to −2 ppm.<sup>42</sup> Thus, a CIP structure predominates for  $\text{I}^{2-}/\text{Li}^+$  in THF even at relatively low temperature. We also found that the average  $\delta^{13}\text{C}$  for the dianion ring of  $\text{I}^{2-}/\text{Li}^+$  was 89.89, 89.66 and 89.44 ppm at −47, −5 and +24 °C, respectively. This is in agreement with an increased  $\text{Li}^+$ –dianion interaction and a small shift towards a tighter ion pair when the temperature is increased.

To summarize the ion pairing, the average  $\delta^{13}\text{C}$  of the dianion ring for the three salts and the  $\delta^7\text{Li}$  of the Li salt indicate true CIPs with  $\text{Na}^+$  and  $\text{K}^+$ , while the Li cation seems to be slightly more solvated. We believe that  $\text{I}^{2-}/\text{Li}^+$  forms a CIP–looser IP equilibrium clearly in favor of the CIP structure. We hesitate to use the SSIP term in the equilibrium, since it indicates that both cations are in a SSIP state. A thermodynamically stable structure with one cation in a CIP state and the other in a SSIP state probably exists in equilibrium with a triple-ion CIP and a structure with both cations solvent-separated from the dianion.<sup>33</sup> As shown by the marked lowering of the ET barrier that comes from only a minor shift in the ion pair equilibrium of  $\text{I}^{2-}/\text{Li}^+$  when the temperature is changed from +47 to −3 °C, the looser ion pair undergoes ET and cation transfer much faster than the CIP does. The exact structure of the  $\text{I}^{2-}/\text{Li}^+$  looser IP cannot be resolved with the existing data.

Some factors that are of interest in this analysis of the BS, ET and cation transfer processes are: (i) possible combination of inter- and intra-molecular ET/cation transfer; (ii) aggregation of ion pairs and rotational-diffusional dynamics; (iii) disproportionation of the radical anion ( $\text{I}^-$ ) and effects on linewidths of small amounts of radicals in the solutions; (iv) degree of adiabaticity of the ET/cation transfer; (v) simultaneous or stepwise transfer of the two electrons. We have attempted to shed light on these issues through concentration studies, measurements of  $^{13}\text{C}$  NMR longitudinal relaxation times, EPR measurements, and by analysis of the present activation parameters. The results are summarized here: (i) since the same rate constants, to within experimental error, were obtained in repeated measurements on 0.20 M and 0.43 M samples of  $\text{I}^{2-}/\text{Li}^+$ , and on 0.40 M and 0.52 M samples of  $\text{I}^{2-}/\text{K}^+$ , the intramolecular exchange mode is likely to be the only pathway for the ET and cation transfer in the  $\text{I}^{2-}$  systems. (ii) The concentration studies also imply that the state of aggregation is unchanged in these concentration regions. Further information is provided by the  $^{13}\text{C}$   $T_1$  measurements. The  $T_1$  value for a certain carbon in the 0.43 M  $\text{I}^{2-}/\text{Li}^+$  sample is quite similar to that of the 0.52 M  $\text{I}^{2-}/\text{K}^+$

sample at 24 °C (Table 1), and does not give any precedence for differences in the rotational motions of the two compounds,<sup>43</sup> as would be expected with different aggregation states, e.g., a monomer as compared with a larger aggregate.<sup>44</sup> The basis for this is the well established proportionality between the inverse of the C–H dipole–dipole relaxation time ( $T_{1,\text{dd}}$ ) and the rotational diffusional correlation time ( $\tau_c$ ) of the molecular species [eqn. (4)].<sup>43</sup>

$$1/T_{1,\text{d-d}} \propto \tau_c \quad (4)$$

The NOE measurements show the proton-bearing carbons to have NOE factors ( $\eta$ ) that correspond to 70–100% of the maximum NOE (Table 1), which is equivalent to the portion of C–H dipole–dipole relaxation of the total  $^{13}\text{C}$  relaxation. The similarity between the  $\eta$  values justifies the  $T_1$  comparison between the Li and K samples. As expected for carbons that lack directly bonded hydrogens, the contribution from the dipole–dipole mechanism for C-1 and C-1' is less than 50 % of the total relaxation. It should also be noted that the  $T_1$  and NOE values for c-hexane are very similar in the two samples. This adds further confidence in the  $T_1$  comparisons. The long  $T_1$  for c-hexane shows that the radical content and the relaxation contribution due to the dipole–dipole interaction with unpaired electrons is low in the samples. The  $T_1$  and NOE data for the dianion systems are consistent with faster motion of the neutral ring compared with the charged ring, such as more rapid rotation of the neutral ring around the C-1–Si bond and an overall motion of  $\text{I}^{2-}$  where the center of gravity is in the dianion ring. Finally,  $^{13}\text{C}$   $T_1$  measurements for a 0.43 M  $\text{I}^{2-}/\text{Li}^+$  sample at different temperatures were made as an attempt to detect possible changes in the aggregation state. Here, eqn. (4) and the Stokes–Einstein equation,<sup>45,46</sup>

$$\tau = V_m \nu / k_B T \quad (5)$$

where  $\tau$  is a rotational diffusional time constant and  $V_m$  is the volume of the molecular complex,  $\nu$  is the viscosity,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature, provide a simple way to examine the dependence of  $T_1$  on  $T/\nu$ . The viscosities of our solutions were approximated to those of neat THF and calculated from the relationship  $\log \nu = -3.655 + 393/T$ , which is valid in the temperature range −70 to +25 °C.<sup>47</sup> The  $T_1$  values were obtained either as described in the Experimental section for all carbons, or from SST experiments on C-5 and C-5' using eqn. (6),<sup>23</sup>

$$T_1 = T_{1,\text{app}} (I_0/I_\infty) \quad (6)$$

where the factors have the same meaning as in eqn. (2). Approximately linear  $T_1$  vs.  $T/\nu$  dependences were found for all carbons using the three temperatures −48, −11 and +24 °C, and for C-5 and C-5' at seven temperatures in the region −11 to +39 °C. This suggests that a change in the aggregation state does not occur for 0.43 M  $\text{I}^{2-}/\text{Li}^+$  in the range −48 to +39 °C. (iii) In addition

to the long  $T_1$  values of *c*-hexane as an indication of the low content of radicals in the Li and K samples, EPR spectra were also obtained. Weak signals corresponding to the spectrum of the  $1^-$  radical were detected in the Li samples,<sup>11</sup> while no EPR signals could be found in the K samples. Attempts to quantify the radical content in the Li samples by integration was not meaningful owing to a low signal-to-noise ratio, but it was concluded that the concentration of  $1^-$  must be very low. Anion radicals that are associated with a cation generally show an exothermic dissociation to neutral and dianionic species.<sup>48</sup> For the COT radical anion, disproportionation equilibrium constants of  $1 \times 10^8$  and  $3 \times 10^8$  in THF at 22.5 °C have been reported for the Li and K salt, respectively.<sup>49</sup> Hence, because of the tight ion pairing of the  $1^{2-}$  species, an exceedingly low concentration of  $1^-$  is to be expected from the disproportionation of  $1^-$  to  $1$  and  $1^{2-}$ . In this context, we mention the occurrence of a differential  $^{13}\text{C}$  NMR line-broadening in the  $1^{2-}/\text{K}^+$  samples at and above room temperature, i.e., the C-2',4' and C-6', 8' signals were broader than other signals. This was found to have no effect on the SST measurements, and will therefore be dealt with subsequently. (iv) In an adiabatic ET reaction, there must be sufficient interaction between the donor and the acceptor in the TS region so that the reactant and product state energy surfaces avoid crossing. In our types of system, it is reasonable that the larger part of  $\Delta G^\ddagger$  ET should be due to a flattening of the neutral ring, and that this is a prerequisite for ET and cation transfer. The  $\Delta G^\ddagger$  BS for **1** is 0.5–0.6 kcal mol<sup>-1</sup> larger than the  $\Delta G^\ddagger$  BS for the Li and K salts of  $1^{2-}$ , and we infer that the interaction between the dianion and neutral ring, which causes the lower BS barrier in  $1^{2-}$ , also prevails in the TS for ET. It is not unreasonable that this interaction between the neutral and the charged ring of  $1^{2-}$  in the ground state is of the same magnitude as the interaction energy between the initial and final ET states. This hypothesis needs to be treated in more detail, but can justify the use of  $\kappa=1$  in the Eyring equation if it can be supported in forthcoming studies. (v) If sequential ET occurs in  $1^{2-}$ , one would expect the formation of a diradical species in accord with the knowledge that COT and substituted COT compounds generally form stable radicals by the uptake of one electron.<sup>11,34,49</sup> Since long-life diradical intermediates were indicated by radical-induced fast  $^{13}\text{C}$  NMR relaxation or EPR signals in the  $1^{2-}$  samples, we conclude that such diradicals have high energy if they exist. Even if a fully synchronous two-electron transfer is possible, we are not aware of any specific reason for this to occur. It seems likely that the ET takes place stepwise, with a fast transfer for the second electron, perhaps even on the timescale of a vibration ( $10^{-13}$  s). Some support for a sequential ET is found from the electrolytic reduction of COT, where two polarographic waves are found corresponding to the monoanion and the dianion, respectively.<sup>34</sup> Actually, it has been claimed that all thermal multielectron transfers are very likely to occur stepwise.<sup>50</sup>

*Intrinsic electron and cation transfer.* When the energy required for the unfolding of the neutral ring is estimated from  $\Delta G^\ddagger$  BS, the difference between  $\Delta G^\ddagger$  ET and  $\Delta G^\ddagger$  BS provides a measure of the barrier for the ET and cation migration ( $\Delta\Delta G^\ddagger$ , Table 2) without the conformational gating due to the neutral ring. In this model, we assume that the ET process involves a TS structure with approximately planar rings.  $\Delta\Delta G^\ddagger$  term may also contain energetics from geometrical changes that are necessary to reach the TS, such as twistings around the C-1-Si and C-1'-Si bonds and solvent rearrangements.  $\Delta\Delta G^\ddagger$  values for the Na and K salts of more than 5 kcal mol<sup>-1</sup> are likely to be dominated by the cation and electron transfer processes, but with low  $\Delta\Delta G^\ddagger$  values for the Li salt a contribution from solvent dynamics may become significant.<sup>51</sup> The rate constant that can be derived from the  $\Delta\Delta G^\ddagger$  with the Eyring equation and  $\kappa=1$  for  $1^{2-}/\text{K}^+$  is  $2 \times 10^9$  s<sup>-1</sup> at 47 °C (Table 2). This value is of the same magnitude as those reported for both intra- and intermolecular ET reactions involving transfer of a counterion.<sup>3,39</sup> The corresponding rate constants for the intrinsic electron and cation transfer in  $1^{2-}/\text{Li}^+$  approaches exceedingly high values, e.g.,  $1 \times 10^{12}$  s<sup>-1</sup> at -3 °C. This value is probably too high to be realistic but cannot be rejected at this stage. The use of  $\Delta\Delta G^\ddagger$  to probe the intrinsic electron and cation transfer and the orbital interactions through the spacer, will not be further evaluated here. However, we anticipate that our on-going studies will give more information on this subject.

To summarize, we have studied two-electron and cation transfer in  $1^{2-}$  with special emphasis on the Li, Na and K counterion effects. The ground state structure of  $1^{2-}$  has a planar dianion ring and a folded neutral ring. The transfer of charge is found to be an intramolecular process where the unfolding of the neutral ring is a gating step. The choice of cation is also important for the rate of ET and cation transfer, with the fastest rates found for  $\text{Li}^+$ . Since the NMR chemical shifts indicate tight ion pairs, the faster transfer with  $\text{Li}^+$  is explained by an equilibrium between tight and less tight ion pairs, with a predominance of the former, and considerably faster transfer for the looser ion pairs than for the tighter ion pairs. Also, it should be noted that the temperature-induced change of the ion pair structure for  $1^{2-}/\text{Li}^+$  make the evaluation of the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for ET/cation transfer impracticable.

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