

Bond shift and charge transfer dynamics in methylene- and dimethylsilyl-bridged dicyclooctatetraene dianions

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The rate constants for bond shift in dicyclooctatetraenylmethane (**1**), dicyclooctatetraenyldimethylsilane (**2**), and their dianions (**1**²⁻ and **2**²⁻) in [D₈]THF, have been determined from the temperature dependence of their ¹³C NMR linewidths. The corresponding parameters for intramolecular electron and cation transfer (charge transfer) between the dinegative and neutral rings have been measured by ¹³C NMR spin saturation transfer experiments for the dipotassium salts of **1** and **2**. Selected structural features of the neutral compounds and the dianions are discussed on the basis of ¹³C NMR chemical shifts and *ab initio* molecular orbital calculations at the HF/6-31G* and HF/3-21G(*) levels of theory. Energy contributions to the ring flattening in the bond shift process are calculated by molecular mechanics methods. The measured rate constants for both bond shift and charge transfer are larger for the methylene-bridged dianion. Approximately half of this difference is due to the greater ease of “gating” (*i.e.*, ring flattening and distortion to the bond shift transition state) in **1**²⁻–2K⁺. A significant portion of the remainder is attributed to a greater inter-ring through-space interaction in **1**²⁻, although mediation by the cation and/or through-bridge interactions probably also contribute to some extent. A temperature-dependent differential ¹³C NMR line broadening is observed for the dianion ring carbons of the dipotassium salts. Possible mechanisms for this counterion-specific line broadening, which occurs only for carbons with large HOMO coefficients, are discussed.

Introduction

The structural and dynamic properties of annulenes have received considerable attention during the past few decades, with [8]annulene [cyclooctatetraene (COT)] being one of the most studied compounds.^{1–3} Ring inversion (RI) and bond shift (BS) mechanisms (Fig. 1) are among the most investigated topics in COT chemistry.^{2–4} Intermolecular electron transfer (ET) between neutral and anionic COT compounds and related issues about electronic configuration and aromaticity have also been examined.^{3,5,6} Further, dianions of bridged diCOT systems have been utilized to investigate various aspects of intramolecular electron and counterion exchange [here denoted charge transfer (CT)] between the dianion and neutral rings,^{7–11} such as donor–acceptor distance, orientation of the rings, and electronic properties of the spacer. In addition, the influence of counterion and solvent on the rate constant for CT (*k*_{CT}) has been studied.^{8,11} Intramolecular two-electron–cation transfer in such species is relatively slow, with *k*_{CT} in the range of 10^{–2}–10² s^{–1} at ambient temperature, which is explained by the requirement for flattening the neutral ring. Rate constants have been obtained by ¹H and ¹³C dynamic NMR methods. In this study, we compare the BS kinetics for COT–CH₂–COT (**1**) and COT–Si(CH₃)₂–COT (**2**) and the BS and intramolecular CT kinetics for the corresponding dipotassium salts **1**²⁻–2K⁺ and **2**²⁻–2K⁺ (Fig. 2). The CT process is discussed on the basis of calculated structures, spacer-induced electronic perturbations of the COT rings, and spacer- and cation-mediated interactions between donor and acceptor moieties. An unusual selective differential

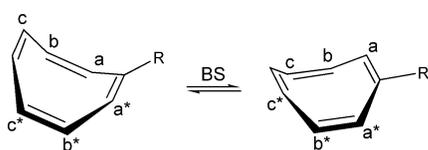


Fig. 1 Bond shift in a monosubstituted COT. Atoms a–c undergo mutual exchange with a*–c*, respectively.

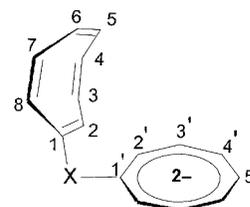
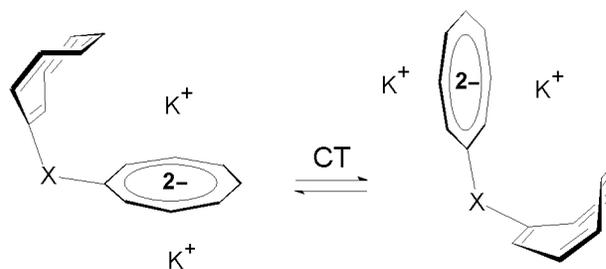


Fig. 2 Numbering of ring carbons in **1**²⁻ (X = CH₂) and **2**²⁻ (X = Si(CH₃)₂).

broadening of ¹³C NMR peaks of the carbons of the dianion ring of the dipotassium salts of **1**²⁻, **2**²⁻, CH₃COT²⁻ (**3**²⁻–2K⁺) and (CH₃)₃SiCOT²⁻ (**4**²⁻–2K⁺) is also reported and discussed.



Experimental

Chemicals and preparation of dianion samples

Compounds **1**,¹² **2**,¹² **3**¹³ and **4**¹⁴ were prepared according to literature procedures. Compound **1** was synthesised by coupling between COTMgBr and COTCH₂Br in tetrahydrofuran (THF) using Li₂CuCl₄ as a catalyst. ¹H NMR ([D₈]THF, 0.5 M, +25 °C): δ 5.71 (br m, 12H), 5.57 (H-2, s, 2H), 2.74 (CH₂, s, 2H). ¹³C NMR ([D₈]THF, 0.5 M, +6 °C): δ 142.24 (C-1), 134.79 (C-8), 132.88, 132.78, 132.56 (C-5), 131.80, 131.71, 129.17 (C-2), 46.95 (CH₂).

The synthesis of **2** was accomplished by reaction of COTLi with dichlorodimethylsilane in diethyl ether. ^1H NMR ($[\text{C}_6\text{H}_6]\text{THF}$, 0.49 M, 27 °C): δ 6.04 (H-2, br s, 2H), 5.92 (d, 2H, $J = 11.4$ Hz), 5.85 (dd, 2H, $J = 2.6, 11.0$ Hz), 5.77–5.63 (m, 8H), 0.14 (methyl, s, 6H).⁸ ^{13}C NMR ($[\text{C}_6\text{H}_6]\text{THF}$, 0.49 M, 27 °C): δ 147.31 (C-1), 141.37 (C-2), 135.51 (C-8), 133.92, 132.70, 132.17, 132.13 (C-5), 129.97, –3.34 (CH_3).⁸

Tetrahydrofuran- d_8 ($[\text{C}_6\text{H}_6]\text{THF}$) was purchased from Glaser AG Basel and used without further purification. THF employed for the NMR analysis of bond shift in **2** was refluxed over K metal and distilled prior to use. Dianions were prepared directly in the NMR tubes by reduction of the neutral compound with potassium metal. The samples were degassed and sealed according to standard vacuum techniques. Details of this procedure are given elsewhere.^{8,9}

The progress of reduction was followed by ^1H NMR and (in some cases) by ^{13}C NMR spectroscopy. Because of extensive disproportionation of the radical anion to the neutral compound and dianion,⁵ reduction does not have to proceed until exactly two equiv. of alkali metal have been consumed and was generally stopped after the reaction of approximately 1.9–2.0 equiv. of metal. Reduction with slightly less than two equiv. of the metal gave NMR signals for the neutral species together with those for the dianion, but the BS and CT rate constants were the same as for more reduced samples. The rate constants were also unaffected by a small excess of K metal (*ca.* 2.05–2.1 equiv.), which gave tetraanion together with dianion.

The possibility of a small line-broadening contribution caused by free radicals to the line broadening due to BS cannot be excluded for certain samples. However, when such a contribution originates from electron–nucleus dipole–dipole coupling (modulated by translation and diffusion) it should largely be compensated for by using NMR lines from other carbons in the dianion or from internal cyclohexane as linewidth references (*vide infra*), *i.e.*, we assume that different resonances are broadened to the same extent by radicals. When NMR lines showed differential broadening (*vide infra*), probably due to electron exchange with radicals, CT rate constants were obtained from magnetisation transfer experiments rather than from linewidth measurements. It has been shown earlier that added radicals (a relaxation reagent) have no effect on the rate constant obtained by magnetisation transfer.¹⁰ The samples of $1^{2-}-2\text{K}^+$ had limited thermal stability at ambient temperature and were investigated within 1–2 days, while samples of $1^{2-}-2\text{Na}^+$ were not sufficiently stable for dynamic NMR studies. Samples of $2^{2-}-2\text{Na}^+$ and $2^{2-}-2\text{K}^+$ were much more stable.⁸

General methods

^1H and ^{13}C NMR spectra were recorded with Bruker AC-P 250, Bruker AMX2-500 and General Electric GN-300 instruments. Cyclohexane was used as an internal chemical shift standard (δ ^1H 1.43 and δ ^{13}C 27.70). The digital resolution in the 1D spectra was generally about 0.2 Hz after zero filling. $^1\text{H}/^{13}\text{C}$ dual 5 mm probeheads were used on all of the instruments. The temperature for the Bruker instruments was controlled with a Bruker BVT 1000 or a BVT 2000 temperature unit and was measured with a methanol sample before or after each experiment.¹⁵ As reported earlier,⁸ heating due to ^{13}C homodecoupling was assumed to be negligible and a maximum error of ± 1 °C was estimated in the measured temperatures. All experiments were performed at least twice on each sample. Molecular orbital (MO) calculations were performed with Spartan 5.1¹⁶ and Gaussian 94W¹⁷ software using the 3-21G(*)¹⁸ or 6-31G*¹⁹ basis sets. Energy minima and transition states were confirmed by analytical frequency analysis. Several of the HF/3-21G(*) calculations were performed using both software packages with identical results. Molecular mechanics calculations were performed with Spartan 5.1¹⁶ (MMFF94 force field)²⁰ and Chem3D Pro 5.0²¹ (MM2 force field).²²

NMR signal assignment

At room temperature **1** and **2** show ^1H NMR signals from the COT-ring hydrogens in the region of δ 5.5–6.1 and eight ^{13}C NMR resonances in the region of δ 129–147 (Table 1). The H-2 resonances for the two compounds were easily assigned since these appear as singlets (J_{23} is small). The C-2 and C-8 signals were assigned on the basis of coupling to H-2 and saturation transfer from C-2, respectively. The C-1 and C-5 assignments followed from their narrow linewidths during BS broadening of the other peaks of the neutral ring and from longer T_1 and smaller NOE values for C-1.⁸

Assignment of the ^{13}C signals of $1^{2-}-2\text{K}^+$ and $2^{2-}-2\text{K}^+$ was achieved by ^{13}C homodecoupling (see SST experiments below), 2D H–C correlation²³ and relayed H–H–C coherence transfer spectroscopy.^{24,25} Pulse delays were optimised for $^1J_{\text{CH}} = 125$ Hz and $^3J_{\text{HH}} = 10$ Hz. The ^{13}C signals of $1^{2-}-2\text{Na}^+$ and $2^{2-}-2\text{Na}^+$ were assigned on the basis of the chemical shift similarities with the corresponding K salts,⁸ while the signals for $3^{2-}-2\text{K}^+$, $4^{2-}-2\text{K}^+$ and $4^{2-}-2\text{Cs}^+$ were assigned by analogy with those for $1^{2-}-2\text{K}^+$ and $2^{2-}-2\text{K}^+$.

^{13}C NMR linewidth (LW) measurements and spin saturation transfer (SST) experiments

The complexity of the ^1H NMR spectra resulting from overlapping signals made ^{13}C NMR preferable for the exchange analyses. The LWs were obtained using the Lorentzian line-fit routines in the standard Bruker UXNMR and GE software. Rate constants for BS and CT were determined from the exchange broadening of the ^{13}C NMR peaks and from spin saturation transfer data,²⁶ respectively. The former method uses the equation $k = \pi\Delta\nu_{1/2}^{\text{exch}}$, where $\Delta\nu_{1/2}^{\text{exch}}$ is the exchange broadening obtained as described below. The SST method uses $k = (I_0 - I_\infty)/(I_0 T_{1\text{app}})$, where $T_{1\text{app}}$ is the apparent relaxation time of one of the exchanging carbons with homodecoupling of the other carbon, and I_∞ and I_0 are the intensities of the signal for the observed carbon with and without homodecoupling of the carbon with which it exchanges, respectively.^{27,28}

Typically, the rate constant for BS is obtained by subtracting from the LW of the specific peak its LW at a lower temperature where exchange is absent, and by correcting for effects due to changes of solvent viscosity and magnetic field homogeneity by using the LW of internal cyclohexane. The natural LWs of C-5 and the other proton-bearing carbons could not be determined at temperatures with slow BS for **1** and **2** because of broadening due to ring inversion (RI). However, similar natural LWs of **1** and **2** and the neutral rings of their dianions were assumed, and values of k_{BS} for **1** and **2** were derived after correction for RI broadenings.²⁹

For 1^{2-} and 2^{2-} it was found from spectra acquired at low temperature, where BS exchange broadening of the ^{13}C peaks was absent, that the natural LW of C-5 (for which the magnetic environment is not changed by BS) was very similar to those of the other proton-bearing carbons in the neutral ring of 1^{2-} and 2^{2-} . Therefore, the LW of C-5 at higher temperatures was subtracted from the LWs of C-2, C-3, C-4, C-6, C-7 and C-8 to give the broadenings due to BS exchange. The BS rate constants were calculated from the average of the exchange broadening of at least five of the six signals.

In the spin saturation transfer (SST) experiments, the power of the ^{13}C homodecoupling output signal was set with a Bruker AMX2-500 linear amplifier or a Bruker BFX-5 amplifier connected to the AC-P 250 instrument. The saturation sequence was looped for the required duration of the homodecoupling. In the experiment without homodecoupling the pulsing was not switched off, but its frequency was changed to the opposite side of the observed carbon, with the offset being the same as the difference between the two exchanging carbons. The T_1 measurements in the SST experiments were performed with the inversion–recovery method with the homodecoupling gated off

Table 1 ^{13}C NMR chemical shifts for the Na and K salts of 1^{2-} – 4^{2-} in $[\text{D}_8]\text{THF}$ ^a

Carbon	1^{2-} – 2Na^+ ^b	1^{2-} – 2K^+ ^c	2^{2-} – 2Na^+ ^d	2^{2-} – 2K^+ ^e	3^{2-} – 2K^+ ^f	4^{2-} – 2K^+ ^g
C-1	150.63	150.40	156.00	156.34		
C-2	122.08	122.27	136.75	136.39		
C-3	134.60	134.69	135.32	135.43		
C-4	130.34	130.25	130.75	130.59		
C-5	132.06	132.40	131.69	131.75		
C-6	132.85	132.59	133.04	132.92		
C-7	128.27	128.46	126.78	126.57		
C-8	137.07	137.73	138.91	139.22		
C-1'	91.90	95.99	81.68	85.68	92.68	89.16
C-2',8'	89.47	92.81	91.40	94.82	92.06	93.16
C-3',7'	86.60	90.19	90.77	94.10	89.07	93.63
C-4',6'	87.35	91.10	86.34	90.06	91.20	90.07
C-5'	86.43	90.32	90.00	93.72	89.50	94.13
Average						
C-1–C-8	133.49	133.60	136.16	136.15		
Average						
C-1'–C-8'	88.15	91.81	88.59	92.17	90.86	92.13

^a In ppm, using cyclohexane ($\delta = 27.7$) as internal reference. ^b -5 °C, 0.30 M. ^c 5 °C, 0.53 M. ^d 27 °C, 0.55 M. ^e 24 °C, 0.52 M. ^f 6 °C, 0.59 M. ^g 20 °C, 0.40 M.

during acquisition. For 2^{2-} – 2K^+ , the SST measurements were performed on C-1 and C-1', since these carbons were the only ones with long enough T_1 s to show appreciable intensity changes due to homodecoupling and exchange.

For 1^{2-} – 2K^+ , the SST experiments were undertaken with observation of C-5, C-2' and C-8'. Signals from C-1' and C-5' were not used because of a reduced signal-to-noise ratio due to broadening (see Results and discussion, Differential line broadening section) at temperatures where CT became measurable. Further details are given in previous work.^{8–10} Note that CT is an *intramolecular* process since k_{CT} does not change with a change in concentration.^{8,9,11} The ΔG^\ddagger values were derived from the Eyring equation $k = \kappa k_{\text{B}} T/h \exp(-\Delta G^\ddagger/RT)$, where the transmission coefficient κ is taken as unity and the other quantities have their usual meanings.

Results and discussion

We first consider structural characteristics from MO calculations and ^{13}C NMR chemical shifts, and then discuss BS dynamics for the neutral compounds and the dianions. Together, these form the basis for the analysis and understanding of intramolecular CT in the dianions. Finally, we conclude with a discussion of differential line broadening in the ^{13}C NMR spectra and its possible origin in intermolecular electron exchange with paramagnetic species.

Structure and ion pairing of dianions

Earlier work has demonstrated that alkali metal salts of bridged dicyclooctatetraene dianions attain a structure with a neutral tub-shaped ring and a charged planar ring,^{7–11} with the cations above and below the dianion ring in a tight ion pair.³⁰ A tight or contact ion-pair (CIP) structure in $[\text{D}_8]\text{THF}$ appears to be a general feature for dianions of conjugated hydrocarbons with alkali metal cations in THF.^{31,32} The number of ^{13}C peaks for 1^{2-} and 2^{2-} and their chemical shifts are consistent with a structure having a neutral COT ring and a dianion ring with local C_{2v} symmetry (Table 1).

Five ^{13}C peaks from the charged ring are observed at all temperatures. In 1^{2-} and 2^{2-} , the average ^{13}C chemical shift of the neutral ring carbons is almost the same as in the corre-

sponding neutral compound (133.60 for 1^{2-} – 2K^+ and 133.50 for **1**; 136.15 for 2^{2-} – 2K^+ and 135.63 for **2**). The average signal for the carbons in the charged ring (91.81 for 1^{2-} – 2K^+ and 92.17 for 2^{2-} – 2K^+) is about 40 ppm upfield from that of the average for the neutral ring. This is similar to other substituted COT dianions such as the K salts in THF of $\text{CH}_3\text{COT}^{2-}$ (δ 90.86)³³ and $(\text{CH}_3)_3\text{SiCOT}^{2-}$ at 20 °C (δ 92.13),³³ and the Li salt–THF adduct of 1,4- $[(\text{CH}_3)_3\text{Si}]\text{COT}^{2-}$ in $[\text{D}_6]\text{benzene}$ (δ 91.8). These values are in accord with the description of one ring in 1^{2-} and 2^{2-} being a dianion ring, in conformity with correlations between ^{13}C chemical shifts and π -charge.^{35–37}

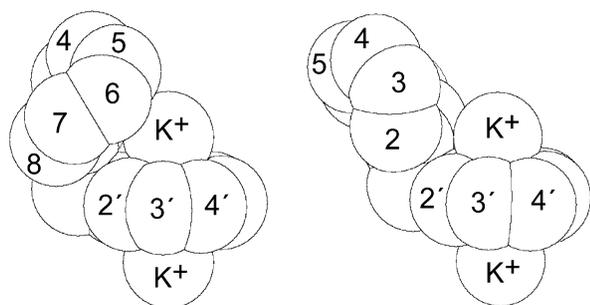
Some information about the ion-pair structure may be gained from a qualitative relationship between the strength of the cation–anion interaction and the average ^{13}C chemical shift for the carbons in the dianion ring.^{8,10,11} In this simple model, a stronger interaction with the cation is assumed to involve some stabilization of the highest occupied MOs of the anion while the levels of the virtual MOs should be less affected by the interaction. As a result, the average excitation energy of magnetic field-induced mixing of certain filled and virtual MOs will become larger and the paramagnetic moment will decrease according to the Karplus–Pople equation for the paramagnetic contribution to the nuclear shielding.³⁸ The effect of a stronger anion–cation interaction is therefore to cause *upfield* shifts of the relevant ^{13}C resonances.

The average ^{13}C chemical shift for C-1'–C-8' changes from δ 91.81 for 1^{2-} – 2K^+ to 88.15 for 1^{2-} – 2Na^+ (Table 1) and from δ 92.17 for 2^{2-} – 2K^+ to 88.59 for 2^{2-} – 2Na^+ ,⁸ which is consistent with a stronger interaction when Na^+ , instead of K^+ , is the counterion. However, note that this should not be interpreted as an indication of differences in the type of ion pairing between the Na^+ and K^+ salts of 1^{2-} and 2^{2-} , since Na^+ is expected to interact more strongly than K^+ with the dianion because of its smaller size. The upfield shift being the same for 1^{2-} and 2^{2-} (3.6 ppm) on going from Na^+ to K^+ is a clear indication of a very similar degree of ion-pair tightness for the two dianions when paired with a specific cation. In contrast, the earlier reported average ^{13}C chemical shift for 2^{2-} – 2Li^+ of δ 89.44 at 24 °C is consistent with a weaker cation–anion interaction and either a more solvated cation in a CIP or the presence of solvent-separated ion pairs owing to the downfield

Table 2 Activation parameters for bond shift and charge transfer in **1**, **2**, $1^{2-}-2K^+$ and $2^{2-}-2K^+$ in $[^2H_8]THF$ at 22 °C

Parameter ^a	1	2	$1^{2-}-2K^+$	$2^{2-}-2K^+$
k_{BS}	29 ^b (41 at 25 °C) ^c	2.3 ^d (8.3 at 33 °C)	249 ^e (57 at -3 °C)	13 ^f (14 at 23 °C)
ΔG_{BS}^\ddagger	15.3 ± 0.1	16.8 ± 0.1	14.0 ± 0.1	15.8 ± 0.1
$\Delta\Delta G_{BS}^\ddagger$ ^g			-1.3 ± 0.2	-1.0 ± 0.2
k_{CT}			1.8	3.7×10^{-3} ^h (4.6×10^{-3} at 27 °C)
ΔG_{CT}^\ddagger			16.9 ± 0.1	20.6 ± 0.1
$\Delta\Delta G_{CT}^\ddagger$ (intrinsic) ⁱ			2.9 ± 0.2	4.8 ± 0.2

^a k in s^{-1} ; ΔG^\ddagger in $kcal\ mol^{-1}$. ^b Intrapolated value for the region of -1 to 25 °C. ^c Representative k values obtained at a specific temperature are given in parentheses. ^d Extrapolated from the region of 30 to 39 °C. ^e Extrapolated from the region of -27 to -3 °C. ^f Extrapolated from the region of 23 to 48 °C. ^g ΔG_{BS}^\ddagger (dianion) - ΔG_{BS}^\ddagger (neutral). ^h Extrapolated from the region of 27 to 47 °C. ⁱ ΔG_{CT}^\ddagger (dianion) - ΔG_{BS}^\ddagger (dianion).

**Fig. 3** Space-filling models of *syn*- (left) and *anti*- $1^{2-}-2K^+$ (right). Hydrogens are omitted for clarity.

shift relative to $2^{2-}-2Na^+$.⁸ Similar results have been reported for the dianion of COT-COT.¹¹

HF/3-21G(*) structure optimisations of $1^{2-}-2K^+$ and $2^{2-}-2K^+$ locate the cations above and below the planar dianion ring. These structures are to be regarded as models for CIPs. Both $1^{2-}-2K^+$ and $2^{2-}-2K^+$ have energy minima for structures with a *syn* and an *anti* orientation of the neutral ring (Fig. 3). The *syn* conformers of $1^{2-}-2K^+$ and $2^{2-}-2K^+$ are more stable than the corresponding *anti* conformers by 3.8 and 4.2 $kcal\ mol^{-1}$, respectively. One of the cations is located between the rings (in the *endo* position), and appears to fit precisely into the cavity of the *syn* structure, as judged by computer-generated space-filling models [Fig. 3, where the C and (four-coordinate) K^+ radii are 1.7³⁹ and 1.65 Å,⁴⁰ respectively].

The center-to-center distances from the *endo* K^+ to C-5 and C-6 (in the neutral ring) in $1^{2-}-2K^+$ are 3.33 and 3.41 Å, respectively. The corresponding distances for $2^{2-}-2K^+$ are 3.27 and 3.49 Å, respectively. Since the p orbitals on C-1, C-2, C-5 and C-6 are directed towards the *endo* K^+ , an interaction between this cation and both the C-1-C-2 and C-5-C-6 π -bonds is a reasonable explanation for the *syn* preference. The C-1-C-1' distances in the CIPs of $1^{2-}-2K^+$ and $2^{2-}-2K^+$ are the same, within 0.04 Å, as those in the corresponding neutral compounds optimised at HF/6-31G*,²⁹ i.e., 2.55, 2.52, 3.08 and 3.04 Å for **1**, $1^{2-}-2K^+$, **2** and $2^{2-}-2K^+$, respectively.

Bond shift

The kinetic data and activation parameters for **1**, **2** and their dipotassium salts are given in Table 2. (The disodium salt of 1^{2-} was not stable enough for kinetic studies.) Note that the BS barriers are lower in the dianions than in the corresponding neutral compounds (see $\Delta\Delta G_{BS}^\ddagger$ values in Table 2). The dianion rings in $1^{2-}-2K^+$ and $2^{2-}-2K^+$ are clearly enhancing the rate of bond shift in the neutral rings.

The mechanism for bond shift can be broken down into two steps: 1) ring flattening and 2) equalisation of the CC bond lengths (π -bond delocalisation) in the neutral COT ring. The first step corresponds to reaching the RI transition structure (TS) and is discussed in this section. Possible mechanisms by

which the dianion ring might influence the second step are discussed in the section after next.

The TS for RI of COT compounds is generally described as having a planar ring with localised π -bonds.^{2,3,41,42} The TS in the BS process in COT is more controversial. Previous workers have proposed a planar delocalised structure,^{4,43} a flattened bond-equalised, saddle-shaped structure,^{2,44} and a crown geometry.⁴⁵ However, recent *ab initio* MO calculations at the CASSCF//HF/6-31G* level⁴⁶ and a photoelectron spectroscopy study⁴⁷ provide strong support for a planar TS with D_{8h} symmetry. Such a TS (with a symmetry plane through C-1 and C-5 perpendicular to the ring plane) is not necessarily valid for substituted COTs but is assumed for BS in this study.

The major contributions to the energy for ring flattening of methyl-substituted COTs have been a source of controversy. Ganis *et al.* determined the free energy of activation for bond shift (ΔG_{BS}^\ddagger) in 1,3,5,7-tetramethylCOT (**5**) to be 22.5 $kcal\ mol^{-1}$ at 120 °C.⁴⁸ These authors concluded, based on rough calculations of the van der Waals (vdW) energy in the ground state (GS) and TS of COT and **5**, that vdW interactions were not the cause of the greater barrier in **5** compared to COT. They were not able to pinpoint the origin of the “methyl effect” in **5**, but suggested that it might lie in bond angle strain and/or resonance energy.

Subsequently, Allinger *et al.*⁴⁹ performed molecular mechanics (MM) calculations on ring flattening in COT and **5** and calculated the differential strain energy on going from the GS to the RI TS in **5** compared to COT ($\Delta\Delta E$) to have the following components: vdW, 2.3; stretching, 1.0; bending, 7.7; torsion, -1.6 $kcal\ mol^{-1}$. However, even though the differential vdW energy was similar to that calculated by Ganis *et al.*, these authors reached exactly the opposite conclusion, *viz.*, that extra vdW strain in the TS is the origin of the higher barrier in **5**. They also argued that the major term (bond angle bending), while due in part to increased $\angle CCC$ vs. $\angle CCH$ bending force constants on going from COT to **5**, is primarily a result of distortions within the methyl groups caused by increased vdW interactions.

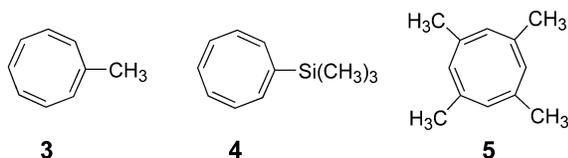
We have previously discussed⁵⁰⁻⁵² how the electronegativity of a substituent influences the barrier for bond shift (ΔG_{BS}^\ddagger) in substituted COTs on the basis of angular substituent parameters (ASPs),⁵³ which have been rationalized on the basis of both the Walsh-Bent hybridization⁵⁴ and valence-shell electron-pair repulsion (VSEPR)⁵⁵ models. According to the Walsh-Bent model, substitution of a methyl group at C-1 of COT causes the substituted carbon to shift s character into the C-CH₃ bond. This, in turn, shifts C-1 p character into the adjacent CC bonds of the ring and causes $\angle C-2-C-1-C-8$ to decrease. This effect is clearly seen in X-ray structures, where $\angle C-2-C-1-C-8$ decreases from 126.7° in COT⁵⁶ to 124.7° in **5**.⁵⁷ Similar decreases are calculated to occur in the RI TSs where the effect on energy is greater owing to the more strained planar ring. The reduced electronegativity of silicon relative to carbon causes a further reduction of $\angle C-2-C-1-C-8$ (as seen in the

Table 3 Components of the change in internal energy on ring flattening calculated by molecular mechanics

Component	ΔE_{RI}^a							
	MMFF94				MM2			
	COT	3	5	4	COT	3	5	4
van der Waals	-4.1	-2.5	5.2	-1.8	2.7	3.9	8.4	5.2
Bend	25.0	26.3	29.6	27.4	20.3	22.4	27.4	21.9
Torsional	-6.1	-7.2	-10.5	-7.8	-11.0	-13.0	-17.7	-13.5
Stretch	-0.3	0	1.0	3.8	0.2	0.3	0.9	0.1
Stretch-bend	-0.5	-0.5	-0.6	-4.2	-0.3	-0.3	-0.4	-0.3
Electrical	2.2	2.3	2.4	2.6	0	0	0	0
Total	16.1	18.4	26.1	19.8	11.9	13.2	18.6	13.4
$\Delta\Delta G_{\text{BS}}^{\ddagger}(\text{exptl})$	13.3 ^b	15.6 ^c	22.5 ^d	16.4 ^c				

^a $E_{\text{GS}} - E_{\text{TS}}$; in kcal mol⁻¹. ^b The value of 13.3 kcal mol⁻¹ is calculated from data in ref. 76, with the correction that lifetime $\tau = 1/2k$ instead of $\tau = 1/k$, as recognised Goldman *et al.* in ref. 77; see also ref. 3. ^c Ref. 52. ^d Ref. 48.

X-ray diffraction structures of *para*-disubstituted benzenes⁵³) and a greater barrier to planarity of the COT ring. From this model, the latter is expected to contribute to the observed increases in $\Delta G_{\text{BS}}^{\ddagger}$ of 1.4 and 0.8 kcal mol⁻¹ on going from **1** to **2** and **3** to **4**,⁵¹ respectively.



In order to test these ideas, we performed MM geometry optimisations of the GS and RI TS of COT and **3–5**. The MM method gives components of the steric energy, which is the potential energy of the molecule over and above the sum of the energies of the unstrained bonds. Note that the partitioning of the steric energy into its component parts is not unique, in that different force fields give different values for the several components.⁵⁸ Nevertheless, we felt that it would be useful to obtain at least approximate values for the different steric energy contributions to the RI/BS barrier, information not easily obtained by molecular orbital calculations. We employed two widely used MM force fields (MM2 and MMFF94) in order to see whether there was any consistency in the partitioning of the energy terms.

The components of the change in internal energy for ring flattening [$\Delta E_{\text{RI}}(\text{total})$] are listed in Table 3 along with the experimental $\Delta G_{\text{BS}}^{\ddagger}$ values. Note that $\Delta G_{\text{BS}}^{\ddagger}$ is systematically *ca.* 3 kcal mol⁻¹ less than $\Delta E_{\text{RI}}(\text{total})$ for the MMFF94²⁰ force field but *greater* by 1.4–3.9 kcal mol⁻¹ for the MM2²² force field. Since $\Delta G_{\text{BS}}^{\ddagger}$ is typically 2–4 kcal mol⁻¹ greater than $\Delta G_{\text{RI}}^{\ddagger}$ in monosubstituted COTs where both RI and BS can be measured^{3,4,9,33,59,60} (in line with CASSCF/6-31G* calculations⁴⁶), the values of $\Delta E_{\text{RI}}(\text{total})$ calculated by MM2 are to be preferred.

The components of the change in internal energy on ring flattening relative to those in COT ($\Delta\Delta E_{\text{RI}}$) are listed in Table 4. The MMFF94 $\Delta\Delta E_{\text{RI}}(\text{total})$ values differ by less than 1 kcal mol⁻¹ from the corresponding values of $\Delta\Delta G_{\text{BS}}^{\ddagger}$, whereas $\Delta\Delta E_{\text{RI}}(\text{total})$ from MM2 is systematically 1–2.5 kcal mol⁻¹ less than $\Delta\Delta G_{\text{BS}}^{\ddagger}$. At first sight, the MMFF94 values appear to be more reasonable. However, substituent effects should differ in the BS TS (more delocalization and perhaps slightly different steric effects) relative to the RI TS. If this serves to increase $\Delta\Delta G_{\text{BS}}^{\ddagger}$ relative to $\Delta\Delta E_{\text{RI}}(\text{total})$, then the MM2 values might be preferred. Whichever method is employed, $\Delta\Delta E_{\text{RI}}(\text{vdW})$ and $\Delta\Delta E_{\text{RI}}(\text{bend})$ have similar magnitudes, consistent with the conclusion that *both contribute substantially to the increase in $\Delta G_{\text{BS}}^{\ddagger}$ for **3**, **4** and **5** relative to COT.*

Charge transfer

In all the cases studied so far, the rate of intramolecular CT in

diCOT dianions is less than the rate of BS.^{7–11} This is consistent with the hypothesis that conformational changes similar to those needed to reach the BS TS are required for CT to occur, *i.e.*, both rings are planar or nearly planar in the CT TS. Support for ring flattening in the CT process comes from EPR and ¹H NMR studies, which have shown that intermolecular CT between the planar radical anion of COT and the planar dianion is fast while CT of the radical anion with a folded neutral COT ring is slow.^{5,6,61}

The increase in $\Delta G_{\text{CT}}^{\ddagger}$ on going from **1**²⁻-2K⁺ to **2**²⁻-2K⁺ [$\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{total})$] (Table 2) can be broken down into the following components [eqn. (1)]: 1) the difference in energy required

$$\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{total}) = \Delta\Delta G_{\text{BS}}^{\ddagger}(\text{neutral}) + \Delta\Delta G_{\text{BS}}^{\ddagger} + \Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic}) \quad (1)$$

to flatten the ring and reach the BS TS in **1** vs. **2** [$\Delta\Delta G_{\text{BS}}^{\ddagger}(\text{neutral})$], 2) the differential lowering of the BS barrier (primarily due to stabilization of the BS TS) on going from the neutral compound to the corresponding dianion [$\Delta\Delta G_{\text{BS}}^{\ddagger} = \Delta\Delta G_{\text{BS}}^{\ddagger}(\text{dianion}) - \Delta\Delta G_{\text{BS}}^{\ddagger}(\text{neutral})$], and 3) the “intrinsic” barrier to charge transfer [$\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic}) = \Delta\Delta G_{\text{CT}}^{\ddagger}(\text{total}) - \Delta\Delta G_{\text{BS}}^{\ddagger}(\text{dianion})$].

Because k_{CT} for **1**²⁻-2K⁺ was measured only at 21 and 22 °C owing to the instability of this compound, we have calculated eqn. (1) at 22 °C. The choice of this temperature also minimizes the extrapolations required since it lies 25 °C above but only 5 and 1 °C below the temperature ranges employed for BS in **1**²⁻-2K⁺ and CT and BS in **2**²⁻-2K⁺, respectively. On inserting the appropriate values from Table 2, eqn. (1) becomes: 3.7 = 1.5 + 0.3 + 1.9 kcal mol⁻¹ (obtained from: (20.6 – 16.9) = (16.8 – 15.3) + [(15.8 – 16.8) – (14.0 – 15.3)] + $\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$). Thus, *only about half* of $\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{total})$ at 22 °C (1.9/3.7) is due to an intrinsic barrier to transfer of charge from one planar delocalised COT ring to another, *i.e.*, the barrier after correction for conformational gating due to ring flattening and COT bond equalization and for charge polarization and/or delocalisation in the BS TS.

The value of $\Delta\Delta G_{\text{BS}}^{\ddagger}(\text{neutral})$ can be further broken down into the difference in energy required to flatten the ring [$\Delta\Delta G_{\text{RI}}^{\ddagger}(\text{neutral})$] and the difference in energy required to change the COT bond lengths from those of the RI TS to those of the BS TS in the neutral compounds [$\Delta\Delta G_{\text{BS}}^{\ddagger}(\text{neutral}) - \Delta\Delta G_{\text{RI}}^{\ddagger}(\text{neutral})$]. This is not central to the mechanism of CT and is discussed elsewhere.²⁹

Cation transfer and low energy conformational changes, such as bond length changes, bond rotations and solvent reorganisation, apart from those involved in the BS process, should all be considered in a refined analysis. However, it is likely that these effects are almost identical in **1**²⁻ and **2**²⁻ since the ¹³C NMR chemical shifts indicate that the tightness of the CIP is very

Table 4 Components of the change in internal energy relative to COT on ring flattening

Component	$\Delta\Delta E_{\text{RI}}^a$					
	MMFF94			MM2		
	3	5	4	3	5	4
van der Waals	1.6	9.3	2.3	1.1	5.6	2.4
Bend	1.3	4.6	2.4	2.1	7.1	1.6
Torsional	-1.1	-4.4	-1.7	-2.0	-6.7	-2.5
Stretch	0.3	1.3	4.1	0.2	0.7	-0.1
Stretch-bend	0	-0.1	-3.7	0	0	0
Electrical	0.1	0.2	0.4	0	-0.1	0
Total	2.3	10.0	3.7	1.4	6.7	1.5
$\Delta\Delta G_{\text{BS}}^{\ddagger}(\text{exptl})$	2.3 ^b	9.2 ^b	3.1 ^b			

^a $\Delta E_{\text{RI}} - \Delta E_{\text{RI}}(\text{COT})$; in kcal mol⁻¹. ^b See Table 3.

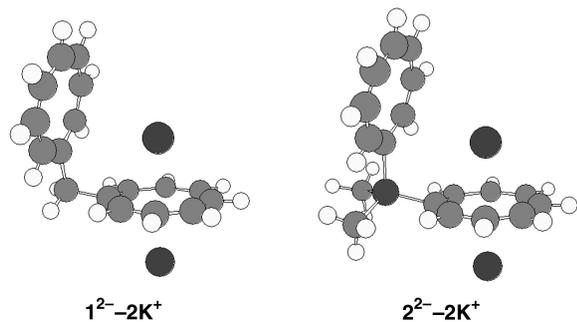


Fig. 4 HF/3-21G(*) geometry-optimised ring inversion transition structures for $1^{2-}-2\text{K}^+$ and $2^{2-}-2\text{K}^+$.

similar in these two systems. Thus, electronic properties associated with the bridge should be the most important contributor to $\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$.

In order to gain insight into possible mechanistic events leading up to the CT TS, we optimised the RI TSs for $1^{2-}-2\text{K}^+$ and $2^{2-}-2\text{K}^+$ at the HF/3-21G(*) level (Fig. 4). Note that the *endo* K^+ is closely connected with both rings in the two structures. In fact, this K^+ is shifted towards C-1' and away from C-5' of the dianion rings of $1^{2-}-2\text{K}^+$ and $2^{2-}-2\text{K}^+$ ($r_{\text{K}^+\dots\text{C}-1} = 2.90$ and 2.94 Å, $r_{\text{K}^+\dots\text{C}-5} = 3.00$ and 3.00 Å, respectively), while the *exo* K^+ is almost equidistant between these two carbons in both compounds. This circumstance suggests that the *endo* K^+ can be transferred as a contact ion pair (CIP) with only minimal motion. It also raises the possibility that such a transfer might be triggered by dissociation of the contact ion-paired *exo* K^+ to form a solvent-separated ion pair (SSIP).

We recently postulated that the dipotassium, dirubidium and dicaesium salts of the more nearly planar bicyclooctatetraenyl dianion (COT^{2-}) undergo charge transfer predominantly through CIPs.¹¹ This conclusion was based on the observation that k_{CT} for these salts decreases [$k(\text{Cs}^+) > k(\text{Rb}^+) > k(\text{K}^+)$] as the degree of tightness of their CIPs increases.^{11,32} A completely CIP mechanism seems less likely in 1^{2-} and 2^{2-} unless the *exo* K^+ first converts to an *endo* K^+ . The latter can be envisaged to occur *via* the following sequence: 1) transfer of the *endo* K^+ to the neutral ring, 2) rotation about the C-CH₂ (or C-Si) bonds of the two rings, either simultaneously or sequentially, to effectively exchange the two K^+ ions and 3) transfer of the new *endo* K^+ to the second ring.

A disadvantage of this CIP mechanism is that both rings must be planar or nearly planar at the same time. Alternatively, we postulate a mechanism where: 1) the *exo* K^+ dissociates to an SSIP, 2) the *endo* K^+ transfers as a CIP and 3) the solvent-separated K^+ desolvates and complexes with the second ring. This mechanism might avoid a structure with two planar rings if the “dianion” ring can fold as the “neutral” ring flattens during transfer of the *endo* K^+ . One does not expect to find a

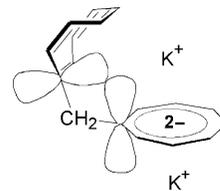


Fig. 5 Illustration of overlap between basis p orbitals on C-1 and C-1' in $1^{2-}-2\text{K}^+$.

significant concentration of SSIPs in the K^+ , Rb^+ or Cs^+ salts of COT^{2-} in THF.^{11,32} Nevertheless, an SSIP TS should be considered for CT in bridged diCOT dianions. We plan to test this mechanism in future work.

Electronic communication across CH₂ vs. Si(CH₃)₂

Two key entries in Table 2 indicate that electronic communication is greater across the CH₂ bridge in $1^{2-}-2\text{K}^+$ compared with the Si(CH₃)₂ bridge in $2^{2-}-2\text{K}^+$. First, the intrinsic barrier to charge transfer [$\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$] is almost 2 kcal mol⁻¹ greater in 2^{2-} than in 1^{2-} and, second, the absolute value of $\Delta\Delta G_{\text{BS}}^{\ddagger}$ is 0.3 kcal mol⁻¹ greater in $1/1^{2-}$ than in $2/2^{2-}$. In the discussion that follows, we consider four potential influences on electronic communication: a) electrostatic interaction of the BS TS with the electric field of the dianion ring as the origin of $\Delta\Delta G_{\text{BS}}^{\ddagger}$ and, for the origin of *both* $\Delta\Delta G_{\text{BS}}^{\ddagger}$ and $\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$, b) π -electron interaction through the bridging group (through-bond interaction), c) through-space interaction between the π -orbitals at C-1 and C-1' (Fig. 5) and d) interaction between the rings mediated by a bridging alkali metal cation.

In a recent study of BS and CT in di(COTethynyl)benzene dianions, we concluded that the rate of BS in the neutral ring of the *ortho* isomer is probably enhanced by *ca.* 0.5 kcal mol⁻¹ relative to the *meta* and *para* isomers by the electric field of the COT dianion ring.¹⁰ This conclusion was based on decreases in $\Delta G_{\text{BS}}^{\ddagger}$ for the dianions compared to the corresponding neutral molecules and on calculated π -charge shifts on going from the GS to the RI TS.

The chemical shift ranges of C-1 to C-8 in the *neutral rings* of **1** and **2** are greater in the dianions than in the corresponding neutral compounds (Table 1 and Experimental).^{8,10,11} This is most apparent for the first double bond, where $\delta\text{C}-1 - \delta\text{C}-2$ increases by 15.06 ppm on going from **1** to 1^{2-} and by 14.01 ppm from **2** to 2^{2-} (Table 1). However, these data give no indication of a larger value of $\Delta\Delta G_{\text{BS}}^{\ddagger}$ in 1^{2-} relative to 2^{2-} (Table 2). Even greater interactions in the corresponding BS TSs might account for these relative values, but we have no evidence that supports this point.

An attractive possibility is that through-space interaction (Fig. 5) is greater in $1^{2-}-2\text{K}^+$ than in $2^{2-}-2\text{K}^+$ owing to a smaller value for $r_{\text{C}-1\dots\text{C}-1'}$ in the former (2.51 vs. 3.01 Å, respectively). Although $\angle\text{C}-\text{Si}-\text{C}$ in $2^{2-}-2\text{K}^+$ is smaller than $\angle\text{C}-\text{CH}_2-\text{C}$ in $1^{2-}-2\text{K}^+$ due to the methyl groups on Si, the C-Si bonds are longer than the C-CH₂ groups and this is the determining factor. The HOMO of $1^{2-}-2\text{K}^+$ and the HOMO-1 of $2^{2-}-2\text{K}^+$ both have contributions from the atoms of the bridge, so electronic communication probably also occurs to some extent *through* the bridge. However, to what extent, if any, this favors CT in 1^{2-} is unknown.

A number of groups have considered the possibility that alkali metal cations catalyse the transfer of an electron from an inorganic polyanion⁶² or an organic anion⁶³ to an anionic or neutral acceptor by serving as an electron conduit. It has been suggested that one role of the cation is to provide low-lying unoccupied orbitals^{62,63-65} that overlap with the appropriate orbitals of the donor and acceptor. As seen in Fig. 6, an unoccupied orbital on the *endo* K^+ makes the major contribution to the LUMO+1 of $1^{2-}-2\text{K}^+$, which also involves p orbitals on carbons in the neutral ring, and could indeed serve as a conduit for electron transfer. (The LUMO is localized solely on

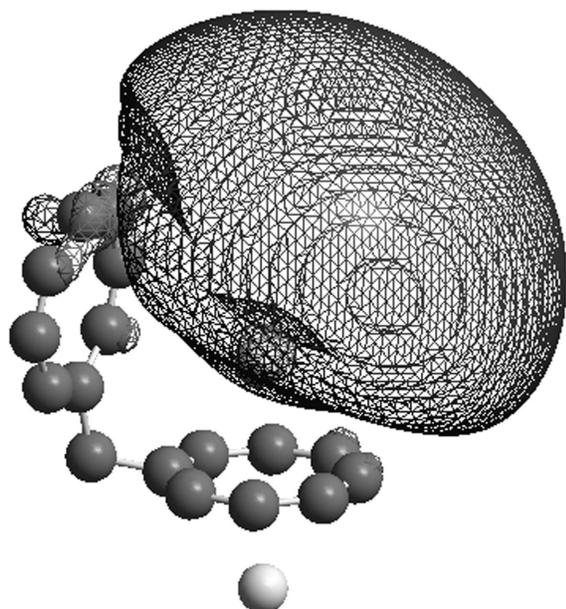


Fig. 6 LUMO+1 isocharge ($0.01 \text{ electrons bohr}^{-3}$) surface of the ring inversion transition state of $1^{2-}-2K^+$ calculated at HF/3-21G(*)//HF/3-21G(*)

the *exo* K^+ .) Because we are using a relatively small basis set, it is likely that the LUMO+1 orbital is physically significant. If so, then it is interesting to ask whether this pathway plays a greater role in $1^{2-}-2K^+$ compared to $2^{2-}-2K^+$ owing to the greater distance between COT rings in the latter compound. This is an important problem that requires further investigation.

Several groups have recently studied the relative degree of electronic communication from one ring across a $\text{Si}(\text{CH}_3)_2$, CH_2 or $\text{C}(\text{CH}_3)_2$ bridge to a second ring. Fourmigué and Huang found that the difference between the first two oxidation waves ($\Delta E_{1/2}$) of bridged trimethyltetrafulvalene and ferrocene dimers was greater when the monomeric units were bridged by CH_2 compared with $\text{Si}(\text{CH}_3)_2$.⁶⁶ The through-space and through-bond overlaps, given by the energy difference between the π -HOMOs ($\Delta \epsilon_{\text{HOMO}}$) of the tetrafulvalene (TTF) rings, were also calculated. They considered the latter to be negligible and concluded that the dominant influence on $\Delta E_{1/2}$ is due to coulombic repulsion. However, the calculated values of $\Delta \epsilon_{\text{HOMO}}$ are actually 43–133% of the value of $\Delta E_{1/2}$ for the bridged TTF dimers, so these calculations do not exclude a significant through-space and/or through-bond contribution.

Through-space interactions are expected to be more important in negatively charged species where the frontier orbitals are more diffuse and have greater long-range overlap. This effect has been seen in the energies of the LUMOs of unsaturated hydrocarbons as determined from the attachment energies of negative ion resonance states measured by electron transmission spectroscopy.⁶⁷ This is in accord with two recent studies which concluded that through-space overlap is greater across a CH_2 or $\text{C}(\text{CH}_3)_2$ bridge than across a $\text{Si}(\text{CH}_3)_2$ bridge.^{12,68}

In a study of the EPR spectra of extensively solvated radical anions of **1** and **2**, Echegoyen *et al.* observed that electron spin density was equally distributed between the two COT rings in $1^{\cdot-}$ on the EPR time scale, while $2^{\cdot-}$ showed a hyperfine-coupling pattern expected for spin localization in one ring.¹² This led these authors to propose a through-space overlap between the π -orbitals at C-1 and C-1' in the two COT rings for CT in $1^{\cdot-}$.

van Walree *et al.* inferred from radiative decay rates of a series of $\text{C}(\text{CH}_3)_2$ - and $\text{Si}(\text{CH}_3)_2$ -bridged *para*-substituted diphenyl compounds in acetonitrile that the electronic coupling between CT and locally excited states and between the ground and CT states is larger for the carbon-bridged compounds.⁶⁸ This was attributed to through-space overlap between the π - and π^* -orbitals at C-1 and C-1' in the phenylene rings.

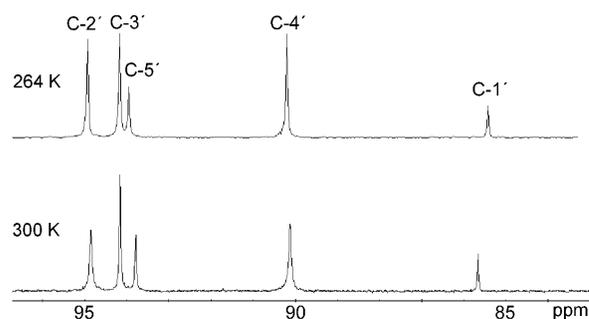


Fig. 7 ^{13}C NMR spectra of the dianion ring carbons of $2^{2-}-2K^+$ showing DLB. The signals for C-2',-8' and C-4',-6' broaden and shorten at higher temperatures while those for C-1', C-3',-7' and C-5' remain narrow.

Interestingly, other investigations have led to different or opposite conclusions. In a ^{29}Si and ^{13}C NMR study of the same series of compounds (along with the corresponding CH_2 -bridged series), van Walree *et al.* concluded that $\text{Si}(\text{CH}_3)_2$ is a better transmitter of substituent effects (by a σ -bond polarization mechanism) than the carbon bridges. However, as these authors point out,⁶⁸ this is an effect primarily associated with the σ -bonds and not with the π -bonds as in the previous study. It is interesting to note that the long-range substituent effect (from C-4 in one ring to C-4' in the second ring) is greater for the CH_2 -bridged compound than for the $\text{Si}(\text{CH}_3)_2$ -bridged compound.^{69a} This could be indicative of a through-space π -polarization mechanism.

Zehnacker *et al.* recently investigated the laser-induced excitation and dispersed fluorescence spectra of the same series of bridged diphenylenes under solvent-free conditions in a supersonic expansion.⁷⁰ In seeming contradiction to the van Walree study,⁶⁸ these authors concluded that a $\text{Si}(\text{CH}_3)_2$ bridge mediates electronic coupling in the excited state better than a $\text{C}(\text{CH}_3)_2$ bridge. However, the situations in the gas phase and solution are fundamentally different. Because only the conformations with perpendicular phenylene rings are populated under jet-cooled conditions, the through-space mechanism is not possible for the $\text{C}(\text{CH}_3)_2$ -bridged compounds, but becomes possible for the $\text{Si}(\text{CH}_3)_2$ -bridged compounds owing to more facile distortions (rotation around the Si-aryl bonds) on excitation.⁷⁰

Wang *et al.* recently observed that the acidity of carborane protons in bridged indenyl anion-carboranes is qualitatively greater for the $\text{Si}(\text{CH}_3)_2$ - compared to the $\text{C}(\text{CH}_3)_2$ -bridged compound and suggested that a silicon atom might function as an “electron conductor” (probably due to Si 3d orbitals) and a carbon atom as an “electron insulator”.⁷¹ However, if the negative charge in the adjacent indenyl anion is transmitted to the carborane ring (thereby reducing the acidity of the carborane proton), then the lower acidity of the $\text{C}(\text{CH}_3)_2$ -bridged compound could be interpreted on the basis of a *greater* electronic communication across the latter bridge.

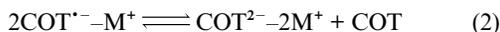
Differential line broadening

In the course of this investigation it was observed that the NMR peaks for C-1', C-3'/C-7' and C-5' in $1^{2-}-2K^+$ (Fig. 7) and for C-2'/C-8' and C-4'/C-6' in $2^{2-}-2K^+$ started to broaden at temperatures just below where broadening was observed due to CT, while the other resonances for the dianion ring remained sharp. This differential line broadening (DLB) was also present in two related COT dianions, $\text{CH}_3\text{COT}^{2-}-2K^+$ and $(\text{CH}_3)_3\text{SiCOT}^{2-}-2M^+$ ($M = K$ and Cs), that lack the possibility of intramolecular CT. This argues against broadening due to dynamics of the neutral ring. Further, DLB was not observed for samples of $1^{2-}-2\text{Na}^+$ or for the Li^+ or Na^+ salts of 2^{2-} , and the ^{13}C T_1 and NOE values for 2^{2-} were similar for all proton-bearing carbons in the dianion ring for both the Li^+ and K^+

salts.⁸ The latter result shows that DLB is due to slow dynamics that affect only the spin–spin relaxation and does not originate from high frequency processes of importance for spin–lattice relaxation.

To investigate whether scalar relaxation from the nearby potassium quadrupoles was present, *i.e.*, ¹³C spin–spin relaxation induced by scalar coupling to the fast relaxing ³⁹K, decoupling experiments were performed on the latter nucleus. This is analogous to nitrobenzene, where we observed that the broadening of the *ipso* carbon is diminished on decoupling ¹⁴N. These experiments gave no indication of a scalar interaction between potassium and the broadened carbons in the dianion ring.

The ¹³C NMR signal assignments and MO calculations (*vide supra*) show that the broadened signals correspond to nuclei with large HOMO coefficients. (The broadened signals are different in **1**²⁻ and **2**²⁻ because the CH₂ bridge is a donor whereas the Si(CH₃)₂ bridge is an acceptor relative to the COT⁻ π-electron system.¹²) At intermediate stages during the reduction of several COT compounds, we observed that the NMR lines were broader than in fully reduced dianion samples. This indicates that exchange with radicals should be considered.^{33,61} EPR measurements on samples used for NMR studies indicated the presence of **2**^{•-} at low concentration in the Li but not in the K sample.⁸ This is in accord with an expected lower concentration of radicals in the latter sample since an EPR study of COT^{•-} in THF has shown that the equilibrium in eqn. (2) is



shifted to the right on going from M = Li to M = K.⁵ However, it cannot be excluded that radicals are also present in the K samples since weak and broad EPR lines can be undetectable.

One possible mechanism for DLB occurring through electron exchange with radicals involves increased cation motion upon increasing the temperature. As a result of fluctuations in the interionic distance, mixing of orbitals of the dianion and K⁺ may occur,⁷² with a possibility of reversible electron transfer from dianion to cation. If this primarily involves the dianion HOMO, electron density changes will occur at the carbons that give the broadened signals in **1**²⁻ and **2**²⁻. The absence of DLB in the Li⁺ and Na⁺ salts could be explained by solvation effects. Although these ionic systems exist predominantly as tight ion pairs, Li⁺ and Na⁺ should have stronger solvent coordination than K⁺ and Cs⁺.⁷³ Orbital mixing with concurrent charge transfer would thus be less favourable for the smaller cations because of a loss of solvation energy.

Still another mechanism that can induce line broadening in the NMR spectrum of a diamagnetic species (D) is electron exchange of D with a paramagnetic species (P).⁷⁴ Exchange that gives DLB effects in ¹H NMR spectra has been investigated for D and P of the same parent compound, *e.g.*, *p*-xylene.^{74,75} In these studies, DLB was detected when the different hydrogens in P had different hyperfine interactions with the unpaired electron. Eqn. (3) describes the exchange contribution to NMR

$$\Delta T_2^{-1} = f_{\text{P}} t_{\text{P}} a_{\text{N}}^2 / 4 (1 + f_{\text{D}} t_{\text{P}}^2 a_{\text{N}}^2 / 4 + 2 t_{\text{P}} T_{1\text{e}}^{-1}) \quad (3)$$

linewidths, and is valid when the lifetime of P is much less than that of D, *i.e.*, $t_{\text{P}} \ll t_{\text{D}}$.⁷⁴

Here f is the fraction of D or P, a_{N} is the hyperfine coupling in angular frequency, $T_{1\text{e}}$ is the spin–lattice relaxation time of the unpaired electron, t_{P} is the lifetime of P, and $t_{\text{P}} = 1/k [\text{D}]$, where k is the rate constant for exchange between P and D. Eqn. (3) could be further simplified to eqn. (4) when $f_{\text{D}} t_{\text{P}}^2 a_{\text{N}}^2 /$

$$\Delta T_2^{-1} = k [\text{P}] \quad (4)$$

$4 \gg (1 + 2 t_{\text{P}} T_{1\text{e}}^{-1})$. This is denoted the “slow exchange case” or “strong pulse limit” by de Boer *et al.*⁷⁴ When $(f_{\text{D}} t_{\text{P}}^2 a_{\text{N}}^2 /$

$4 + 2 t_{\text{P}} T_{1\text{e}}^{-1}) \ll 1$, eqn. (5) is obtained, and this is denoted the

$$\Delta T_2^{-1} = [\text{P}] a_{\text{N}}^2 / ([\text{D}]^2 4k) \quad (5)$$

“rapid exchange case” or “weak pulse limit”. In eqns. (4) and (5), [P] and [D] are the concentrations of P and D. When the conditions for eqn. (4) or eqn. (5) are fulfilled, an increase in the rate constant will cause a broadening or narrowing of the signals, respectively. In accord with this, DLB was analysed for the ¹H NMR spectra of *p*-xylene partially reduced with potassium.⁷⁴

EPR and ¹H NMR studies have revealed that electron exchange between COT^{•-} and COT²⁻ in THF is rather fast.⁵ In addition, a large increase in the rate of CT between COT^{•-} and COT²⁻ is observed when the cation is changed from Li⁺ to K⁺ in THF.⁶ It has also been observed that upon reduction of COT with K, the ¹H signal from the dianion is very broad while the signals for the neutral COT and the solvent remain sharp throughout the reduction. The dianion signal sharpens just before complete reduction.⁶¹ If the parameters for the COT radical anion/dianion systems are transferable to the substituted COT systems in this study, the DLB for the potassium salts seems reasonable. The use of eqns. (2) and (3) for explaining the ¹³C NMR DLB in this study requires that the ¹³C hyperfine coupling constants are of the same magnitude as the ¹H hyperfine couplings. Literature data on COT²⁻–2Li⁺ indicate that the magnitudes are indeed similar ($a_{\text{H}} = 3.2$ G, $a_{\text{C}} = 1.34$ G).⁵ Since the larger ¹H hyperfine couplings in **1**^{•-} and **2**^{•-} are assigned to the protons attached to carbons with large SOMO coefficients,¹² this is fully consistent with the expected DLB for the carbons with large HOMO coefficients in the dianions.

In summary, the ¹³C NMR DLB that is observed in both the partially and fully reduced dianion samples of substituted COT compounds using potassium is probably best explained by exchange with a small amount of the corresponding radical anion. Since the dianions exist as contact ion pairs, intermolecular electron and cation exchange (between the dianion and monoanion salts) may occur through the transfer of a K atom. The reason why a faster exchange between the dianion and a radical compound is observed for K⁺ as compared to Li⁺ or Na⁺ in **2**²⁻ is probably because the former ion has a weaker solvation shell in THF. With more strongly (externally) solvated cations, *e.g.*, Li⁺, a COT dianion and a COT radical anion would have more difficulty in approaching each other.⁶³

Summary

The smaller free energy of activation for charge transfer in **1**²⁻–2K⁺ as compared to that in **2**²⁻–2K⁺ is attributed about equally to the lower energy required to reach the BS TS and a lower intrinsic energy barrier for CT [$\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$] in **1**²⁻. The first factor is due to easier ring flattening (due to the greater electronegativity of C relative to Si) and greater electronic communication in the BS TS of **1**²⁻ ($\Delta\Delta G_{\text{BS}}^{\ddagger}$). Both $\Delta\Delta G_{\text{BS}}^{\ddagger}$ and $\Delta\Delta G_{\text{CT}}^{\ddagger}(\text{intrinsic})$ probably arise to a significant extent from a greater through-space interaction primarily at the *ipso* carbons (C-1 and C-1') in **1**²⁻, although differential cation mediation and through-bond interactions might also contribute.

The differential line broadening (DLB) in the ¹³C NMR spectra of **1**²⁻–2K⁺ and **2**²⁻–2K⁺ at ambient temperature is best explained by an exchange with very small amounts of radicals in the solutions of the dianions. However, DLB does not affect the measurement of the rate constants for bond shift and charge transfer.

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