Factors Determining Ion-pair Formation. Studies of the Radical Anions of 2,5-Bis(tricyanovinyl)furan and 2,5-Bis(tricyanovinyl)thiophene

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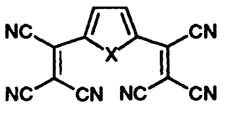
The specificity of ion-pair formation of the radical anions of 2,5-bis(tricyanovinyl)furan (**1**) and 2,5-bis(tricyanovinyl)thiophene (**2**) has been studied using solvents covering a broad range on the polarity scale and Li^+, Na^+, K^+ and Cs^+ as the counter-ions. The EPR/ENDOR spectra show that $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ can exist as the free radical anions in which the tricyanovinyl groups have a *syn*/*anti* conformation, but under appropriate conditions $\mathbf{2}^{\bullet-}$ can also exist in a *syn*/*syn* conformation in an ion-pair with the metal cation. This is rationalised in terms of a selectivity for the formation of ion pairs depending on the size of the alkali-metal cation and of the cavity presented by the proximate pair of cyano groups.

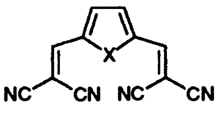
In recent years it has been established that a high number of chemical reactions proceed *via* electron-transfer processes.[1] Obviously a one-electron transfer reaction leads to the formation of a radical ion. As most of the reactions are performed in fluid solution, such charged species are capable of interacting with the solvent and counter-ions. When well defined counter-ions are provided in a solution containing the radical ion, insight into the factors directing such 'guest–host communications' can be gained.

When, for example, radical anions are formed by reductive electron transfer from metals, the metal cation formed in the redox process serves as the well defined counter-ion. Depending on solvation, this counter-ion influences the stability and the structure of the negatively charged molecule. The extent of such an influence can be studied readily by EPR spectroscopy.[2] This was demonstrated for, *inter alia*, 1,2-diones,[3] but-2-ene-1,4-diones,[4] thiophenecarbaldehydes,[5] alkylidene-bridged π-systems[6] and cyano-substituted furans and thiophenes.[7]

In this contribution we investigate the radical anions of 2,5-bis(tricyanovinyl)furan (**1**) and 2,5-bis(tricyanovinyl)thiophene (**2**) in various environments and relate these results to those established for the tetracyano derivatives $\mathbf{3}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$.[7]



1 X = O
2 X = S



3 X = O
4 X = S

It has been shown for $\mathbf{3}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$ that the contact ion pairs with alkali cations Li^+, Na^+, K^+ and Cs^+ possess a higher (C_{2v}) symmetry than the free ions (C_s). Moreover, it has been found that $\mathbf{3}^{\bullet-}$ preferentially forms ion pairs with Na^+ whereas $\mathbf{4}^{\bullet-}$ favours K^+.

The two additional CN groups in **1** and **2** improve the electron-accepting properties compared with **3** and **4**.[8] The radical anions $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$ offer additional sites for complexation for the alkali-metal counter-ions and, moreover, the distances between facing N atoms differ from those of the tetracyano counterparts.

In the light of these characteristics we will discuss the structure of the radical ion pairs of $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ and investigate whether their formation depends upon the nature of the counter-ion.

Results

Furan Derivative **1**.—Owing to its 'low' first reduction potential (−0.205 V *vs.* ferrocene[9]), **1** is isolated as the radical-anion salt $\mathbf{1}^{\bullet-}/K^+$.[10] For the EPR and ENDOR/Triple measurements the salt was dissolved in HMPA (*N*,*N*,*N'*,*N'*,*N''*,*N''*-hexamethylphosphoric acid triamide)–DME (1, 2-dimethoxyethane) mixtures, DME, THF (tetrahydrofuran), MTHF (2-methyltetrahydrofuran) and benzene. The solutions directly gave the EPR spectrum shown in Fig. 1.

Introduction of Li^+, Na^+ and Cs^+ as the counter-ions was achieved by addition of an excess of LiCl, $NaBPh_4$ and CsCl, respectively, to the solutions of $\mathbf{1}^{\bullet-}/K^+$. The ENDOR technique indicates that the proton hyperfine coupling constants, a_H, remain almost unchanged for all solvent–counter-ion combinations (Table 1). In all cases two a_H are detected, one of 0.02 mT (1 H), the other of 0.07 ± 0.01 mT (1 H). The hyperfine coupling constants of the ^{14}N nuclei, a_N, could not be distinguished by ENDOR and were therefore determined by simulations of the EPR spectra (Table 1). This type of spectrum will be denoted as *A*.

Thiophene Derivative **2**.—Neutral thiophene **2** was converted into its radical anion ($\mathbf{2}^{\bullet-}$) by chemical reduction with a Na, K or Cs metal mirror. Li^+ as the counter-ion was introduced by addition of an excess of LiCl to the K-reduced solutions of $\mathbf{2}^{\bullet-}$. HMPA–DME mixtures, DME, THF and MTHF were used as the solvents. Depending on the solvent/counter-ion combination, two different types of EPR/ENDOR spectrum were observed.

The first type, denoted as *M* (Fig. 2), was recorded in the solvents HMPA–DME and DME, in THF at low temperatures and with Li^+ in MTHF (see also Fig. 4). These EPR spectra possess non-identical low- and high-field wings and the ENDOR spectra indicate three a_H. One pair of ENDOR signals, belonging to a_H = 0.079 mT, is identical with the coupling constant detected for the *A*-type spectra (see below). The two remaining pairs of lines (a_H = 0.031 and 0.093 mT, Table 1) have the same intensity which is lower than that of the former pair of lines. Together with the asymmetric shape of the EPR signal, this suggests the presence of two radicals. An unequivocal simulation of the *M*-type spectra could not be achieved (see the Discussion).

The second type of EPR spectrum labelled *S* (Fig. 3) was observed in THF and MTHF as the solvent at higher temperatures with Na^+ and Cs^+. With K^+ as the counter-ion, however, the *A*-type spectra were detected above 263 K in THF

Table 1 Experimental and HMO calculated a_H of $1^{\bullet -}$ and $2^{\bullet -}$

	a_H/mT[d]			a_N/mT[e]			g Factor[f]
$1^{\bullet -}$ (exp.)	0.02 (1 H)	0.07 (1 H)		0.04 (2 N)	0.10 (4 N)[g]		2.00293
$1^{\bullet -}$ (calc.)[a,b]	0.07 (1 H)	0.09 (1 H)		0.06 (2 N)	0.08 (4 N)		
$2^{\bullet -}$ (exp.) *M*	0.031	0.079	0.093	*g*			*h*
$2^{\bullet -}$ (exp.) *S*		0.079 (2 H)		0.042 (2 N)	0.082 (2 N)	0.104 (2 N)	2.00347
$2^{\bullet -}$ (calc.)[a,b]	0.088 (1 H)		0.100 (1 H)		0.05–0.08(6 N)		
$2^{\bullet -}$ (calc.)[b,c]		0.090 (2 H)		0.051 (2 N)		0.076 (4 N)	

[a] Values calculated for *syn*/*anti* conformation. [b] For parameters, see the text. [c] Values calculated for *syn*/*syn* conformation. [d] Error ±0.004 mT. [e] Error ±0.01 mT. [f] Error ±0.000 04. [g] a_N cannot be unambiguously determined, see the text. [h] The *g* factor cannot be determined because of the superposition of two EPR spectra.

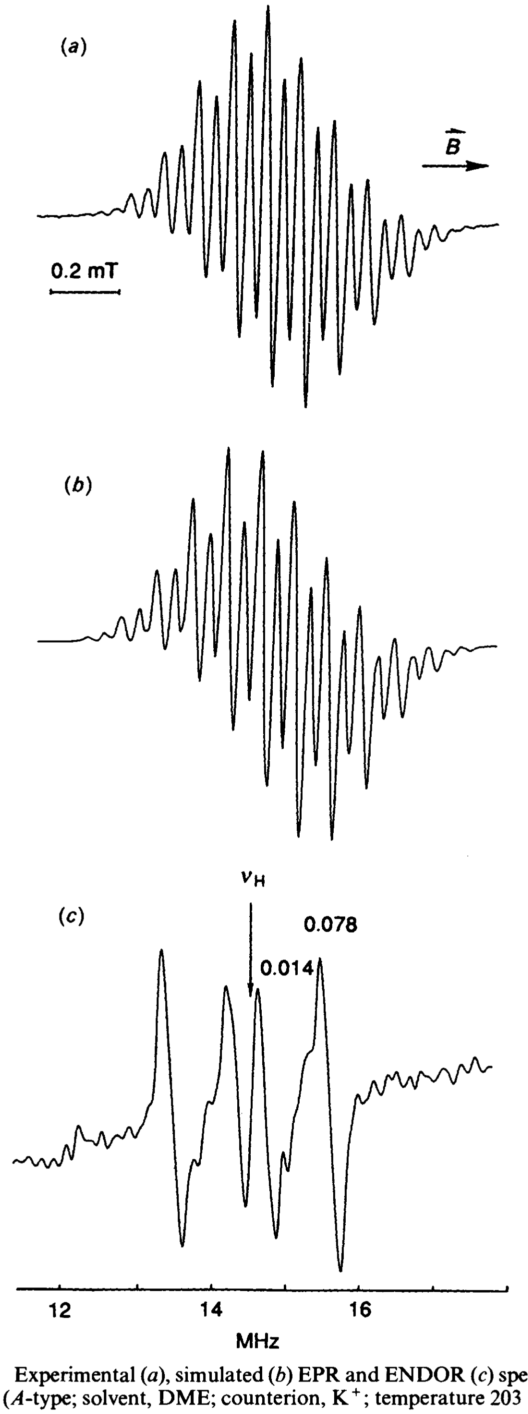


Fig. 1 Experimental (*a*), simulated (*b*) EPR and ENDOR (*c*) spectrum of $1^{\bullet -}$ (*A*-type; solvent, DME; counterion, K$^+$; temperature 203 K)

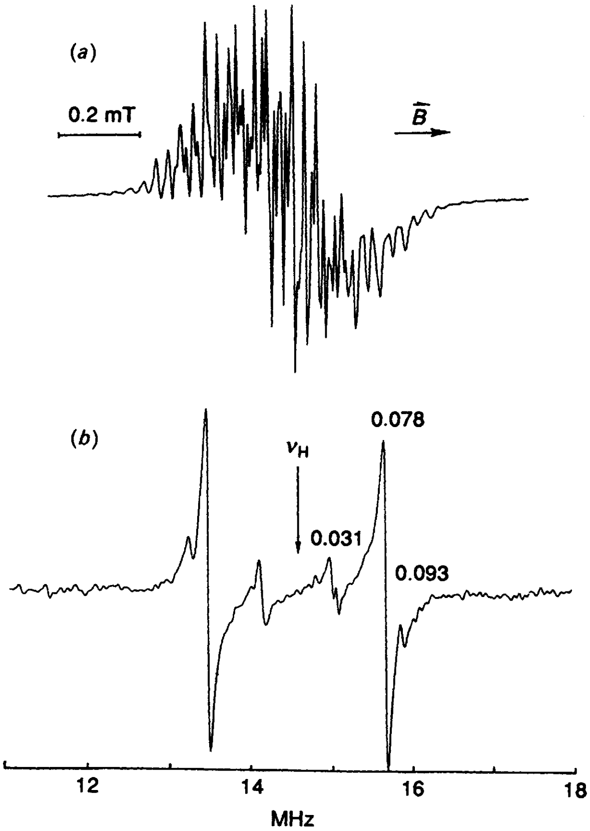


Fig. 2 EPR (*a*) and ENDOR (*b*) spectrum of $2^{\bullet -}$ (*M*-type; solvent, DME; counterion, K$^+$; temperature 203 K)

and over the whole temperature range covered (203–298 K) in MTHF (Fig. 4). Here, only one a_H of 0.079 mT was established by the ENDOR spectrum. The simulation of the EPR spectrum reveals that it belongs to a pair of equivalent protons. Moreover, three a_N of 0.042, 0.082 and 0.104 mT stemming from pairwise equivalent N-atoms were deduced from the simulations of the EPR spectra (Fig. 3, Table 1).

Discussion

AM1[11] Calculations predict energy minima for almost planar conformations of $1^{\bullet -}$ and $2^{\bullet -}$ which consequently should predominate on the hyperfine timescale of the EPR experiment and are thus relevant for the discussion. Three such geometries are conceivable: two possessing C_{2v} symmetry denoted *syn*/*syn* and *anti*/*anti* and one of C_s symmetry (*syn*/*anti*). The acronyms *syn* and *anti* represent the orientation of the dicyanomethylidene moiety towards and away from the five-ring heteroatoms, respectively (Fig. 5).

Assignment of Coupling Constants. HMO Calculations.— Assuming the preference for (almost) planar geometries of $1^{\bullet -}$

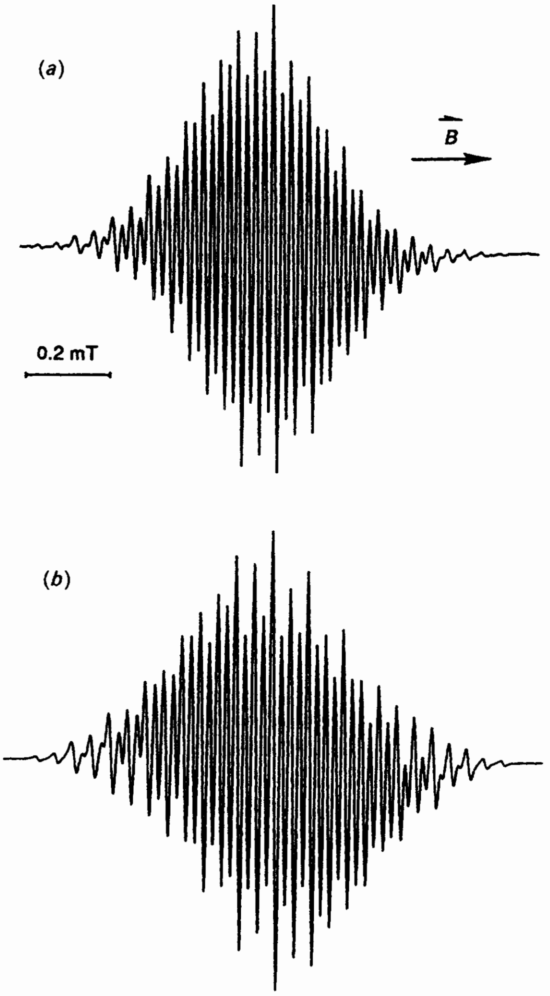


Fig. 3 Experimental (*a*) and simulated (*b*) EPR spectrum of $\mathbf{2}^{\cdot -}$ (*S*-type; solvent, MTHF; counter-ion, K^+; temperature 263 K)

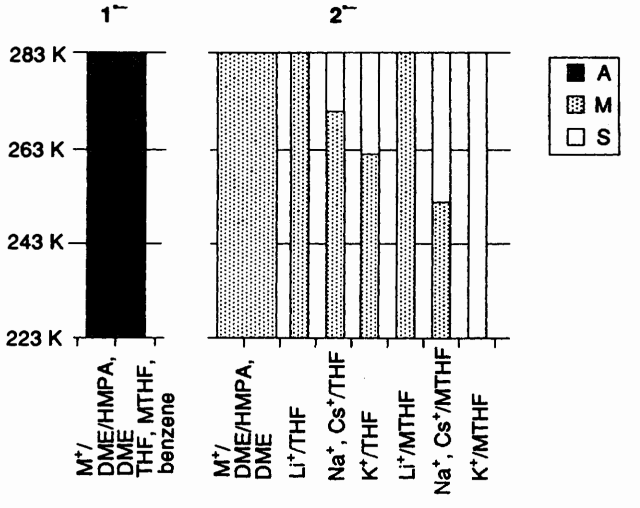


Fig. 4 Temperature, solvent and counter-ion dependence of the EPR/ENDOR spectral types of $\mathbf{1}^{\cdot -}$ and $\mathbf{2}^{\cdot -}$

and $\mathbf{2}^{\cdot -}$, it is justified to use the HMO[12] method for the calculation of the hyperfine coupling constants for the three preferred conformations. To account for the heteroatoms and their different bond lengths, the following corrections of the Coulomb ($\alpha' = \alpha + h_a\beta$, a = index for centre) and the resonance ($\beta' = k_{ab}\beta$, ab = index for bond) integrals were chosen: $h_O = 2.0$, $h_S = 1.0$, $h_N = 1.0$ and $k_{CO} = 1.0$, $k_{CS} = 0.65$, $k_{CN} = 2.0$. The O and S atoms contribute two electrons to the π system. Consequently, **1** and **2** have to be regarded as 22-electron π systems. In the McConnell equation, $a_X = Q_x{\cdot}\rho$ (X = H or N), $Q_H = -2.5$ (ref. 13) mT and $Q_N = +1.9$ (ref. 14) mT was used. The steric congestion between the furan (thiophene) 3-H atoms and the close CN groups of an *anti* arrangement (Fig. 5) was modelled by $h_{st} = -0.1$ at C(3) of the ring. The agreement between the thus calculated values and the experimental a_H and a_N is satisfactory (Table 1).

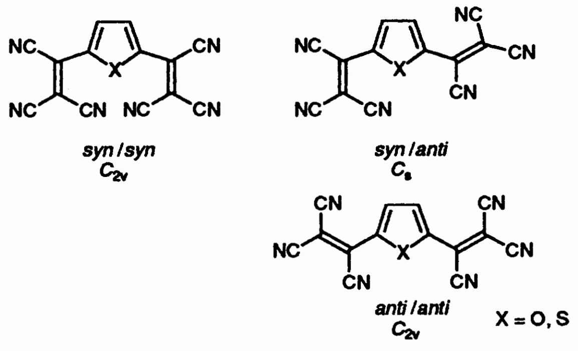


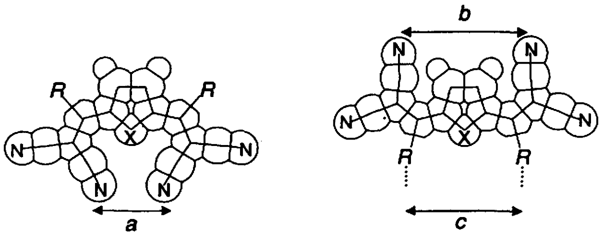
Fig. 5 Planar conformations of $\mathbf{1}^{\cdot -}$ and $\mathbf{2}^{\cdot -}$

Furan Derivative **1**.—Under all experimental conditions (Table 1 and Fig. 4) two a_H (EPR type *A*) each due to one proton were determined for $\mathbf{1}^{\cdot -}$ pointing to C_s symmetry on the hyperfine timescale. Thus neither the counter-ion nor the degree of solvation affect the structure of $\mathbf{1}^{\cdot -}$ on the hyperfine timescale. This means that either the free ion predominates, or an ion pair $\mathbf{1}^{\cdot -}/\mathbf{M}^+$ of low symmetry is present under all experimental conditions.

Thiophene Derivative **2**.—In contrast with $\mathbf{1}^{\cdot -}$, the EPR spectra of $\mathbf{2}^{\cdot -}$ were of type *M* or *S* depending upon the combination of temperature, solvent and counter-ion. The *M*-type EPR spectra with their non-symmetrical shape (Fig. 2) point to the presence of two paramagnetic species with marginally differing *g* factors. The three different a_H represented by three pairs of lines in the ENDOR spectrum corroborate the presence of two species, because two pairs of lines possess identical intensity which is weaker than that of the pair of lines belonging to the a_H of 0.079 mT (Fig. 2). Conditions promoting the formation of contact-ion-pairs, *i.e.*, less polar solvents and higher temperatures (Fig. 4), lead to the evolution of *S*-type spectra. This spectral type represents pairwise equivalent a_H and a_N and therefore reveals a twofold symmetry of $\mathbf{2}^{\cdot -}$. The a_H found in the *S*-type spectra is 0.079 mT, identical with one of the a_H of the *M*-type spectra. Hence it is straightforward to assume that the *M*-type spectra represent the mixture of one C_{2v} (*S*-type EPR, *syn*/*syn* or *anti*/*anti*) and one C_s(*A*-type EPR, *syn*/*anti*) conformation of $\mathbf{2}^{\cdot -}$. The three different proton coupling constants due to the two components of the *M*-type spectra are derived from the ENDOR signals. The three pairwise equivalent nitrogen coupling constants belonging to the *S*-type component are known, but six additional one-atom a_N from the C_s-symmetric components have to be introduced. The differences between these latter a_N lie within the linewidths of the EPR spectrum which itself indicates line broadening effects in the narrow temperature range (*ca.* 10 K) where the spectral type changes from *M* to *S*. Owing to these superimposed effects an unambiguous determination of these a_N and the exchange process is impossible and thus a simulation of the EPR spectra does not provide any conclusive information.

Geometry of Free Ions and Ion-pairs.—AM1[11] Calculations predict barriers of *ca.* 13 and 10 kJ mol^{-1} between the three local

Table 2 N ⋯ N distances in *syn/syn* and *anti/anti* conformations of $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ calculated by AM1 and preferred counter-ions



	X	R	*a*/pm	*b*/pm	*c*/pm	Ion pair with
$\mathbf{1}^{\bullet -}$	O	CN	294	788	484	—
$\mathbf{2}^{\bullet -}$	S	CN	405	746	615	$K^+ > Na^+ \approx Cs^+$
$\mathbf{3}^{\bullet -}$	O	H	307	814		$Na^+ > K^+, Li^+ \approx Cs^+$
$\mathbf{4}^{\bullet -}$	S	H	458	777		$Cs^+ \approx K^+ > Na^+ > Li^+$

minima *syn/syn*,† *anti/anti* and *syn/anti* of $\mathbf{1}^{\bullet -}$ and $\mathbf{2}^{\bullet -}$. The energy differences between these three conformations are *ca.* 1–2 kJ mol^{-1} and thus insignificant for a definite prediction of the preferred conformation of $\mathbf{1}^{\bullet -}$ and $\mathbf{2}^{\bullet -}$. The only clear-cut distinction which can be drawn is that a planar *syn/syn* arrangement is unrealisable for $\mathbf{1}^{\bullet -}$ because the N ⋯ N distance between the two facing CN groups is 294 pm, just below twice the van der Waals radius of an N atom (300 pm[15]) (Table 2).

The two one-proton a_H established by the EPR and ENDOR spectra (type *A*) testify to the C_s symmetry of $\mathbf{1}^{\bullet -}$. As the multiplicity of these a_H remains unchanged irrespective of the use of a polar (HMPA–DME) or a non-polar (MTHF) solvent, it is reasonable to assign these spectra to the free ion of $\mathbf{1}^{\bullet -}$.

On the other hand, the presence of two species reflected by the *M*-type EPR/ENDOR spectra of $\mathbf{2}^{\bullet -}$ agrees very well with the almost identical energies of the three planar conformations of $\mathbf{2}^{\bullet -}$ exhibiting C_{2v} and C_s symmetry (Fig. 5). The use of solvents of low polarity (THF, MTHF) or/and higher temperatures induces a change in the EPR spectra. For example, upon warming of a sample of $\mathbf{2}^{\bullet -}$ in MTHF and with Na^+ (or Cs^+) as the counter-ion a change from the non-symmetric *M*-type to a symmetric *S*-type spectrum takes place around 253 K over a *ca.* 10 K range (Fig. 4). Hence promotion of conditions favouring contact-ion pair formation leads to the observation of EPR spectra representing one unique species with a two-fold symmetry axis and an a_H of 0.079 (2 H) mT (Table 1). Thus the ion pair $\mathbf{2}^{\bullet -}/M^+$ must have at least C_2 symmetry and consequently has to be derived from the *anti/anti* or *syn/syn* conformations (Fig. 5). To resemble the experimental observations, the metal cation M^+ either has to flip between two equivalent positions of these conformations (fast on the hyperfine timescale) or has to reside in a position preserving the overall C_{2v} symmetry. The first assumption can be ruled out because the N ⋯ N distances inside the two di- or tricyanoethene moieties are almost identical in $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ and thus do not account for the different behaviour of alkali-metal cations. The almost indetectable coupling constants of the alkali-metal nuclei point to the metal cation occupying a position in the nodal plane of the π system of $\mathbf{2}^{\bullet -}$–$\mathbf{4}^{\bullet -}$.[7] Thus it is reasonable to assume that M^+ resides between two facing N atoms each belonging to one of the two di- and tri-cyanovinyl moieties.

In Table 2 the C_{2v} symmetric conformations of **1**–**4** are shown together with the distances between the pairs of facing N-atoms. It is apparent that the N ⋯ N distances, *b* and *c* in the *anti/anti* conformations are too extended (484–814 pm) selectively to accommodate an alkali-metal cation (radius[15] 60–139 pm). However the distances *a* in *syn/syn* $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ correlate very well with the sizes of M^+. Whereas $\mathbf{3}^{\bullet -}$ with an N ⋯ N distance *a* of 307 pm preferentially forms ion pairs with Na^+ the corresponding values of 405 and 458 pm in $\mathbf{2}^{\bullet -}$ and $\mathbf{4}^{\bullet -}$ account for the preference for K^+ and Cs^+, respectively. Such an ion-pair shape also explains that for $\mathbf{1}^{\bullet -}$ no ion-pair formation could be observed: for $\mathbf{1}^{\bullet -}$ the distance *a* is only 294 pm and this does not allow the formation of a planar *syn/syn* conformation (see above). This supports the idea that contact (or tight) ion pairs are exclusively formed when the metal cation can attach to the two facing N atoms of the *syn/syn* conformation. It is also likely that the O or S atom of the furan (thiophene) ring serves as an additional ligand.‡

Conclusions

Hitherto, predominately the hard–soft relationship has been applied to explain interactions between radical anions and metal counter-ions.[2] A distinct cation selectivity could only be established when crown ethers were attached to a radical ion.[17]

Our study of the ion pairs of $\mathbf{1}^{\bullet -}$ and $\mathbf{2}^{\bullet -}$ and comparison with the previously reported tetracyanovinyl derivatives $\mathbf{3}^{\bullet -}$ and $\mathbf{4}^{\bullet -}$ indicates a specific interaction of the ligands $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ with the alkali-metal cations. This remarkable cation selectivity of $\mathbf{2}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ particularly can be traced back to the different distances between the facing cyano N atoms of the *syn/syn* conformations of $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$.§ To our knowledge these results for the first time clearly establish the size of the counter-ion as a crucial factor for radical-ion-pair formation.

Experimental

The syntheses of **1**–**4** are given in ref. 10. All solvents used were refluxed with Na–K alloy for three days and stored under high vacuum over Na–K alloy.

The radical anions were prepared (except $\mathbf{1}^{\bullet -}$, see the Results section) by direct contact of the solutions of the neutral compounds with the alkali-metal mirrors. The K mirror was produced directly from K metal whereas the Na and Cs mirrors were generated from NaN_3 and CsN_3. Special precautions were necessary for the Na mirrors in order to avoid K-enriched surfaces.[18]

EPR spectra were recorded on a Varian E9 spectrometer and *g*-factors were determined using a Marconi Instruments 2440 microwave counter and a Bruker ER 035 M NMR gaussmeter. ENDOR spectra were taken on a Bruker ESP 300 spectrometer system.

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† The minimum of $\mathbf{1}^{\bullet -}$ deviates from a complete planar arrangement by *ca.* 30° of the tricyanovinyl groups.

‡ The observations of ion-pair formation were independent of the concentration of the radicals, thus the formation of higher aggregates can be discarded. If the position of the metal cation were above/below the furan/thiophene π system, the coupling constants particularly of ^{133}Cs should have far higher values.[16]

§ Selectivity due to different excesses of charge at the cyano groups of $\mathbf{1}^{\bullet -}$–$\mathbf{4}^{\bullet -}$ does not explain the experimentally established behaviour.

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