Isolated Free-radical Pairs in Rb^+ 18-Crown-6 $TCNQ^-$ Single Crystals (TCNQ = Tetracyanoquinodimethane)†

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An *X*-ray crystallographic study of Rb^+ 18-crown-6 $TCNQ^-$ reveals the presence of localised pairs of radical anions rather than the stacks commonly encountered in salts of $TCNQ^-$; the spin–spin tensor of the excited triplet observed and measured by EPR spectroscopy of a single crystal has principal values and directions appropriate for the location of the intrinsic pair within the crystal structure.

Ion-radical salts of the powerful electron acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) show unusual electrical and magnetic properties[1—3] which are undoubtedly associated[4—10] with the presence of one-dimensional stacks of the acceptor molecule within the crystal structure. Site inequivalence can lead to charge localisation and a pairwise antiferromagnetic coupling of electron spin, *i.e.*, the formation of a complex of two or more TCNQ anions which has a singlet ground state and an excited triplet state. The triplet excitation energy is usually sufficiently small that the paramagnetic state (the 'triplet exciton') can be observed by EPR spectroscopy at or below room temperature, although the fine-structure (zero-field) splitting characteristic of triplet EPR spectra is only detectable at low temperatures. The collapse of the fine structure at elevated temperatures is associated with collisions between the excitons, which can migrate through the crystal *via* weak electron exchange.[6,8]

We have recently synthesised a number of crown ether-complexed alkali-metal salts of TCNQ which exhibit powder EPR spectra at *ca.* 100 °C consisting of six weak fine-structure features, characteristic of a rhombic spin–spin interaction,[7] centred about a strong featureless absorption at *g* 2.0023. The intensity of the fine-structure features increases with increasing temperature, showing that they are due to an electronically excited triplet.

In the case of Rb^+ 18-crown-6 $TCNQ^-$, we have been able

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Table 1. Experimental[a] and calculated[b] fine-structure tensors for the $(TCNQ^-)_2$ pair in Rb^+ 18-crown-6 $TCNQ^-$ single crystal at 140 °C.

	Tensor			Principal values[c] and direction cosines			
	$X(a^*)$	$Y(b)$	$Z(c)$	x	y	z	
				214.9	84.7	−295.1	MHz
$D_{expt.}$	−136.5	0	−202.0	−0.2932	0.5495	0.7823	
	0	165.5	±78.0	±0.8080	±0.5799	∓0.1044	
	−202.0	±78.0	−24.5	0.5111	−0.6015	0.6140	
				$D = -442.7$	$E = 65.1$		MHz
				225.9	121.8	−347.7	MHz
$D_{calc.}$	−137.5	±26.9	−241.9	−0.2807	0.5928	0.7549	
	±26.9	180.8	±86.2	±0.8117	±0.5663	∓0.1429	
	−241.9	±86.2	−43.3	0.5121	−0.5727	0.6401	
				$D = -522$	$E = 52$		MHz

[a] $g\mu_B\Delta H/3$ in MHz, where $g = 2.00227$, μ_B is the Bohr magneton, and ΔH is the fine-structure splitting. [b] Calculated for the actual geometry of the pair and the unpaired spin densities of ref. 13 using the relation[9] $D_{pq} = \frac{1}{2}g^2 \mu_B{}^2 \Sigma o_i o_j (r^2{}_{ij}\delta_{pq} - 3p_{ij}q_{ij})r_{ij}{}^{-5}$. [c] Units of MHz.

to obtain single crystals sufficiently large to determine the structure by X-ray crystallography‡ and to establish the fine-structure anisotropy by EPR spectroscopy. The solid-state structure is characterized (Figure 1) by isolated pairs of nearly planar TCNQ units that are related by inversion and separated by 3.23 Å along the line joining their centres. The constituent TCNQ units are displaced only 9° from the perpendicular to their least-squares planes,[11] with one nitrogen only from each end of a TCNQ co-ordinated to a crown ether-complexed Rb cation. Bond distances in the TCNQ moieties are appropriate for $TCNQ^-$, rather than for $TCNQ^0$ or $TCNQ^{-1/2}$. This arrangement of close pairs of anions is distinct from the stacking pattern which is typical of many ion-radical salts.[4—10] Furthermore, the constituents of the $(TCNQ^-)_2$ pair have nearly perfect ring overlap (Figure 1).

EPR measurements made on single crystals of established structure can be used[12] to locate the principal directions of the spin–spin tensor, and thus help to establish which acceptor molecules constitute a given triplet. Surprisingly little work of this nature has been undertaken, although it is clearly much more definitive[9] than attempts to correlate observed principal values with those calculated from assumed spin distributions on the constituent radicals.

Table 1 gives the measured spin–spin interaction tensor in the orthogonal XYZ (a^*bc) axis system of the monoclinic ($A2/n$) crystal, together with the principal values and directions in the same axis system. Figure 2 shows the EPR spectrum as a function of angle in the only plane (YZ) which showed significant site-splitting. g Anisotropy was negligible both for the species exhibiting fine structure splitting (**A**) and for the carrier (**B**) of the strong central feature.

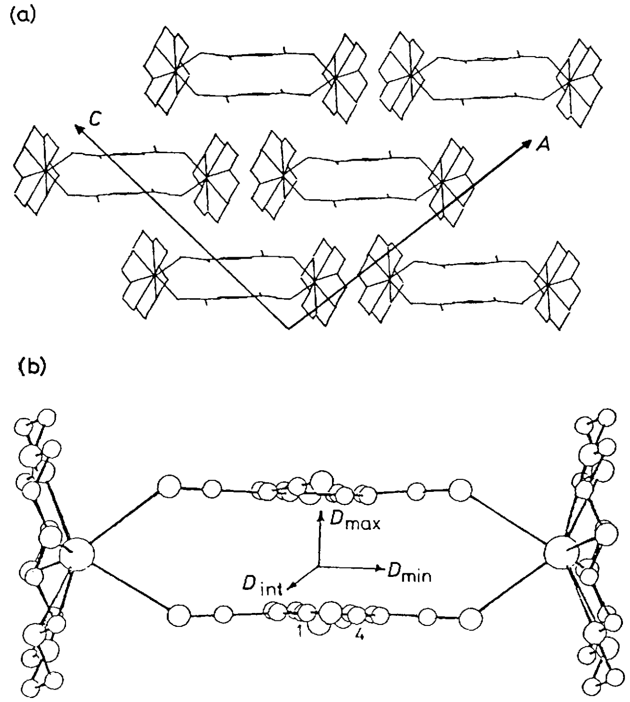

Figure 1. (a) Packing arrangement present in (**1**), showing the brickwork lattice of dimers; (b) structure of the TCNQ dimer pair showing the orientation dependence of the EPR signal.

Consideration of the measured principal directions of the fine-structure tensor shows that they all lie only 3° from certain directions within a close pair, namely the line joining the centres of each constituent $TCNQ^-$, the long axis of both constituents, and the cross-product of those directions [Figure (1b)]. For a perfectly overlapped pair, these are the expected principal directions of the spin–spin tensor. The calculated principal directions for an assumed spin-density distribution[13] in $TCNQ^-$ and the crystallographically established geometry are in even better agreement with the experimental values (Table 1). We can therefore assign the triplet exciton with

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‡ *Crystal data:* a crystal measuring 0.3 × 0.3 × 1.1 mm was mounted on an Enraf-Nonius CAD-4F diffractometer equipped with Cu-K_α radiation (λ = 1.5418 Å). $C_{24}H_{28}N_4O_6Rb$. Space group $A2/n$ (a non-standard setting of $C2/c$), monoclinic, a = 27.028(6), b = 8.239(4), c = 24.430(7) Å, β = 99.60°, Z = 8, D_c = 1.37 g cm^{-3}, U = 5363 Å^3. Data were collected in an ω–2θ scan mode from 1 to 75° (2θ) to yield 5525 unique reflections of which 2946 were considered observed having $I > 3\sigma(I)$. The structure was solved using SHELXS-86 (G. M. Sheldrick, 'Crystallographic Computing, 3' eds. G. M. Sheldrick, C. Krüger, and R. Goddard, Oxford University Press, 1985, pp. 175—189) and refined by least-squares techniques to give a final R = 8.52% (R_w = 8.91%). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

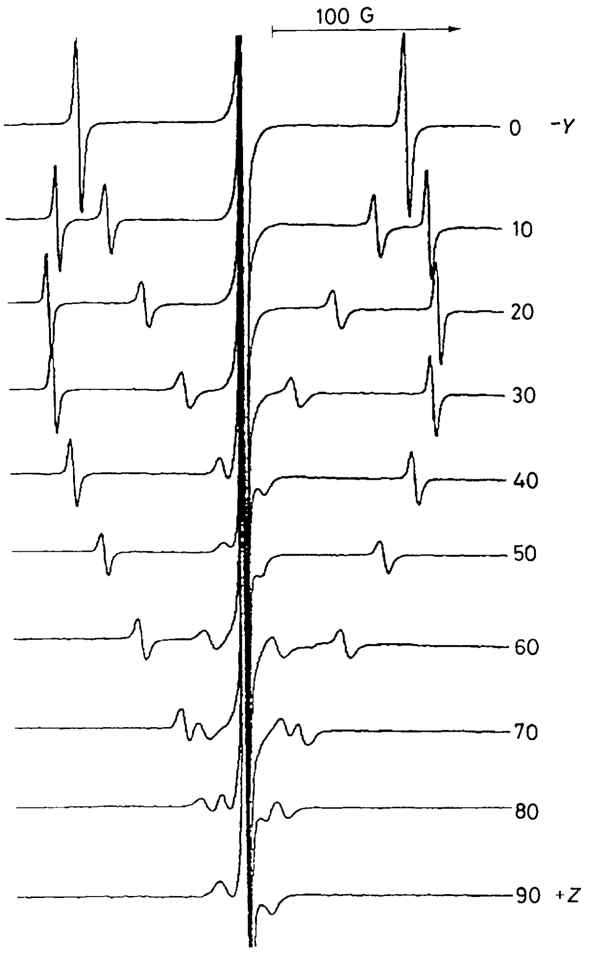

Figure 2. First-derivative EPR spectra as a function of angular displacement from $-Y$ in the YZ plane of an Rb$^+$ 18-crown-6 TCNQ$^-$ crystal (1 G = 10^{-4} T).

considerable confidence to a localised pair of radicals consisting of nearest-neighbour anions. The estimated (Table 1) principal values are some 18% higher than observed. We ascribe this discrepancy to inadequacies of the point-dipole approximation rather than to a sharing[14] or extension[9] of the exciton to neighbouring pairs. The close correlation of principal directions with crystal directions shows that the triplet **A** approximates a pure Frenkel exciton.

Line intensities were measured using the product of height and the square of the line width. From the temperature dependence of the spectral intensity of **A** we estimate a singlet–triplet energy separation (J) of 3082 ± 27 cm^{-1}, a value which contradicts the widely held belief that good ring overlap in a pair of TCNQ units is not conducive to efficient electron exchange.[9,10,15] The temperature dependence of the central spectral feature shows that it also is due to an excited triplet state (**B**; J 1464 ± 120 cm^{-1}) with minimal contamination from doublet species. Evidently, this is a migrating triplet exciton.

Electrical measurements reveal that Rb$^+$ 18-crown-6 TCNQ$^{\cdot-}$ has much lower conductivity ($\sigma_{293\,\text{K}}$ 1.8 $\times 10^{-8}$, $\Delta\varepsilon$ 0.96 eV, compressed powder) than RbTCNQ itself and a.c. dielectric spectroscopic measurements (over the range 10^4—10^{-3} Hz) indicate low-frequency dispersive behaviour and suggest that the crown ether complex is an ionic rather than an electronic conductor. The magnetic properties of this material are currently under investigation.

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