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N-CARBENIOPYRIDINIUM SALTS: CHARGE-TRANSFER COMPLEXES WITH THE $C_5(COOMe)_5$ ANION; C—C BOND FORMATION WITH THE TCNQ RADICAL ANION

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N-[2,3-Bis(dimethylamino)cyclopropenylio]- and N-(tetramethylamidinio)pyridinium salts (trifluoromethanesulphonates and tetrafluoroborates) form 1:1 and 1:2 charge-transfer complexes with the pentakis(methoxycarbonyl)cyclopentadienide anion. The x-ray crystal structures of 1-[2,3-bis(dimethylamino)cyclopropenylio]pyridinium pentakis(methoxycarbonyl)cyclopentadienide tetrafluoroborate hydrate and of 1-[2,3-bis(dimethylamino)cyclopropenylio]pyridinium bis[pentakis(methoxycarbonyl)cyclopentadienide] were determined. In constrast, the tetracyano-*p*-quinodimethane (TCNQ) radical anion reacts with the first-mentioned salts by C—C bond formation to give novel dicationic salts. Thereby, the radical anion attacks the pyridinium γ-position of the N-(tetramethylamidinio)pyridinium dication, but the three-membered ring of the N-[2,3-bis(dimethylamino)cyclopropenylio]pyridinium system.

INTRODUCTION

N-Carbeniopyridinium salts such as **1** and **2** (Scheme 1) may react with nucleophiles at either the α- or γ-position of the pyridinium ring or at the (C_5N^+)-C^+ atom. With resonance-stabilized carbanions as nucleophiles, α- and C^+-attack at **1a**,[1] but α- and γ-attack at **2a**,[2] are observed. It appears that these cases of ambifunctional reactivity cannot be interpreted satisfactorily by the concept of charge vs orbital control; rather, some findings suggest that acceptor–donor complexes between the respective dication and the anionic carbon nucleophile have a decisive influence on the reaction pathway[3] (it has been suggested that similar acceptor–donor complexes are on the reaction pathway to C—C bond formation between simple pyridinium ions and enolates[4]).

In order to shed light on the question of which of the two cationic subunits in dications **1a** and **b** provides the more favourable interaction with an approaching resonance-stabilized carbanion, we decided to synthesize salts of these dications with carbanions of low nucleophilicity, namely pentakis(methoxycarbonyl)cyclopentadienide $\{[C_5(COOMe)_5]^-\}$ and the tetracyano-*p*-quinodimethane (TCNQ) radical anion, and to examine the spectral and structural properties of these model systems.

Pentakis(methoxycarbonyl)cyclopentadienide has been the counter ion in a number of salts with organic cations, such as tropylium,[5] pyrylium,[5] pyridinium,[5,6] quinolinium[5] and tetralkylammonium.[7] The salts with the planar organic cations have been characterized spectroscopically as charge-transfer (CT) complexes.[5,8] The crystal structure of the tropylium complex is characterized by infinite columns of interleaved cations and anions with an interplanar spacing of ca 3·5 Å.[9] On the other hand, no close cation–anion contacts were observed in the crystal structure of $Me_4N^+ [C_5(COOMe)_5]^-$.[7]

The TCNQ radical anion forms charge-transfer complexes with a number of onium cations, including pyridinium and quinolinium ions.[10] On the other hand, the parent tropylium ion[10,11] and certain of its derivatives[11] undergo C—C bond formation with $TCNQ^{-\cdot}$, whereas other substituted tropylium ions again form CT complexes.[11] The reduction potentials of the tropylium ions play an important role in determining the reaction pathway.[11]

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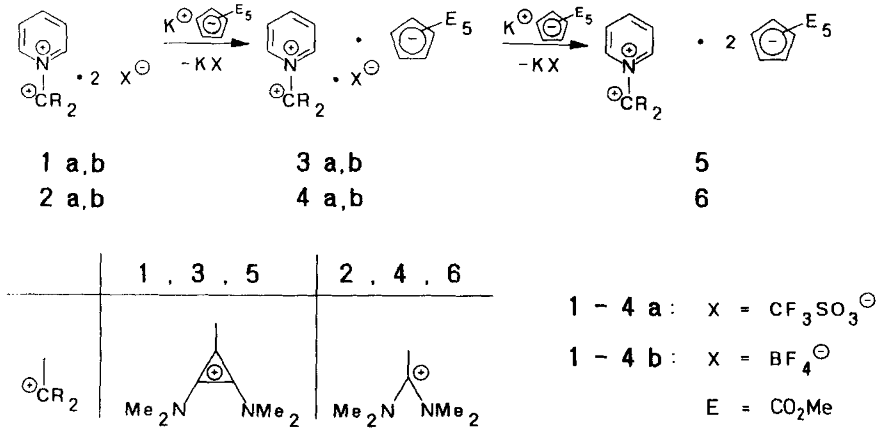
RESULTS AND DISCUSSION

Charge-transfer complexes with $[C_5(COOMe)_5]^-$

When *N*-[2,3-bis(dimethylamino)cyclopropenylio]pyridinium ditriflate (**1a**) is added to a suspension of $K[C_5(COOMe)_5]$ in acetone in a 1 : 1 ratio, a yellow precipitate of the mixed salt **3a** is formed. On the other hand, a 1 : 2 molar ratio of the reactants cleanly yields the dication dicyclopentadienide (**5**). Anion exchange in the ditriflate **1a** with $Bu_4N^+BF_4^-$ provides the *N*-cyclopropenylio-pyridinium bis(tetrafluoroborate) **1b**. In complete analogy with **1a**, this salt reacts with $K[C_5(COOMe)_5]$ to produce **3b** and **5**, respectively. On the other hand, combination of *N*-(tetramethylamidinio)pyridinium ditriflate (**2a**) and $K[C_5(COOMe)_5]$ according to the procedure described above does not give access to isolable metathesis products **4a** and **6**, respectively. If, however, the BF_4^- salt **2b** is used instead of the ditriflate **2a**, precipitates of **4b** and **6**, respectively, are formed. In both cases, coprecipitated KBF_4 can be removed largely, but not completely, by repeated recrystallization.

Salts **3a**, **3b**, **4b**, **5** and **6** represent CT complexes which also exist in solution. In the UV–visible spectra, a low-intensity, broad absorption, which is not present in the starting materials, is considered to be the CT band. The molar absorptivity of this absorption is concentration dependent; in the case of **3a**, **3b** and **5**, the position of this band also varies slightly depending on the concentration (Table 1). The absorption appears



Scheme 1

Table 1. UV–visible spectra of CT complexes 3–6 (in acetonitrile)

		CT band		
Compound	λ_{max}(nm) (log ε)	Concentration (mol l^{-1})	λ_{max} (nm)	ε (l mol^{-1} cm^{-1})
3a[a]	216(4·07), 258(4·36), 291(4·06), 334(3·69)	3·297	424[b]	446
		2·454	415	439
		1·648	406	427
5	216(4·10), 258(4·89), 291(4·49), 334(3·81)	2·785	426	483
		1·946	416	471
		1·392	405	447
4b	258(4·47), 291(3·93)	6·849	426	136
		4·714	426	129
		3·425	426	112
6	258(4·99), 291(4·42)	5·054	426	154
		4·358	426	148
		2·527	426	127

[a] Spectra of **3a** and **3b** are identical.

[b] ±5 nm. The band appears as a shoulder in the absorption band at λ_{max} = 334 nm.

at significantly longer wavelength than in *N*-methylpyridinium pentakis(methoxycarbonyl)cyclopentadienide.[5] The CT interactions appear to be the same in both the 1 : 1 and 1 : 2 complexes, since the position of the CT band is not affected and a new absorption does not become visible on going from 1 : 1 to the 1 : 2 complex. The latter argument must be used with care, however; such an absorption may be covered by the stronger short-wavelength absorptions of the system. In fact, it has been suggested that this is the case for triphenylcylopropenylium pentakis(methoxycarbonyl)cyclopentadienide.[5]

In the ^{1}H NMR spectra of **3**–**6**, small but significant high-field shifts with respect to the precursor salts are found for all signals (Table 2). That these changes are indeed due to the formation of 1 : 1 and 1 : 2 complexes is exemplified by Figure 1: addition of increasing amounts of $[C_5(COOMe)_5]^-$ to **1a** results in high-field shifts of the cation's resonance signals, until two molar equivalents of the anion are present. No significant change is observed at higher anion/cation ratios.

Formation of the complex salts **3b** and **5** also results in small high-field shifts of the ^{13}C resonances of the dication (except for N*Me*) (Table 3). It has been suggested that the ^{13}C NMR changes observed on formation of CT complexes between aromatic donors and acceptors result both from charge transfer and from anisotropy effects, as is the case in ^{1}H NMR spectroscopy.[12]

If the anionic donor is to interact with either one of the two cationic subunits of the acceptor part of **3** or **4**, arrangements such as **7A** and **7B** seem likely, in which the planar rings of both the acceptor and the donor assume an approximately parallel orientation (Figure 2). The second donor molecule may coordinate to the same or the other cationic site, but on the opposite face. Further, an arrangement according to **7C** is conceivable for the 1 : 2 complex **5**. Such a structure is impossible for **6**, since the two rings of the *N*-(tetramethylamidinio)pyridinium dication cannot be coplanar for steric reasons.[3]

The NMR data (Tables 2 and 3) do not allow one to

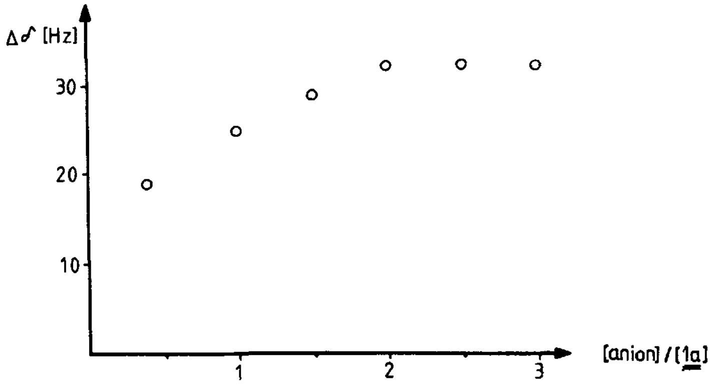


Figure 1. High-field shifts (Δδ) of δ(2,6-H) of **1a** on addition of $K[C_5(COOMe)_5]$ (in CD_3CN, [**1a**] = 0.05 mol l^{-1})

Table 2. ^{1}H NMR data for **3**–**6** (CD_3CN, δ in ppm, TMS as internal standard)[a]

	pyridinium				
Compound	NMe$_2$	3,5-H	4-H	2,6-H	COOMe
3a	3·30, 3·36	8·16	8·66	8·80	3·60
	(−0·08, −0·08)	(−0·17)	(−0·21)	(−0·33)	(−0·10)
3b	3·23, 3·33	8·10	8·63	8·75	3·60
	(−0·15, −0·11)	(−0·23)	(−0·24)	(−0·38)	(−0·10)
5	3·20, 3·30	7·97	8·53	8·62	3·57
	(−0·18, −0·14)	(−0·36)	(−0·34)	(−0·51)	(−0·13)
4b	2·87, 3·46	8·33	8·80–9·10[b]		3·63
	(−0·10, −0·11)	(−0·17)			(−0·07)
6	2·80, 3·40	8·25	8·77–9·00[b]		3·65
	(−0·17, −0·17)	(−0·25)			(−0·05)

[a] In parentheses: Δδ values with respect to the precursor salts.
[b] Values for **2b**: 8·83–9·27 ppm.

Table 3. ^{13}C NMR data for **1b**, **3b** and **5** (CD_3CN), δ in ppm, TMS as internal standard)

	C_3^+ ring			C_5N^+ ring			Anion		
Compound	NMe_2	C-1′	C-2′,3′	C-2,6	C-3,5	C-4	C-ring	OMe	C=O
1b	44·2 44·5	99·4	131·7	146·0	130·5	151·2			
3b	44·1 44·4	99·0	129·6	144·5	129·9	149·8	117·4	51·9	168·0
5	44·2	98·9	128·8	144·3	128·9	149·3	117·8	51·8	167·9

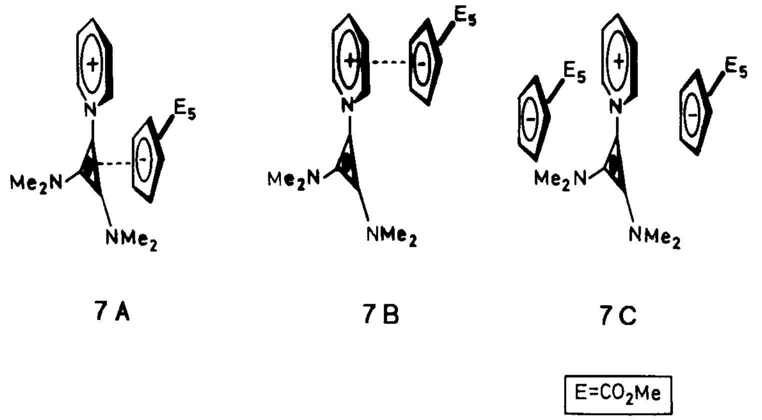


Figure 2. Structures of **7A–C**

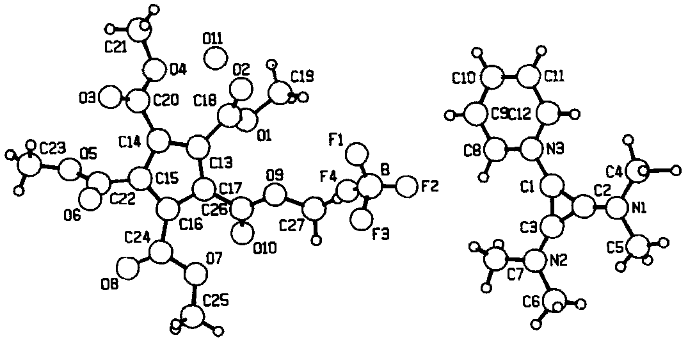


Figure 3. PLUTO plot of complex salt **3b**·H_2O; O-11 belongs to the water molecule

distinguish between structures such as **7A–C**. Further, equilibration of such structures is likely to occur on the NMR time scale.

X-ray crystal structures of 3b and 5

Suitable crystals of **3b** were obtained by slow evaporation of a solution in acetone. Thereby, **3b** crystallizes with one molecule of water per formula unit. Crystals of **5** were obtained from acetone.

Plots of the two complexes are given in Figures 3 and 4. Heavy-atom parameters are listed in Tables 4 and 5 and some relevant structural data in Table 6.

The most important feature to be discussed here is the shapes of both the dications and the anions. The cyclopropenylium and the pyridinium rings in the two dications are more or less close to coplanarity, the interplanar angle being 2·0° for **3b** and 17·1° for **5**. The NMe_2 planes are only slightly tilted against the plane of the three-membered ring (**3b**, 2·3° and 2·3°;

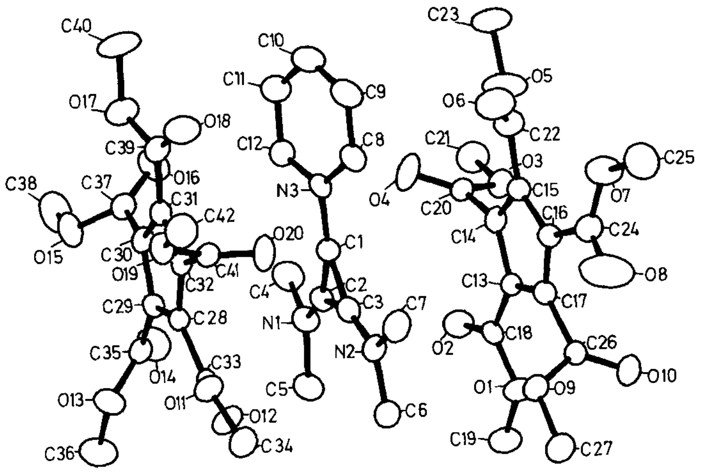


Figure 4. ORTEP plot of complex salt **5**

Table 4. Positional parameters of heavy atoms in **3b**·H_2O (estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
F1	0·3612(4)	0·5204(10)	0·8049	C7	0·4660(3)	0·3072(13)	0·0844(6)
F2	0·4213(3)	0·6496(14)	0·7367(10)	C8	0·4690(3)	0·3291(13)	0·3215(6)
F3	0·3688(5)	0·5168(13)	0·6642(5)	C9	0·4953(3)	0·2910(13)	0·3953(6)
F4	0·3459(3)	0·7403(10)	0·7222(8)	C10	0·4752(3)	0·3296(11)	0·4758(6)
O1	0·2935(2)	0·2265(6)	0·3612(4)	C11	0·4281(3)	0·4077(11)	0·4808(6)
O2	0·2954(2)	0·0205(7)	−0·4309(4)	C12	0·4016(3)	0·4383(11)	0·4037(5)
O3	0·4548(2)	0·2098(7)	−0·4088(4)	C13	0·3484(3)	0·0193(9)	0·3035(4)
O4	0·4047(2)	0·0091(7)	−0·4675(3)	C14	0·3964(3)	−0·0578(8)	0·3167(5)
O5	0·5064(2)	0·0823(6)	−0·2494(4)	C15	0·4175(2)	−0·0943(8)	0·2348(5)
O6	0·4747(2)	0·3180(7)	−0·1896(4)	C16	0·3833(2)	−0·0409(9)	0·1698(5)
O7	0·3458(2)	0·0685(8)	−0·0305(3)	C17	0·3403(2)	0·0333(8)	0·2137(5)
O8	0·4307(2)	0·0920(9)	−0·0395(4)	C18	0·3110(3)	0·0673(9)	0·3723(5)
O9	0·2514(2)	0·0429(6)	0·2053(4)	C19	0·2532(4)	0·2783(11)	0·4207(7)
O10	0·2953(2)	0·2199(6)	0·1177(4)	C20	0·4225(2)	−0·1016(9)	0·4010(5)
N1	0·3094(2)	0·5793(7)	0·2058(4)	C21	0·4243(4)	−0·0512(15)	0·5527(6)
N2	0·4149(2)	0·3845(9)	0·0845(4)	C22	0·4680(2)	−0·1805(9)	0·2219(5)
N3	0·4221(2)	0·4007(7)	0·3257(4)	C23	0·5554(3)	−0·1627(14)	0·2591(7)
C1	0·3948(2)	0·4339(8)	0·2482(5)	C24	0·3904(3)	−0·0693(10)	0·0761(5)
C2	0·3530(2)	0·4984(9)	0·2060(5)	C25	0·3484(4)	−0·0927(14)	−0·0615(6)
C3	0·3938(3)	0·4238(9)	0·1596(5)	C26	0·2946(3)	0·1095(9)	0·1724(5)
C4	0·2834(3)	0·6292(11)	0·2879(6)	C27	0·2039(3)	0·1187(13)	0·1754(8)
C5	0·2811(3)	0·6114(11)	0·1243(6)	B	0·3763(4)	0·6093(13)	0·7352(7)
C6	0·3890(4)	0·4127(14)	−0·0004(6)	O11	0·3215(2)	−0·3421(8)	0·5006(4)

5, 9·0° and 6·7°). This arrangement seems not to be enforced by the packing in the crystal, since a similar geometry has been found in the crystal structure of **1a**, which has totally different anions.[3]

None of the cyclopentadienide rings deviates significantly from planarity. The ester side-groups assume conformations with respect to the ring plane, for which the following seemingly irregular sequences of interplanar angles between O=C—O and the C_5 ring were found: **3b**, 21·7, 66·0, 22·6, 127·4, 128·6°; **5**, 6·7, 90·6, 16·3, 36·3, 75·2° and 13·5, 78·6, 27·6, 46·3, 55·8°. Interestingly, a similar sequence to that for **5**, although with values differing from ours by up to ca 14°, has been found in another crystal structure containing this anion.[7] In both that structure and ours, specific interactions between the ester groups and the cation do not exist.

In the crystal structures of **3b** and **5**, the rings of the dication and of the organic anion are in an approximately parallel orientation. The crystal of

Table 5. Positional parameters of heavy atoms in **5** (estimated standard deviations in parentheses)

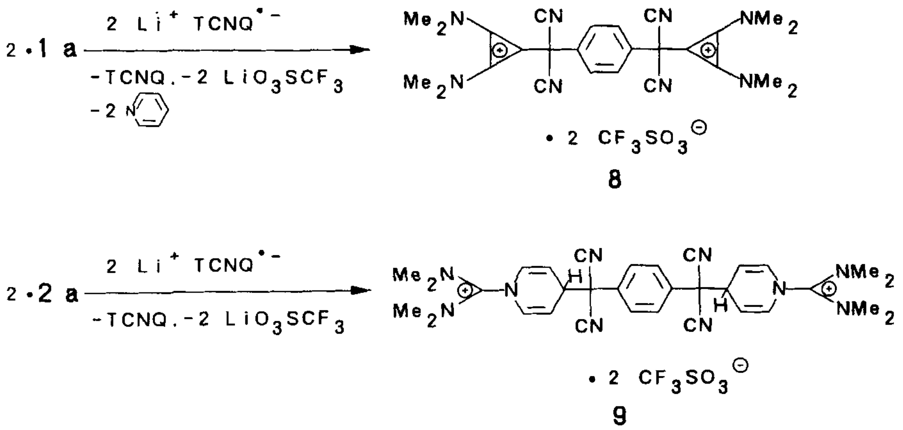
Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O1	0·3459(2)	0·4545(2)	0·2410	C11	0·5011(4)	0·0669(3)	0·2840(5)
O2	0·3057(2)	0·3536(2)	0·2967(4)	C12	0·4587(3)	0·1127(3)	0·2282(4)
O3	0·3742(2)	0·2931(2)	0·5035(3)	C13	0·4354(3)	0·3849(2)	0·3212(4)
O4	0·4100(3)	0·2176(2)	0·3844(4)	C14	0·4634(3)	0·3286(2)	0·3783(4)
O5	0·5603(2)	0·2508(2)	0·5158(4)	C15	0·5422(3)	0·3354(2)	0·3930(4)
O6	0·6567(2)	0·2707(2)	0·4072(4)	C16	0·5653(3)	0·3972(2)	0·3428(4)
O7	0·6886(2)	0·4095(2)	0·4128(4)	C17	0·4999(3)	0·4265(2)	0·3013(4)
O8	0·6540(3)	0·4809(3)	0·2928(5)	C18	0·3568(3)	0·3939(2)	0·2863(4)
O9	0·5064(3)	0·4900(2)	0·1456(3)	C19	0·2704(4)	0·4699(3)	0·2059(6)
O10	0·4871(3)	0·5465(2)	0·2959(3)	C20	0·4144(3)	0·2732(2)	0·4192(4)
O11	0·4715(2)	0·2305(2)	−0·2166(3)	C21	0·3227(3)	0·2444(3)	0·5481(5)
O12	0·3541(2)	0·2511(2)	−0·1544(3)	C22	0·5930(3)	0·2865(3)	0·4416(5)
O13	0·2599(2)	0·1322(2)	−0·1971(3)	C23	0·6034(4)	0·1983(3)	0·5648(6)
O14	0·2213(2)	0·1187(2)	−0·0309(4)	C24	0·6392(3)	0·4329(3)	0·3463(5)
O15	0·2853(2)	−0·0208(2)	−0·0080(3)	C25	0·7621(4)	0·4422(4)	0·4180(7)
O16	0·3398(2)	0·0043(2)	0·1464(3)	C26	0·4976(3)	0·4940(3)	0·2507(4)
O17	0·4970(2)	−0·0373(2)	0·0718(4)	C27	0·5050(5)	0·5525(3)	0·0873(5)
O18	0·5916(2)	0·0371(2)	0·0462(4)	C28	0·4163(3)	0·1488(2)	−0·1086(4)
O19	0·6018(2)	0·1104(2)	−0·1608(3)	C29	0·3535(3)	0·1098(2)	−0·0722(4)
O20	0·5914(2)	0·1920(2)	−0·0397(4)	C30	0·3837(3)	0·0572(2)	−0·0101(4)
N1	0·2991(2)	0·2308(2)	0·1275(4)	C31	0·4665(3)	0·0634(2)	−0·0101(4)
N2	0·4649(2)	0·3291(2)	0·0435(4)	C32	0·4845(3)	0·1201(2)	−0·0734(4)
N3	0·4912(2)	0·1715(2)	0·2007(3)	C33	0·4082(3)	0·2147(2)	−0·1619(4)
C1	0·4449(3)	0·2183(2)	0·1489(4)	C34	0·4756(4)	0·2971(3)	−0·2578(5)
C2	0·3722(3)	0·2389(3)	0·1229(4)	C35	0·2726(3)	0·1208(2)	−0·0941(4)
C3	0·4377(3)	0·2766(3)	0·0901(4)	C36	0·1826(4)	0·1491(4)	−0·2265(7)
C4	0·2638(3)	0·1801(3)	0·1971(5)	C37	0·3367(3)	0·0105(3)	0·0514(5)
C5	0·2474(3)	0·2746(3)	0·0696(5)	C38	0·2245(4)	−0·0544(4)	0·0458(6)
C6	0·4137(3)	0·3799(3)	−0·0001(5)	C39	0·5250(3)	0·0221(3)	0·0368(4)
C7	0·5476(3)	0·3424(3)	0·0414(5)	C40	0·5519(4)	−0·0807(3)	0·1256(7)
C8	0·5644(3)	0·1867(3)	0·2272(5)	C41	0·5635(3)	0·1455(2)	−0·0882(4)
C9	0·6082(3)	0·1408(3)	0·2813(5)	C42	0·6821(3)	0·1243(3)	−0·1715(6)
C10	0·5757(4)	0·0811(3)	0·3109(5)				

3b·H_2O consists of infinite stacks in which dications and cyclopentadienide rings alternate in a sandwich-type manner (Figure 5). The BF_4^- ions are between these columns, and the water molecule is associated with a C=O group and a BF_4^- anion by hydrogen bonds [O-11···O-2, 2·831(7) Å; O-11···F-3, 2·98(1)Å]. In the stacks, it is the cyclopropenylium and not the pyridinium ring which is flanked by the anionic C_5 ring with an intermolecular spacing of ca 3·39–3·46 Å (see Table 6). In the crystal of **5**, columns consisting of discrete anion–cation–anion units, as depicted in the correct orientation in Figure 4, are found (Figure 6). Within the columns, neighbouring units of this type are related by a glide plane, and the rings are oriented approximately parallel to the translational component of this symmetry element. Thus, the walls of the columns consist of cyclopentadienide rings, whereas the channels between them are filled by dications. As in **3b**·H_2O, the anions are associated with the cyclopropenylium rather than the pyridinium ring, again with an intermolecular spacing of 3·44–3·51 Å (Table 6), but the anionic rings are now shifted in the direction of the C_5N ring. Such an arrangement approaches the situation drawn schematically as **7C** (Figure 2).

According to the intermolecular spacing, **3b** and **5** represent weak donor–acceptor complexes. Obviously, the orientation of the ester groups with respect to the C_5 ring prevents a closer approach of the latter to the dication.

C—C bond formation with the TCNQ radical anion

When equimolar amounts of **1a**, or **2a**, and LiTCNQ are combined, no isolable charge-transfer complexes are obtained. Rather, the novel dicationic salts **8** and **9** are formed (Scheme 2), the constitution of which follows from their elemental analysis and ^1H NMR data (see Experimental). Surprisingly, the C≡N stretching vibration in the IR spectrum is found at 2185 cm^{-1} for **8** and at 2195 cm^{-1} for **9**, i.e. not different from $TCNQ^{-\bullet}$.



Scheme 2

Table 6. Selected structural features of salts **3b**·H_2O and **5**

	Bond length (Å)			Bond length (Å)	
Bond	**3b**·H_2O	**5**	Bond	**3b**·H_2O	**5**
C-1—C-2	1·358(8)	1·368(6)	C-13—C-14	1·399(8)	1·419(6)
C-1—C-3	1·345(8)	1·381(6)	C-14—C-15	1·386(8)	1·387(6)
C-2—C-3	1·400(9)	1·424(6)	C-15—C-16	1·391(8)	1·441(6)
C-2—N-1	1·299(7)	1·282(6)	C-16—C-17	1·423(8)	1·381(6)
C-3—N-2	1·299(8)	1·289(5)	C-17—C-13	1·380(8)	1·415(6)
C-1—N-3	1·395(8)	1·394(5)	C-13—C-18	1·473(8)	1·447(6)
N-3—C-8	1·342(8)	1·350(6)	C-14—C-20	1·486(8)	1·485(6)
C-8—C-9	1·345(10)	1·371(7)	C-15—C-22	1·487(7)	1·450(6)
C-9—C-10	1·359(11)	1·367(7)	C-16—C-24	1·450(8)	1·468(6)
C-10—C-11	1·372(10)	1·370(8)	C-17—C-26	1·470(8)	1·487(6)
C-11—C-12	1·376(9)	1·367(7)	C=O	1·195(7)	1·193(5)
C-12—N-3	1·328(8)	1·343(6)		–1·204(7)	–1·211(5)[a]

	Interplanar angles (°)[b]	
	3b·H_2O	**5**
C_3 ring/C_5N ring	1·9	17·1
C_3 ring/C_5 ring	3·0	7·2, 2·9[c]
C_5N ring/C_5 ring	2·1	9·9, 18·3[c]

	Distance (Å) of some ring atoms of cation from C_5 ring plane of anion	
	3b·H_2O	**5**
C_5 ring—C-1	3·463	3·505, 3·439[c]
—C-2	3·439	3·388, 3·467
—C-3	3·394	3·563, 3·508
—N-3	3·534	3·523, 3·395

[a] Range is given for the two anions, except O-6—C-22 [1·230(6) Å].

[b] Only ring planes within the same molecular complex are considered.

[c] First value, ring C-13—C-18; second value, ring C-28—C-32.

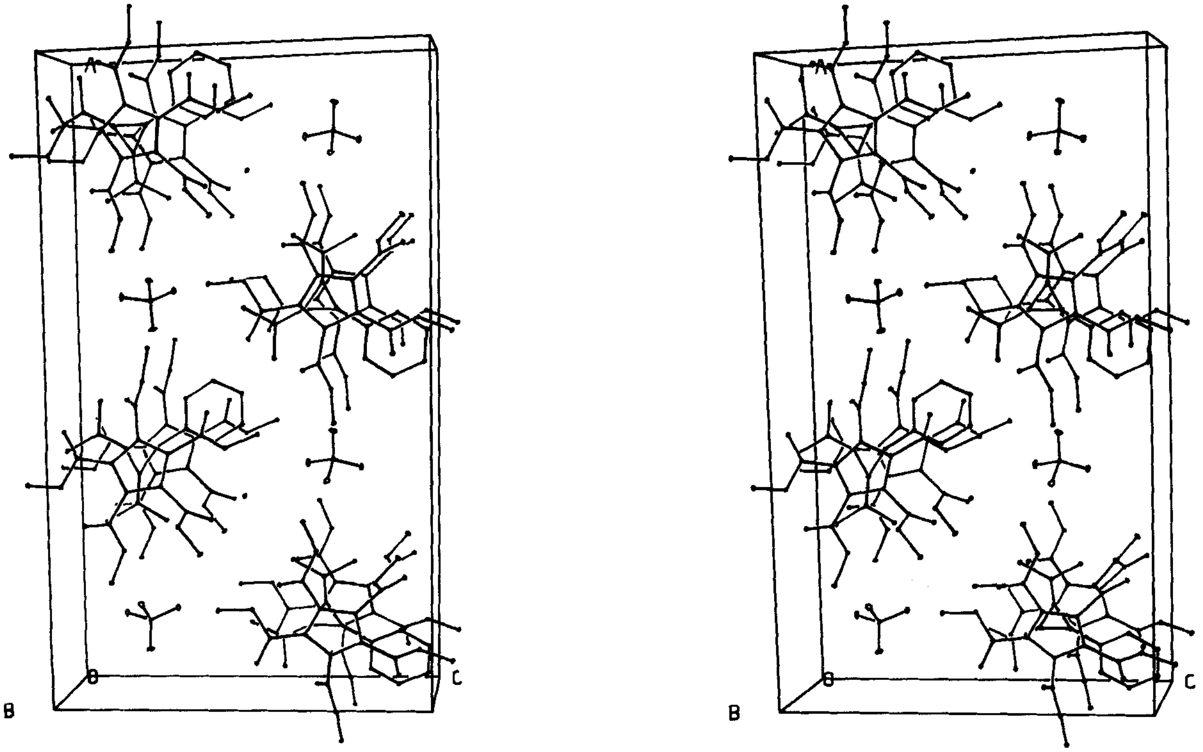


Figure 5. Stereoview of the unit cell of **3b**·H_2O

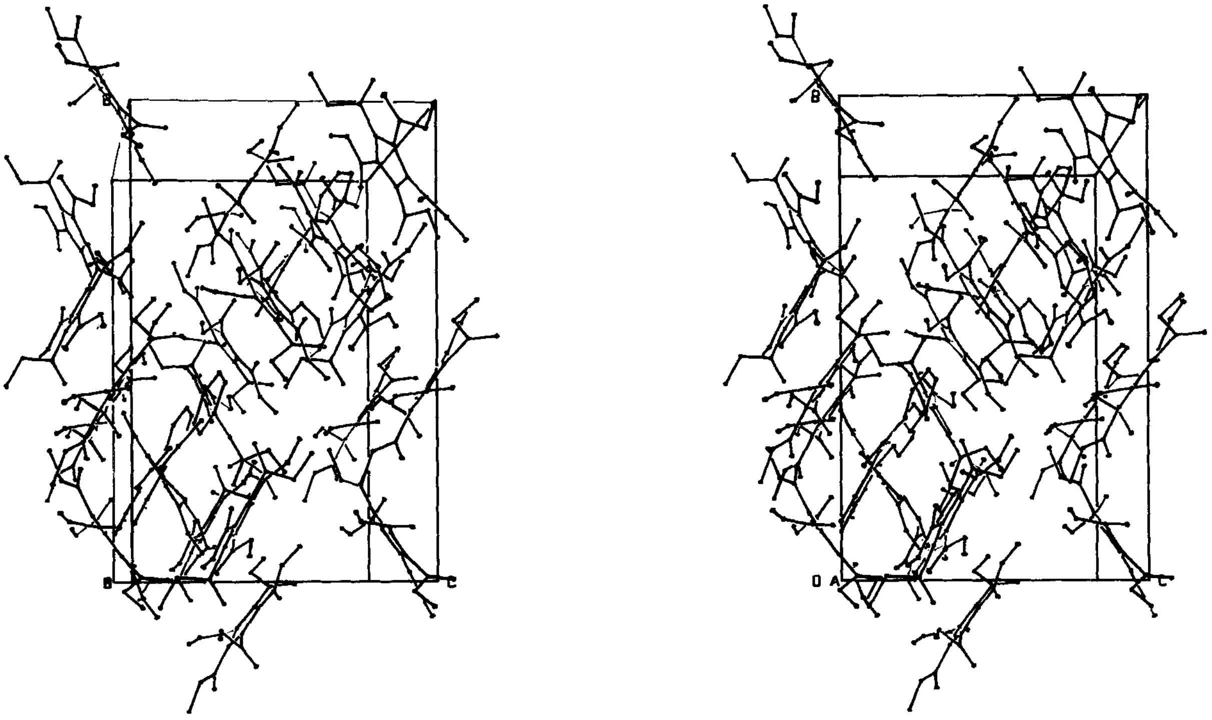


Figure 6. Stereoview of the unit cell of **5**

Salt **8** results from an addition–elimination reaction of TCNQ$^{-\cdot}$ at the three-membered ring of **1a**, whereas with **2a** attack at the γ-position of the pyridinium ring occurs to form a 1-carbenio-1,4-dihydropyridine derivative. C—C bond formation between TCNQ$^{-\cdot}$ and organic cations has been observed before, namely for certain tropylium ions which in general had a reduction potential E^{red} (vs SCE) $\geqslant -0{\cdot}2$ V.[11] Two possible pathways have been proposed, one in which the TCNQ$^{-\cdot}$ attacks the cation as an anionic nucleophile (the missing electron for the two-fold reaction being transferred from a second TCNQ radical anion), and another which begins with electron transfer from TCNQ$^{-\cdot}$ to the dication, followed by C—C coupling of the radical pair thus formed.[10,11] The fact that mainly tropylium ions with a high E^{red} undergo the chemical reaction, whereas others form CT complexes, favours the electron transfer pathway. Therefore, we became interested in the first reduction potential of dications **1** and **2**.

Cyclic voltammograms of **1b** and **2b** indicated that electron transfer was not reversible. Reduction of both dications to the radical cations by transfer of one electron was followed by a fast reaction so that the true E_1^{red} could not be obtained. The following peak potentials for this step were found:

	1b	**2b**
$E_1^{\text{pk,cat}}$ vs ferrocene (V)	$-0{\cdot}73$	$-0{\cdot}90$
[corresponding to $E_1^{\text{pk,cat}}$ vs SCE (V)	$-0{\cdot}35$	$-0{\cdot}52$]

These values are markedly less negative than that of the *N*-methylpyridinium ion ($-1{\cdot}28$ V vs SCE[13]), a fact which can certainly be attributed to the presence of a second positive charge. Since the *N*-methylpyridinium ion forms a stable CT complex with TCNQ$^{-\cdot}$,[10] whereas **1b** and **2b** undergo a chemical reaction, a similar correlation between reduction potential and behaviour towards TCNQ$^{-\cdot}$ as mentioned above for tropylium ions seems to exist for the pyridinium salts. However, it must be pointed out that related cations with comparable or higher peak potentials than **1b** and **2b**, namely *N*-methylacridinium ($-0{\cdot}41$ V vs SCE) and *N*-methylphenazinium ($-0{\cdot}11$ V vs SCE), also form stable CT complexes with TCNQ$^{-\cdot}$.[13] Therefore, it is unlikely that **1** and **2** react with TCNQ$^{-\cdot}$ through an initial electron transfer to the respective dication. Rather, the TCNQ radical anion behaves as a simple nucleophile and the regioselectivity of nucleophilic attack fits the picture obtained with other carbon nucleophiles.[1–3]

EXPERIMENTAL

^{1}H NMR spectra were recorded with Varian EM 390 (90 MHz) and Bruker WP 200 (200 MHz) instruments with TMS as internal standard and ^{13}C NMR spectra with a Bruker WP 200 (50·28 MHz) instrument. IR spectra were measured with a Perkin-Elmer IR 397 and UV–visible spectra with a GCA/McPerson EU 700-32 instrument. For elemental analyses a Perkin–Elmer EA 240 apparatus was used. For x-ray diffraction measurements, an Enraf-Nonius CAD4 diffractometer with monochromatized Cu Kα radiation was employed.

All syntheses were carried out in dried solvents. The following compounds were prepared according to literature procedures: **1a**,[1a] **2a**,[2] potassium pentakis(methoxycarbonyl)cyclopentadienide[14] and LiTCNQ.[10] Other syntheses were carried out as described below.

1-[2,3-Bis(dimethylamino)cyclopropenylio]pyridinium bis(tetrafluoroborate) (1b). A solution of tetrabutylammonium tetrafluoroborate (6·59 g, 20·0 mmol) and of **1a** (2·51 g, 5·0 mmol) in acetonitrile (50 mmol) is stirred for 1 h, then the product is precipitated by addition of diethyl ether; colourless crystals (1·60 g, 85%), m.p. 189–190 °C. UV (acetonitrile): $\lambda_{\max}$ 216 nm ($\log\varepsilon = 4{\cdot}08$), 334 (3·60). IR (KBr): 1943 (s, C_3 ring), 1653 (vs), 1058–1022 cm^{-1} (vs, br, BF_4). Analysis: calculated for $C_{12}H_{17}B_2F_8N_3$ (MW 376·9) C 38·24, H 4·55, N 11·15; found, C 38·2, H 4·63, N, 10·6%.

1-(Tetramethylamidinio)pyridinium bis(tetrafluoroborate) (2b). Prepared from **2a** (2·39 g, 5·0 mmol) according to the synthesis of **1b** (see above); colourless needles (1·63 g, 93%), m.p. 119 °C. UV (acetonitrile): $\lambda_{\max}$ 242 nm ($\log\varepsilon = 3{\cdot}95$). IR (KBr): 1691 (s), 1053–1029 cm^{-1} (vs, br, BF_4). Analysis calculated for $C_{10}H_{17}B_2F_8N_3$ (MW 352·9), C 34·04, H 4·86, N 11·91; found, C 33·7, H 4·90, N 11·8%.

1-[2,3-Bis(dimethylamino)cyclopropenylio]pyridinium pentakis(methoxycarbonyl)cyclopentadienide trifluoromethanesulphonate (3a). A solution of **1a** (0·501 g, 1·0 mmol) in acetone (20 ml) is added to a suspension of potassium pentakis(methoxycarbonyl)cyclopentadienide (0·394 g, 1·0 mmol) in acetone (30 ml). After stirring for 1 h, the yellow solid is filtered off and recrystallized from acetone (20 ml); orange crystals (0·631 g, 89%), m.p. 127–129 °C. IR (KBr): 1938 (m, C_3 ring), 1704 (s), 1670 (s), 1271 (s), 1220–1205 (s, br), 1159 (s), 1029 cm^{-1} (m). Analysis: calculated for $C_{28}H_{32}F_3N_3O_{13}S$ (MW 707·6), C 47·52, H 4·56, N 5·94; found, C 47·0, H 4·64, N 5·6%.

1-[2,3-Bis(dimethylamino)cyclopropenylio]pyridinium pentakis(methoxycarbonyl)cyclopentadienide tetrafluoroborate (3b). Prepared from **1b** (0·377 g, 1·0 mmol) according to the synthesis given for **3a** (see above); orange needles (0·505 g, 85%), m.p. 171–172 °C. IR (KBr): 1942 (m, C_3 ring), 1703 (vs), 1676 (vs), 1653 (s), 1050 cm^{-1} (vs, BF_4). Analysis: calculated for $C_{27}H_{32}BF_4N_3O_{10}$ (MW 645·4), C 50·25, H 5·00, N 6·51; found, C 50·2, H 5·02, N 6·4%.

1-[2,3-Bis(dimethylamino)cyclopropenylio] pyridinium pentakis(methoxycarbonyl)cyclopentadienide tetrafluoroborate hydrate (3b·H$_2$O). Salt **3b** is dissolved in acetone and the solvent is allowed to evaporate slowly; orange crystals, m.p. 150–151 °C. Analysis: calculated for $C_{27}H_{32}BF_4N_3O_{10}\cdot H_2O$ (MW 663·4), C 48·88, H 5·17, N 6·33; found C 48·7, H 4·96, N 6·3%.

1-(Tetramethylamidinio)pyridinium pentakis(methoxycarbonyl)cyclopentadienide tetrafluoroborate (4b). A solution of **2b** (0·353 g, 1·0 mmol) and potassium pentakis(methoxycarbonyl)cyclopentadienide (0·394 g, 1·0 mmol) in acetonitrile (50 ml) is stirred for 1 h. After addition of diethyl ether (20 ml), a yellow oil separates which is isolated by decanting off the supernatant liquid. The oil is dissolved in acetonitrile and the procedure is repeated three times. Drying the oil at 0·001 Torr/25 °C yields a yellow solid (0·36 g, m.p. 109–110 °C) of **4b**, which is not analytically pure, however (contamination with KBF_4 and CH_3CN).

1-[2,3-Bis(dimethylaminocyclopropenylio] pyridinium bis[pentakis(methoxycarbonyl)cyclopentadienide] (5). A solution of **1b** (0·377 g, 1·0 mmol) in acetone (20 ml) is added to a suspension of potassium pentakis (methoxycarbonyl)cyclopentadienide (0·789 g, 2·0 mmol) in acetone (30 ml) and the mixture is stirred for 1 h. The solid is filtered off and recrystallized from acetone; orange crystals (0·828 g, 91%), m.p. 152 °C. IR (KBr): 1940 (w, C_3 ring), 1706 (s), 1684 (s), 1668 (s), 1199 (vs), 1170 cm^{-1} (vs). Analysis: calculated for $C_{42}H_{47}N_3O_{20}$ (MW 913·8), C 55·20, H 5·18, N 4·60; found, C 55·0, H 5·13, N 4·6%.

1-(Tetramethylamidinio)pyridinium bis[pentakis(methoxycarbonyl)cyclopentadienide] (6). Prepared from **2b** (0·353 g, 1·0 mmol) and potassium pentakis(methoxycarbonyl)cyclopentadienide (0·789 g, 2·0 mmol) according to the procedure described for **4b**. A yellow solid (0·477 g, m.p. 118–119 °C) of **6**·0·5 KBF_4 is obtained. IR (KBr): 1712 (br, vs), 1472 (s), 1230, 1201, 1186 (all vs), 1080 (s), 1050 cm^{-1} (br, m). Analysis: calculated for $C_{40}H_{47}N_3O_{20}\cdot 0\cdot 5\ KBF_4$ (MW 952·2), C 50·45, H 4·98, N 4·41; found, C 49·9, H 4·93, N 4·2%.

1,1′-(7,7,8,8-Tetracyano-1,4-xylene-7,8-diyl)bis[2,3-bis(dimethylamino)cyclopropenylium] bis(trifluoromethanesulphonate) (8). A mixture of **1a** (0·251 g, 0·5 mmol) and LiTCNQ (0·106 g, 0·5 mmol) in acetonitrile (70 ml) is stirred until the suspension and the dark-green colour have disappeared (24 h). The product is precipitated by addition of diethyl ether as a beige powder (0·171 g, 91%), m.p. 243–245 °C. IR (KBr): 2185 (m, C≡N), 1939 (s, C_3 ring), 1628 (br, s) 1409 (s), 1280–1250 (vs, br), 1140 (s), 1028 cm^{-1} (s). ^1H NMR (CD_3CN): $\delta = 3\cdot 13$ (s, 12 H, NMe), 3·23 (s, 12 H, NMe), 8·03 ppm (s, 4 H). Analysis calculated for $C_{28}H_{28}F_6N_8O_6S_2$ (MW 750·7) C 44·80, H 3·76, N 14·93; found, C 44·7, H 3·78, N 15·1%.

1-(4-{(7,7,8,8-Tetracyano-8-[1-(tetramethylamidinio) -1,4-dihydropyridin-4-yl])-1,4-xylen-7-yl}-1,4-dihydropyridin-1-yl)tetramethylamidinium bis(trifluoromethanesulphonate) (9). A mixture of **2a** (0·239 g, 0·50 mmol) and LiTCNQ (0·106 g, 0·5 mmol) in acetonitrile (70 ml) is stirred for 1 h, when a clear solution has formed. The product is precipitated by addition of diethyl ether as a beige powder (0·144 g, 67%), m.p. 128–129 °C. IR (KBr): 2195 (m, C≡N), 1688, 1628, 1530, 1428 (all s), 1280 (vs), 1258 (vs), 1162 (s), 1030 cm^{-1} (vs). ^1H NMR (200 MHz, CD_3CN): $\delta = 2\cdot 93$ (s, 12 H, NMe), 3·09 (s, 12 H, NMe), 4·65 [m, 2 H, ^3J(3-H,4-H) = ^3J(4-H,5-H) = 3·0 Hz, 4-H, dihydropyridine], 5·42 [m, 4 H, ^3J(2-H,3-H) = ^3J(5-H,6-H) = 7·6 Hz, 3-,5-H], 6·74 (d, 4 H, 2-,6-H), 7·72 ppm (s, 4 H, aryl). Analysis: calculated for $C_{34}H_{38}F_6N_{10}O_6S_2$ (MW 860·6), C 47·43, H 4·45, N 16·27; found, C 46·3, H 4·23, N 16·1%.

X-ray crystal structure analysis of 3b·H_2O. $C_{27}H_{32}BF_4N_3O_{10}\cdot H_2O$, formula weight 663·39, orthorhombic, space group $Pca2_1$, $a = 25\cdot 930(5)$, $b = 7\cdot 891(2)$, $c = 15\cdot 145(3)$ Å, $Z = 4$, $D_{\text{calc}} = 1\cdot 422$ g cm^{-3}. Data collection: 2740 unique reflections with $4\cdot 0 \leqslant 2\theta \leqslant 130\cdot 0°$, $\omega/2\theta$ scan, scan width $(0\cdot 85 + 0\cdot 14 \tan\theta)°$, scan speed 0·85–5·03° min^{-1}; correction for intensity changes of control reflections, empirical absorption correction. The structure was solved with MULTAN and refined by full-matrix least-squares methods. Hydrogen atom positions (except for those of H_2O, which were not located) were calculated (staggered geometry for methyl groups), and the atoms were treated as riding on their bond neighbours). Convergence was reached at $R = 0\cdot 066$, $R_w = (\Sigma\Delta^2 F/\Sigma F_0^2)^{1/2} = 0.062$ [2281 reflections having $I > 3\sigma(I)$, 414 variables, unit weights, shift/error ratio $\leqslant 0\cdot 38$]. Heavy-atom coordinates are given in Table 4.*

X-ray crystal structure analysis of 5. $C_{42}H_{47}N_3O_{20}$, formula weight 913·85, orthorhombic, space group $Pna2_1$, $a = 17\cdot 375(1)$, $b = 19\cdot 888(2)$, $c = 12\cdot 629(2)$ Å, $Z = 4$, $D_{\text{calc}} = 1\cdot 39$ g cm^{-3}. Data collection: 3606 unique reflections with $4\cdot 0 \leqslant 2\theta \leqslant 124\cdot 4°$, $\omega/2\theta$ scan, scan width $(0\cdot 85 + 0\cdot 14 \tan\theta)°$, scan speed 0·99–5·03° s^{-1}; empirical absorption correction

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*Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG, on quoting the depository number CSD-53968, the names of the authors and the journal citation.

[μ(Cu Kα) $= 9\cdot10\ \mathrm{cm}^{-1}$]. The structure was solved with the SHELX-86 program system (several efforts with MULTAN failed) and refined by full-matrix least-squares methods; hydrogen atom positions were calculated (staggered positions for methyl groups) and not refined [3497 reflections having $I > 2\sigma(I)$, 586 variables, unit weights, $R = 0\cdot047$, $R_w = (\Sigma\Delta^2 F/\Sigma F_0^2)^{1/2} = 0\cdot047$, shift/error ratio $\leqslant 0\cdot12$]. Heavy-atom coordinates are given in Table 5.*

*Cyclicvoltammetry of **1b** and **2b**.* The experimental setup has been described.[15] The undivided cell was equipped with a platinum disc working electrode and a platinium spiral counter electrode. The Ag/AgCl quasi-reference electrode was calibrated with ferrocene[16] after each experiment. The potentials referred to SCE are calculated by adding 385 mV to the values referred to ferrocene.

The measurements were carried out in purified[17] acetonitrile containing 0·1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The values given were obtained at a sample concentration of $1\cdot5\times10^{-3}$ M and a scan rate of 250 mV s^{-1}.

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REFERENCES

1. (a) H. M. Weber and G. Maas, *Synthesis* 604 (1988); (b) H. M. Weber and G. Maas, *Chem. Ber.* **121**, 1791 (1988).
2. (a) G. Maas and B. Feith, *Angew. Chem.* **97**, 518 (1985); *Angew. Chem., Int. Ed. Engl.* **24**, 511 (1985); (b) B. Feith, H. M. Weber and G. Maas, *Chem. Ber.* **119**, 3276 (1986).
3. G. Maas, E.-U. Würthwein, H. M. Weber and G. Wuttke, in preparation.
4. E. M. Kosower, *Prog. Phys. Org. Chem.* 81 (1965).
5. E. LeGoff and R. B. LaCount, *J. Am. Chem. Soc.* **85**, 1354 (1963).
6. A. G. Davies, J. P. Goddard, M. B. Hursthouse and N. P. C. Walker, *J. Chem. Soc., Dalton Trans.* 1873 (1986).
7. M. I. Bruce, P. A. Humphrey, B. W. Skelton and A. H. White, *Aust. J. Chem.* **37**, 2441 (1984).
8. (a) G. Briegleb, J. Trenscéni and W. Herre, *Chem. Phys. Lett.* **3**, 146 (1969); (b) V. Kampars and O. Neilands, *Zh. Org. Khim.* **9**, 2336 (1973); *J. Org. Chem. USSR* **9**, 2350 (1973); (c) C. Párkányi and G. J. Leu, *Z. Naturforsch., Teil B* **30**, 984 (1975).
9. M. I. Bruce, P. A. Humphrey, B. W. Skelton and A. W. White, *Aust. J. Chem.* **39**, 165 (1986).
10. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.* **84**, 3374 (1962).
11. Y. Yamashita, K. Hagiya, G. Saito and T. Mukai, *Bull. Chem. Soc. Jpn.* **61**, 271 (1988).
12. (a) R. C. Griffith, D. M. Grant and J. D. Roberts, *J. Org. Chem.* **40**, 3726 (1975); (b) I. Prins, J. W. Verhoeven and Th. J. de Boer, *Org. Magn. Reson.* **9**, 543 (1977).
13. J. B. Torrance, *Acc. Chem. Res.* **12**, 79 (1979).
14. E. LeGoff and R. B. LaCount, *J. Org. Chem.* **39**, 423 (1964).
15. J. Daub and J. Salbeck, *Chem. Ber.* **122** (1989) 727.
16. G. Gritzner and J. Kutta, *Pure Appl. Chem.* **56** (1984) 462.
17. J. Salbeck, Dissertation, University of Regensburg (1988).

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* See footnote on previous page.