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Donor Properties of the *p*-Tricyanovinylphenyldicyanomethide Ion

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The donor properties of the *p*-tricyanovinylphenyldicyanomethide (TCVPDM) ion are studied by cyclic voltammetry and pi-complex formation with the acceptors 2,4,6-triphenylthiapyrylium and 2,4,7-trinitrofluorenone (TNF). These complexes are electrically insulating and both are photosensitive. The tetramethylammonium salt of $TCVPDM^-$ crystallizes from acetonitrile with solvent of crystallization. The salt $(CH_3)_4N^+TCVPDM^- \cdot TNF$ is the first structurally characterized example of a pi-complex between a closed-shell monoanion donor and a neutral closed-shell acceptor. The crystals are monoclinic, space group $P2_1/C$, $a = 17.190(5)$ Å, $b = 6.879(3)$, $c = 27.458(10)$, $\beta = 107.85(3)°$, $V = 3090$ Å^3, $Z = 4$, $\rho_{obs} = 1.37(1)$ g/cm^3, $\rho_{calc} = 1.357$ g/cm^3. Several short contacts between the donor and acceptor are noted. Other structurally established examples of pi-complexes which arise by donor-acceptor interactions other than the well-known neutral closed-shell donor-neutral closed-shell acceptor interaction are summarized. The neutral molecule *p*-tricyanovinyldimethylaniline (TCVDMA) is analogous to $TCVPDM^-$ in its electrochemical behavior and complex formation with TNF.

INTRODUCTION

The ease of oxidation of the phenyldicyanomethyl anion[1] suggested to us that a suitably substituted derivative of that anion could function as a pi-donor in weak molecular complexes.[2] For our study, we chose the previously reported[3] *p*-tricyanovinylphenyldicyanomethide ion (TCVPDM, **1**). We found that $TCVPDM^-$ functions as a monoanion closed-shell donor by studies of its solution electrochemistry and its formation of complexes with the neutral closed-shell acceptor 2,4,7-trinitrofluorenone (TNF, **2**) and the

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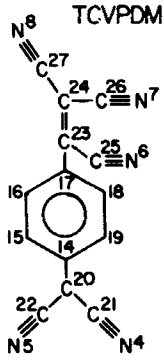

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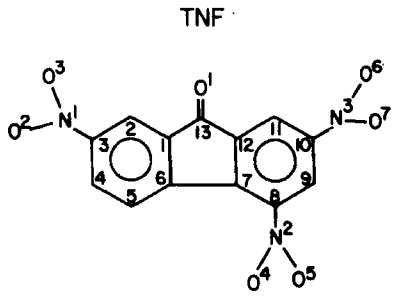

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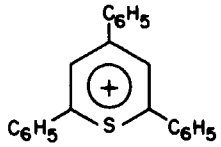

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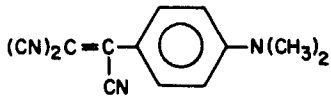

(4)

monocation closed-shell acceptor 2,4,6-triphenylthiapyrylium (TPT, **3**); both of these complexes are insulators and exhibit photosensitivity. We were able to obtain single crystals of the TNF complex suitable for the determination of its crystal structure, and this complex is the first structurally characterized complex between a closed-shell monoanion donor and a neutral closed-shell acceptor. We also noted that the tetramethylammonium salt of the TCVPDM ion crystallizes from acetonitrile with solvent, a finding not observed in earlier work.[3]

RESULTS AND DISCUSSION

A. Preparation and characterization of the complexes

$TCVPDM^-$ was prepared as described by Williams[3] from TCNQ and malononitrile, the latter preferably used in excess. Crystal data for the tetramethylammonium salt of $TCVPDM^-$ was obtained on crystals grown in acetonitrile solution and is presented in Table I. With reference to Table I, it is apparent that the observed density of the crystals is incompatible with the presence of only four molecular units and suggests that solvent may be present in the crystals. The presence of acetonitrile in the crystals grown in this solvent was established by recording solid state infrared spectra of different

TABLE I

Crystal data for $(CH_3)_4N^+TCVPDM^-$ and its TNF complex

	$[(CH_3)_4N^+TCVPDM^-]_4 \cdot nCH_3CN$	$(CH_3)_4N^+TCVPDM^- \cdot TNF$
a	10.736(5) Å	17.190(5) Å
b	28.429(15)	6.879(3)
c	6.764(6)	27.458(10)
α	96.68(5)°	90°
β	108.35(5)	107.85(3)
γ	89.05(4)	90
V	1945 Å^3	3090 Å^3
Space group	P1 or P$\bar{1}$	$P2_1/C$
Z	4	4
ρ_{obs}	1.20(1)	1.37(1)
ρ_{calc}	1.080 g/cm^3 for $n = 0$	1.357 g/cm^3
	1.185 g/cm^3 for $n = 3$	—
	1.220 g/cm^3 for $n = 4$	—

samples of the same material separately crystallized from acetonitrile and ethanol in potassium bromide pellets. The material recrystallized from acetonitrile differs from that from ethanol in the cyano stretching region and between 6.7 and 7.5 μ, a region of strong acetonitrile absorption. The density data suggests that either three or four molecules of acetonitrile crystallize in each unit cell, although the solid could also be non-stoichiometric.

The electrochemical characteristics of the TCVPDM ion in acetonitrile solution were studied by cyclic voltammetry and are displayed in Figure 1.

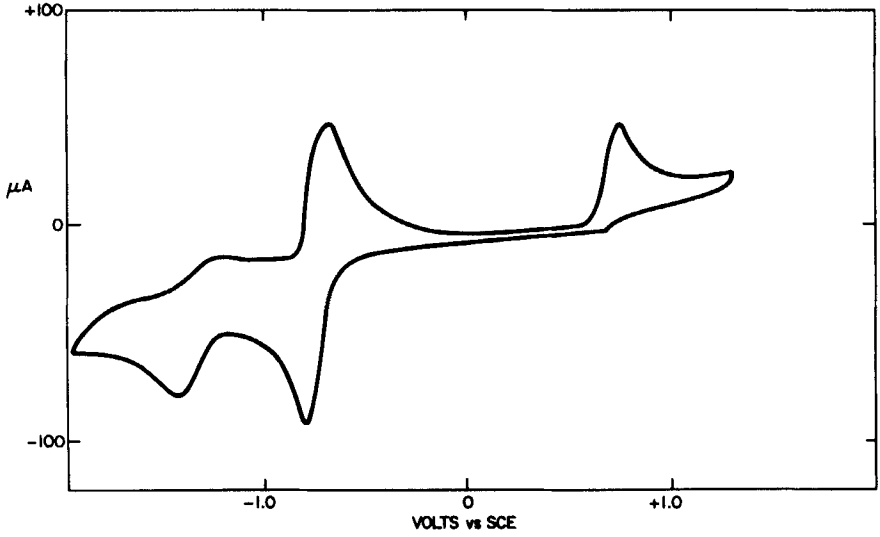

FIGURE 1 Cyclic voltammogram of $(CH_3)_4N^+TCVPDM^-$ in 5×10^{-4} acetonitrile solution.

The donor properties of $TCVPDM^-$ are clearly revealed in the potential of the irreversible anodic wave at +0.80 volts vs. the saturated calomel electrode (SCE), at a 500 mv/sec sweep rate. This potential is significantly lower than that of the neutral closed-shell donors of the *N*-alkylcarbazole class which also exhibit irreversible oxidation at +1.10–1.20 volts vs. SCE[4] and gas phase ionization energies of 7.27 and 7.29 eV for the *N*-ethyl and -isopropyl derivatives,[5] respectively. $TCVPDM^-$ exhibits a reversible one-electron reduction at −0.73 volts vs. SCE and an irreversible reduction with a cathodic peak at −1.40 volts.

The irreversible oxidation of $TCVPDM^-$ cannot be regarded as surprising, since it is an aromatic dicyanomethyl anion whose one electron oxidation would lead to an "unstable" aryldicyanomethyl radical, a species of known reactivity from the work of Hartzler.[1] Irreversible oxidation was also observed in a cyclic voltammetry study of the "ATCNQ" anion.[6]

The electrochemical parameters observed for $TCVPDM^-$ are reminiscent of those reported[7] for *p*-tricyanovinyldimethylaniline (TCVDMA, **4**), $E^{ox}_{1/2}$ + 0.96 V (reversible), $E^{red}_{1/2}$ − 0.70 V (reversible), −1.20 V (irreversible), although in TCVDMA the oxidation is reversible. Thus $TCVPDM^-$ may be simply viewed as the replacement of the neutral dimethylamino donor group in TCVDMA with the anionic donor group $C(CN)_2$. This analogy is pursued further below.

Cyclic voltammetry of the closed-shell aceptor TPT^+ revelas two reversible one electron reductions at −0.23 and −1.22 volts vs. SCE.

Complexes of $TCVPDM^-$ with TNF and TPT^+ were prepared as described in the experimental section. The absorption spectra of these complexes dispersed in potassium bromide are displayed in Figure 2. Between 350 and 800 nm, the spectra largely manifest the features of the separate components of the complexes. While these complexes exhibit no distinct charge-transfer maxima in their spectra, the absorption at energies lower than 800 nm must be due to charge-transfer absorption The intensity of the absorption of the complexes between 800 and 900 nm is substantial since molar extinction coefficients in solution of $TCVPDM^-$ are *ca.* 5×10^4 near 600 nm^3. The position of the charge-transfer maximum was detected in ethanol solution as follows. In half millimeter path length cells, 10^{-3} M solutions of the tetramethylammonium salt of $TCVPDM^-$ in both sample and reference positions give a level baseline. Portionwise solution of TNF in the sample cell revealed a broad absorption with a maximum at 620–625 nm and absorption characteristic of TNF between 350 and 400 nm. Thus, the donor maximum[3] and charge-transfer maximum are at similar wavelengths for the TNF complex. Moreover, the observed charge-transfer maximum is at the energy expected for a donor with $E^{ox}_{1/2}$ of *ca.* +0.80–0.90 volts.[8]

If the analogy noted above between $TCVPDM^-$ and TCVDMA is useful

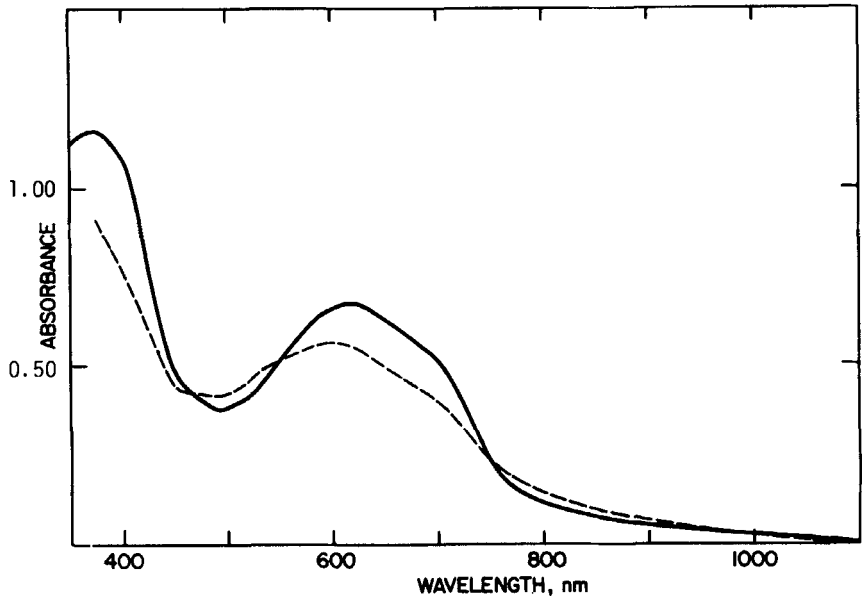

FIGURE 2 Solid state (KBr) absorption spectra of $TPT^+TCVPDM^-$ (———) and $(CH_3)_4N^+TCVPDM^-$. TNF (– – –).

then TCVDMA might form complexes with acceptors such as TNF. Such is the case. The TCVDMA complex of TNF was prepared as described in the experimental section, and lattice constants for single crystals are given. The absorption spectrum of TCVDMA.TNF in potassium bromide exhibits a maximum at 520 nm, blue shifted to higher energy compared to the $TCVPDM^-$ complex; no charge-transfer maximum was detectable. To our knowledge, no solid complexes of TCVDMA have been previously isolated, although an attempt was reported.[9] We have also prepared other solid complexes of TCVDMA, and these will be reported separately.[10]

B. Crystal structure of the TNF complex of the tetramethylammonium salt of TCVPDM

The crystals were grown by slow cooling of an alcohol of the complex, and are reddish-brown with highly reflective surfaces. The best crystal available for data collection had dimensions of 0.05 × 0.075 × 0.175 nm and was mounted on a glass fiber with random orientation. Data were collected using an Enraf–Nonius CAD-4 diffractometer by Molecular Structure Corporation, College Station, Texas 77840, who also solved the structure. The cell parameters, given in Table I, were obtained by least-squares refinement of

diffractometer settings for 16 reflections. A total of 4396 reflections were collected; of these 4291 were independent reflections.

Three standard reflections were monitored periodically during the data collection; no significant changes in intensity were observed. The variance for each observation was calculated on the basis of counting statistics with the p of the $(pI)^2$ term being set equal to 0.03. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu(CuK_\alpha)$ = 22.5 cm^{-1}). The small size of the crystal gave a data set with only 1115 reflections with $F_0^2 > 3\sigma(F_0^2)$ which was used in all subsequent calculations. The structure was solved by direct methods. The final cycle of least-squares refinement gave:

$$R_1 = \frac{\Sigma||F_0| - F_c||}{\Sigma|F_0|} = 0.157$$

$$R_2 = \left[\frac{\Sigma w(|F_0| - |F_c|)^2}{\Sigma w F_0^2}\right]^{1/2} = 0.175$$

A view of the unit cell down the crystallographic b-axis is shown in Figure 3. The b-axis dimension of 6.879(3) Å is common for 1:1 mixed stack pi-complexes which often have a repeat distance along the stack of 7 Å[11]. TNF and $TCVPDM^-$ are not coplanar; there is a dihedral angle of 16.1° between the molecular planes.

The observed bond lengths for $TCVPDM^-$ and TNF are given in Table II with atomic designations. They are not of high precision due to the relatively high discrepancy index for this structure. More precise bond lengths for

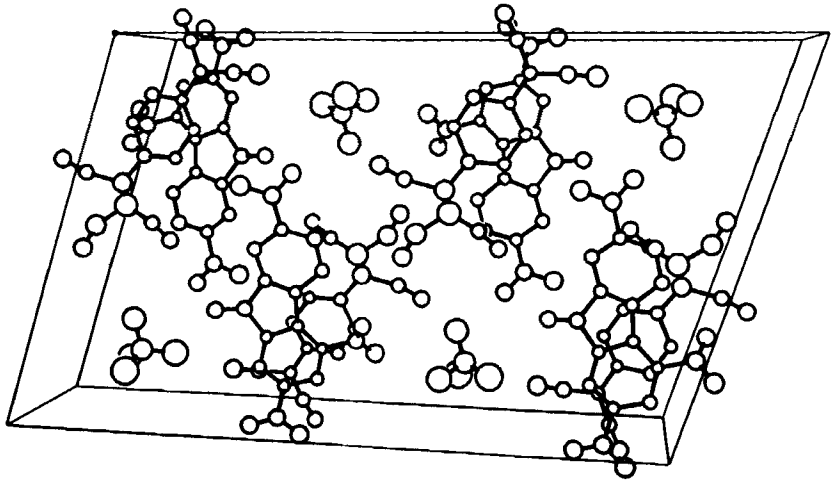

FIGURE 3 View down the crystallographic b-axis of $(CH_3)_4N^+TCVPDM^-$. TNF.

TABLE II

Bond lengths (Å) of $TCVPDM^-$ and TNF in the complex

$TCVPDM^-$		TNF	
Bond	Length	Bond	Length
$C_{26}—N_7$	1.068(13)	$C_1—C_2$	1.400(12)
$N_6—C_{25}$	1.175(13)	$C_2—C_3$	1.391(12)
$N_8—C_{27}$	1.13(2)	$C_3—C_4$	1.409(13)
$C_{15}—C_{16}$	1.413(11)	$C_4—C_5$	1.367(13)
$C_{15}—C_{14}$	1.377(11)	$C_5—C_6$	1.460(11)
$C_{14}—C_{19}$	1.425(12)	$C_6—C_7$	1.461(12)
$C_{14}—C_{20}$	1.419(11)	$C_7—C_8$	1.383(11)
$C_{16}—C_{17}$	1.415(12)	$C_8—C_9$	1.378(11)
$C_{17}—C_{18}$	1.492(12)	$C_9—C_{10}$	1.457(12)
$C_{17}—C_{23}$	1.50(2)	$C_{10}—C_{11}$	1.298(11)
$C_{18}—C_{19}$	1.410(13)	$C_{11}—C_{12}$	1.369(11)
$C_{20}—C_{21}$	1.392(13)	$C_{12}—C_{13}$	1.497(13)
$C_{20}—C_{22}$	1.477(14)	$C_1—C_{13}$	1.526(13)
$C_{23}—C_{24}$	0.94(2)	$C_{13}—O_1$	1.210(12)
$C_{23}—C_{25}$	1.68(2)	$C_3—N_1$	1.457(12)
$C_{24}—C_{26}$	1.38(2)	$N_1—O_2$	1.367(12)
$C_{24}—C_{27}$	1.62(2)	$N_1—O_3$	1.224(10)
$N_4—C_{21}$	1.132(13)	$C_8—N_2$	1.497(12)
$N_5—C_{22}$	1.137(14)	$N_2—O_4$	1.207(11)
		$N_2—O_5$	1.206(12)
		$C_6—N_3$	1.501(12)
		$N_3—O_6$	1.231(11)
		$N_3—O_7$	1.214(12)

TNF may be found in its crystal structure[12] or in that of its complex with hexamethylbenzene.[13]

The non-coplanarity of TNF and $TCVPDM^-$ leads to several short intermolecular contact distances which are given in Table III. With the exception of the contracts of O_2 with C_{15} and C_{16}, the distances in Table V are for contacts between a donor-acceptor pair in the same stack. The contacts between O_2 and C_{15} and C_{16} involve a TNF and a $TCVPDM^-$ in the same sheet. The atomic coordinates are given in Table IV.

The packing pattern of this structure precludes contacts between TNF molecules, a feature of the two previously reported[12,13] structures containing TNF.

While the TNF complex of $TCVPDM^-$ represents the first structural characterization of a Mulliken pi-complex between a closed-shell monoanion donor and a neutral closed-shell acceptor, solid complexes of the pentacarbomethoxycyclopentadienide ion, also a closed-shell monoanion, and neutral acceptors including TNF have been reported.[14] There is an

TABLE III

Short intermolecular contacts between TNF and TCVPDM$^-$

Contact	Distance, Å (±0.015)
C_9—N_4	3.303
C_{15}—O_2	3.189
C_{16}—O_2	3.252
C_{18}—O_4	3.123
C_{18}—O_5	3.007
C_{21}—O_7	3.293
C_{25}—O_4	3.241

extensive literature[11,15] discussing the structural aspects of weak pi-complexes and charge-transfer salts arising by interaction of neutral closed-shell donors and acceptors. In contrast there are relatively few examples of crystal structures involving pi-complexes of other closed-shell species. Several complexes between closed-shell monocation acceptors of the flavin class and neutral closed-shell donors were reviewed earlier.[11] Two structures have been reported of complexes between closed-shell monoanion donors and closed-shell monocation acceptors. They are the complex between the 2,4,6-triphenylpyrylium cation and the 1,1,3,3-tetracyanopropenide anion,[16] and the complex between the 3,5-diphenyl-1,2-dithiolium cation and the 4-phenyl-5-thioxo-1,2-dithiol-3-thiolate anion.[17] The structure of the 2:1 complex between the closed-shell monocation acceptor quinolinium and the closed-shell dianion 2-dicyanomethylene-1,1,3,3-tetracycanopropanediide has been described.[18] The complex between the closed-shell dication acceptor *N*,*N*-dimethyl-4,4′-bipyridylium and the neutral donor hydroquinone and anionic atomic donor iodide has been structurally characterized.[19] A generalized approach to donor-acceptor interactions involving species other than neutral closed-shell donors and acceptors including open-shell species has been developed,[20] and this perspective has been applied to phase formation of segregated stack 1:1 ion-radical structures.[21]

C. Physical properties of the complexes

Consistent with their description as weak pi-complexes, these materials are electrical insulators. Two probe measurements on compressed pellets of these complexes at room temperature revealed conductivities of 5×10^{-12} (ohm-cm)$^{-1}$ for the TPT^+ complex and 3×10^{-13} (ohm-cm)$^{-1}$ for the TNF complex. Both complexes are photosensitive. The best data was obtained for the TPT^+ complex dispersed as a pigment 20% by weight in

TABLE IV

Positional and thermal parameters and their estimated standard deviations

Atom	*X*	*Y*	*Z*	B(1.1)	B(2.2)	B(3.3)	B(1.2)	B(1.3)	B(2.3)
O1	0.6909(9)	0.180(2)	0.2650(6)	7.0(5)					
O2	0.3710(11)	0.155(3)	0.2467(7)	10.2(6)					
O3	0.3397(10)	0.215(3)	0.3164(6)	8.6(5)					
O4	0.7190(10)	0.199(3)	0.4966(6)	8.0(5)					
O5	0.8071(10)	0.429(3)	0.5217(7)	9.1(6)					
O6	1.0017(10)	0.310(3)	0.3658(6)	8.6(5)					
O7	1.0279(10)	0.387(3)	0.4453(7)	9.3(6)					
N1	0.395(1)	0.202(3)	0.2976(7)	8.2(7)					
N2	0.766(1)	0.318(3)	0.4901(7)	7.7(6)					
N3	0.981(1)	0.341(3)	0.4041(7)	7.6(7)					
N4	−0.047(1)	0.397(3)	0.0582(8)	7.6(6)					
N5	0.098(1)	0.269(4)	0.2156(8)	10.4(8)					
N6	0.315(1)	0.265(3)	−0.0569(8)	8.0(6)					
N7	0.516(1)	0.228(3)	0.1575(7)	7.0(6)					
N8	0.544(1)	0.234(4)	0.0206(8)	9.5(7)					
N9	0.194(2)	0.723(4)	0.3355(9)	13.1(9)					
C1	0.613(1)	0.218(3)	0.3257(7)	4.4(6)					
C2	0.531(1)	0.193(4)	0.2959(8)	5.2(7)					
C3	0.482(1)	0.224(3)	0.3266(7)	4.4(6)					
C4	0.504(1)	0.246(4)	0.3801(9)	6.6(7)					
C5	0.585(1)	0.260/4)	0.4064(8)	5.1(6)					
C6	0.642(1)	0.245(3)	0.3766(7)	3.9(5)					
C7	0.731(1)	0.264(3)	0.3957(7)	3.5(5)					
C8	0.790(1)	0.300(3)	0.4421(7)	2.9(5)					
C9	0.872(1)	0.328(3)	0.4481(8)	4.5(6)					
C10	0.893(1)	0.312(3)	0.4007(7)	3.6(6)					
C11	0.842(1)	0.271(3)	0.3560(7)	4.2(6)					
C12	0.761(1)	0.254(3)	0.3529(7)	3.7(5)					
C13	0.688(1)	0.225(4)	0.3071(9)	6.3(7)					
C14	0.163(1)	0.297(3)	0.1048(7)	3.2(5)					
C15	0.237(1)	0.262(3)	0.1410(7)	3.7(5)					
C16	0.308(1)	0.256(3)	0.1251(7)	3.7(5)					
C17	0.304(1)	0.273(4)	0.0730(8)	5.0(6)					
C18	0.220(1)	0.307(3)	0.0363(7)	4.1(6)					
C19	0.150(1)	0.329(4)	0.0517(8)	5.3(7)					
C20	0.091(1)	0.310(3)	0.1196(8)	4.4(6)					
C21	0.013(1)	0.346(4)	0.0865(9)	5.6(7)					
C22	0.094(1)	0.295(4)	0.1739(9)	6.4(7)					
C23	0.374(2)	0.265(5)	0.0515(11)	10.2(9)					
C24	0.430(2)	0.255(6)	0.0687(13)	15.0(13)					
C25	0.349(1)	0.271(4)	−0.0127(8)	6.0(7)					
C26	0.474(1)	0.237(4)	0.1200(8)	5.5(7)					
C27	0.484(2)	0.249(5)	0.0296(11)	11.8(11)					
C28	0.274(2)	0.728(6)	0.3631(13)	15.5(13)					
C29	0.150(3)	0.584(8)	0.3408(17)	22.3(19)					
C30	0.175(2)	0.865(7)	0.2915(16)	20.2(18)					
C31	0.162(2)	0.857(6)	0.3626(14)	16.5(15)					

The form of the anisotropic thermal parameter is: EXP[−(B(1.1)*H*H + B(2.2)*K*K + B(3.3)*L*L + B(1.2)*H*K + B(1.3)*H*L + B(2.3)*K*L)].

poly-*N*-vinylcarbazole in a film 15 microns in thickness on a ball-grained aluminum substrate by xerographic discharge at a field of 10^4 volts/cm. For positive corona, the sample was sensitive over the wide wavelength range of 400–950 nm with an estimated quantum yield of 0.02.

EXPERIMENTAL SECTION

General

Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Lattice constants were determined by Molecular Structure Corporation, College Station, Texas using MoK_α radiation. Absorption spectra were measured on a Cary 17D spectrophotometer. Cyclic voltammetry was measured under the same conditions as previously reported.[22]

Preparation[3] of the tetramethylammonium salt of TCVPDM$^-$

To a dimethylformamide (66 ml) solution of powdered, gradient sublimed TCNQ (4.0 g, 19.6 mmole) was added malonitrile (12.26 g, 34.2 mmole). This solution was heated on a steam bath for 90 minutes. The reaction mixture was poured into cold water (660 ml), and to this solution was added tetramethylammonium bromide (46.9 g, 305 mmole). A dark solid was isolated by suction filtration and recrystallized from absolute alcohol followed by acetonitrile to give 1.6 g (50% yield), mp. 234° (dec).

Preparation of the Triphenylthiapyrylium (TPT$^+$) Salt of TCVPDM$^-$TPT$^+$TCVPDM$^-$

To a warm methanol solution of TPT$^+$ perchlorate[23] (134 mg, 0.32 mmole) was added a methanol solution of the tetramethylammonium salt of TCVPDM$^-$ (100 mg, 0.32 mmole). A dark-colored solid precipitated which was recrystallized from methanol to give a greenish-gold solid (92 mg, 51% yield), m.p. 227.5–229° (dec).

Anal.: Calcd for $C_{37}H_{21}N_5S$: C, 78.29; H, 3.73; N, 12.34; S, 5.65.
Found: C, 78.26; H, 3.89; N, 12.17; S, 5.88.

The Debye–Scherrer pattern of this complex, recorded using CuK_α radiation, exhibits the following *d* spacings in Å: 11.0, 8.6, 6.6–6.8 s, 6.3, 5.7 s, 5.5 s, 4,8, 4.4, 4.20 s, 3.80, 3.70, 3.55 s, 3.33 s, s = strong line.

Preparation of the 2,4,7-Trinitrofluorenone (TNF) Complex of TCVPDM, $(CH_3)_4N^+TCVPDM^-\cdot TNF$

Trinitrofluorenone (0.58 g, 1.8 mmole) was Soxhlet extracted into an ethanol (170 ml) solution of the tetramethylammonium salt of $TCVPDM^-$ (0.63 g, 2 mmole). A precipitate formed in the cooled solution and it was collected by suction filtration to give 0.77 g reddish-gold crystals, m.p. 213–215° (dec.)

Anal.: Calcd for $C_{31}H_{21}N_9O_7$: C, 58.96; H, 3.35; N, 19.96; O, 17.74.
Found: C, 58.85; H, 3.61; N, 19.76.

The Debye–Scherrer pattern, as above, exhibits the following spacings: 13, 12.5 s, 9.0, 8.2, 6.6, 5.5, 4.85, 4.60, 4.30, 4.05, 3.80, 3.45 s, 3.35, 3.20.

Preparation of the complex of 2,4,7-Trinitrofluorenone (TNF) complex of Tricyanovinyldimethylaniline (TCVDMA)

TNF (1.06 g, 0.34 mmole) was Soxhlet extracted into an absolute ethanol (200 ml) solution of TCVDMA[24] (0.75 g, 0.34 mmole) for fifteen hours. The mixture was allowed to cool to room temperature and a red-brown solid (1.34 g, 74% yield) was isolated by suction filtration, m.p. 151° (dec.)

Anal.: Calcd for $C_{26}H_{15}N_7O_7$: C, 58.11; H, 2.81; N, 18.24; O, 20.84.
Found: C, 57.78; H, 3.04; N, 18.00.

The unit cell data for TCVDMA·TNF reveal a triclinic crystal, $a = 7.467(1)$, $b = 11.992(1)$, $c = 14.405(1)$ Å, $\alpha = 107.02(1)°$, $\beta = 102.49(1)°$, $\gamma = 91.38(1)°$, $V = 1198.9$ Å^3, $Z = 2$, $\rho_{calc} = 1.487$, $\rho_{obs} = 1.49(1)$.

SUMMARY AND CONCLUSIONS

The complexes described herein are the first reported for $TCVPDM^-$ and TCVDMA. The role of the large molecular dipole of TCVDMA (10.91D)[7] (and presumably also of $TCVPDM^-$) in complex formation is uncertain at present. $TCVPDM^-$ is the first closed-shell anion donor to be studied by electrochemical techniques. The observation that the charge-transfer maximum in the TNF complex of $TCVPDM^-$ is at an energy comparable to one of the components of the complex is unusual but not unprecedented; recall the classic benzene–iodine complex where the charge-transfer absorption is at higher energy than the iodine absorption. While complex formation involving closed-shell anion donors such as $TCVPDM^-$

is not an extensive subject, it is appropriate to note that there are many closed-shell cyanocarbon anions,[25] to cite one possibility, which have not been studied in this connection.

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