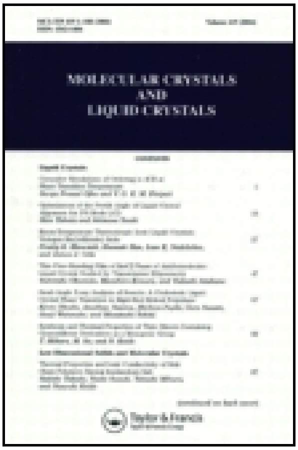

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Solid Complexes of the Pi-Amphoteric Molecule p-Tricyanovinyl-N, N-Dimethylaniline

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Solid Complexes of the Pi-Amphoteric Molecule *p*-Tricyanovinyl-N,N-Dimethylaniline

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Solid pi-complexes of *p*-tricyanovinyl-N,N-dimethylaniline (TCVDMA) have been isolated for the first time. The complexing molecules include the simple aromatic solvents benzene, toluene, chlorobenzene, 1,2,4-trichlorobenzene, and N,N-dimethylaniline (DMA), 2,4,7-trinitrofluorenone (TNF), and *p*-chloranil. Lattice constants are reported for the five complexes with aromatic solvents and TNF. The complexes of TCVDMA with benzene, toluene, and chlorobenzene have the stoichiometry 2TCVDMA (aromatic) and similar lattice constants. The complexes of TCVDMA with DMA and 1,2,4-trichlorobenzene have the unusual stoichiometry 4 TCVDMA (aromatic) with similar lattice constants including a short unit cell dimension of *ca.* 4.0 Å. The complexes with DMA, TNF, and *p*-chloranil are found to have new absorption assigned to charge-transfer transitions and are thus Mulliken donor-acceptor complexes. Based on molecular energy levels and redox potentials, TCVDMA behaves as a donor in its complexes with TNF and *p*-chloranil and as an acceptor in its complex with DMA. Thus TCVDMA is the first example of a molecule to yield well-defined solid complexes in which it behaves as a donor with one molecule and as an acceptor with another. While TCVDMA has long been known to be a solvatochromic, its solvent shifts do not give good correlations with E_T* and Z. The most quantitative correlation found was between the frequency shift and a refractive index function for the solvents benzene, toluene, and chlorobenzene. The sensitivity of the spectra of solid evaporated films of TCVDMA to degree of crystallinity thermal history, and exposure to benzene vapor is reported. A recent claim that *p*-dimethylaminobenzylidene-malononitrile, a molecule similar in structure to TCVDMA, gave different crystalline forms on crystallization from benzene and methanol was found not to be reproducible.

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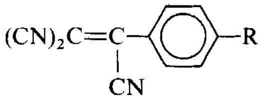
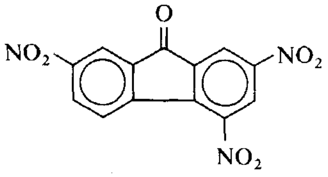
1 INTRODUCTION

From an experiment intended to prepare the 2,4,7-trinitrofluorenone (TNF, **1**) complex of *p*-tricyanovinyl-N,N-dimethylaniline[1] (TCVDMA, **2**) in benzene solution, we isolated a previously unreported crystalline solid found to have the formula 2(TCVDMA)·C_6H_6. This was the first of a series of solid TCVDMA complexes with simple benzene derivatives which we isolated and studied.



R = $-N(CH_3)_2$

2



1

TCVDMA has been known for over twenty years.[2] It has been of interest for its photosensitive properties[3,4] and mechanistic study of the tricyanovinylation reaction.[5] TCVDMA has both a good donor group (dimethylamino) and a good acceptor (tricyanovinyl) group in its molecular structure. Based on its reported[3] solution oxidation and reduction potentials, TCVDMA might be expected to function as either a donor or an acceptor in pi-molecular complexes. However, until our isolation of its TNF complex,[1] such solid complexes had not been reported. A previous report[6] suggested possible intermolecular complex formation involving TCVDMA in solution.

This paper reports our studies of the preparative, thermal, structural, and spectral properties of seven new solid complexes of TCVDMA. The complexing molecules are: benzene, toluene, chlorobenzene, 1,2,4-trichlorobenzene, N,N-dimethylaniline (DMA), *p*-chloranil and TNF.

Other complexes of TCVDMA with pyridine, methylbenzoate and nitrobenzene were isolated but not characterized in detail. In the course of this work, we have found that TCVDMA procides the first clear example of a molecule to yield a *solid* complex with one molecule (TNF) in which it behaves as a donor and a *solid* complex with another molecule (DMA) in which it behaves as an acceptor.[1b]

Solid molecular complexes where aromatic hydrocarbons such as pyrene, anthracene, and perylene behave as donors have been structurally characterized.[7] However, the behavior of these hydrocarbons as acceptors with tetrakis (dimethylamino)ethylene has been detected spectroscopically only in solution studies.[8a] A brief note[8b] reported that dimethylalloxazine was a donor with TCNE and an acceptor with pyrene in solid complexes, but no experimental detail was given.

2 EXPERIMENTAL SECTION

General

Elemental analyses (Table I) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Lattice constants were determined by Molecular Structure Corporation, College Station, Texas, 77840. Solution absorption spectra were measured on a Cary 15 Spectrometer in one cm. cells. Solid state absorbtion spectra were measured on a Cary 17D Spectrometer. Infra-red spectra were measured on a Perkin–Elmer 283 Spectrometer. Endotherm temperatures (Table I) were obtained using a Dupont 900 Differential Scanning Calorimeter. The densities of the complexes were determined by the flotation method using aqueous potassium iodide solution. Stoichiometries were verified by spectrophotometry in acetone solution.[2]

Preparation of 4-(tricyanovinyl)-N,N-dimethylaniline

TCVDMA was prepared from DMA and tetracyanoethylene (Eastman) according to McKusick, *et al.*[2] X-Ray powder diffraction of TCVDMA recrystallized from glacial acetic acid solution showed the same phase as that studied by Chetkina, *et al.*[4] m.p. 173°.

For solid state spectral studies, our samples were purified by gradient sublimation[9] on Kapton at 130° and 10^{-6} mn.

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

TNF (1.06g, 0.34 mmole) was Soxhlet extracted into an absolute ethanol (200 ml) solution of TCVDMA (0.75g, 0.34 mmole) for fifteen hrs. The mixture was allowed to cool to room temperature and red-brown solid (1.34g, 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; 0, 20.84.
Found: C, 57.78; H, 3.04; N, 18.00.

Preparation of the *p*-chloranil complex of TCVDMA

p-Chloranil (0.77g, 3.15 nmole) was Soxhlet extracted into an absolute ethanol solution (190ml) of TCVDMA (0.70g, 3.15 mmole) for 15 hrs. The solution was then cooled to room temperature and the precipitate collected by suction filtration. The product, a homogeneous purple solid, was dried in a vacuum desiccator, m.p. 198.5–200° (dec). The Debye-Sherrer

TABLE I

Visible spectra, elemental analysis[a], and thermal properties

Complex	Solution λ max (nm)	Spectra[b] $\varepsilon \times 10^{-4}$	% Carbon Calc.	% Carbon Found	% Hydrogen Calc.	% Hydrogen Found	% Nitrogen Calc.	% Nitrogen Found	% Chlorine Calc.	% Chlorine Found	Endotherms[c] Temp. °C
2(TCVDMA)·C_6H_6	505	4.27	73.56	73.42	4.48	5.05	21.46	21.55	—	—	70,120
2(TCVDMA)·$C_6H_5CH_3$	502.5	4.15	73.88	73.68	5.23	5.48	20.89	20.02	—	—	80,125
2(TCVDMA)·C_6H_5Cl	517	4.41	69.00	68.89	4.49	4.56	20.13	18.99	6.38	7.60	—
4(TCVDMA)·DMA	517	3.19	71.43	71.41	4.96	5.29	23.61	22.80	—	—	132
4(TCVDMA)·$C_6H_3Cl_3$	514	4.54	65.08	65.24	4.02	4.24	20.94	20.14	9.95	8.28	—

[a] Complexes of TCVDMA with volatile molecules such as those in this table cannot be washed with solvents or vacuum dried without loss of the volatile component.

[b] The solvent is the molecule complexed to TCVDMA.

[c] Measured by differential scanning calorimetry. Additionally each complex exhibits a major endotherm at 173°, the melting point of TCVDMA.

pattern of this solid exhibits the following at *d*-spacings greater than 2 Å: 11.5, 8.2, 7.2, 6.7, 5.8, 4.75, 4.15, 3.40 (Strong), 3.25, 2.95, 2.90, 2.75, 2.37, 2.18, 2.05, 2.00. Acetone spectrophotometry of this solid shows 43.1% TCVDMA by weight. A 1:1 stoichiometry corresponds to 37.6% TCVDMA be weight. A 2:3 stoichiometry corresponds to 47.4% by weight.

Anal. Calcd. for $C_{44}H_{20}Cl_{12}N_8O_6$: C, 44.70; H, 1.71; Cl, 35.99; N, 9.48; O, 8.12. Calcd, for $C_{19}H_{10}Cl_4N_4O_2$: C, 48.72; H, 2.14, Cl, 30.34; N, 11.96; O, 6.84.

Found: C, 43.81; H, 1.77; Cl, 36.18; N, 8.46

Crystals obtained were not suitable for X-Ray diffraction studies.

Preparation of the benzene complex of TCVDMA

TCVDMA was added to hot benzene (10 ml) until the saturation point was reached. The solution was then cooled to room temperature in a stoppered Flask: The red prismatic crystals which precipitated were isolated by suction filtration to give 2 (TCVDMA)-(Benzene) (see Table I).

General preparation of benzene derivative complexes of TCVDMA

The toluene, chlorobenzene, 1,2,4-trichlorobenzene and dimethylaniline (DMA) complexes were formed by the same procedure used for the benzene complex. The toluene and chlorobenzene complexes gave crystals visually similar to the benzene complex. The DMA and trichlorobenzene complex gave steel blue needles. Analytical data for these complexes is given in Table I.

Preparation of *p*-dimethylaminobenzylidenemalononitrile (DCVDMA)

DCVDMA was prepared from *p*-dimethylaminobenzaldehyde and malononitrile according to Kuder *et al.*[3] m.p. 180°, lit.[3] m.p. 179–180°.

Recrystallization of DCVDMA from benzene and methanol

To 10 ml of hot benzene was added enough DCVDMA to reach saturation. The solution was cooled to room temperature in a stoppered flask. The orange-yellow precipitate was isolated by suction filtration m.p. 179–180°.

This procedure was repeated using 10 ml of absolute methanol in place of benzene. An orange-yellow precipitate, m.p. 180°, was obtained.

Debye-Scherrer X-Ray powder patterns show that both products are the same phase. The Debye-Scherrer pattern of these solids exhibits the following at *d*-spacings greater than 2 Å: 8.0(s), 7.0, 5.6(s), 4.70, 4.20, 3.90, 3.75, 3.40(s), 3.35(s), 3.05, 3.00, 2.85, 2.70, 2.38, 2.27, 2.22, 2.17, 2.14, 2.10, 2.01.

3 RESULTS AND DISCUSSION

The preparation of the new complexes is described in the Experimental Section. Given the volatility of the molecules complexed to TCVDMA, the loss of the volatile component on standing is not surprising. For example, "single crystals" of 2TCVDMA. C_6H_6 which have been stored for six months will not diffract X-rays even though they have not visibly changed. The data in Table II were obtained on freshly prepared samples. A previous attempt to detect complex formation between *p*-chloranil and TCVDMA was unsuccessful.[6] We found that TCVDMA readily complexes *p*-chloranil (Experimental Section), but the resultant homogeneous precipitate either contains several phases of different stoichiometry or is non-stoichiometric.

The 4:1 stoichiometry observed in the complexes with DMA and 1,2,4-trichlorobenzene is unusual but not unprecedented[7] in molecular complexes and ion-radical salts. Two structures of 4:1 salts of TCNQ and dications have been reported.[10]

Crystallographic properties

Lattice constants for TCVDMA, its complex with TNF[1] and its five complexes with simple aromatic molecules are given in Table II. The lattice constants of the complexes are markedly different from those of TCVDMA.[4] The complexes of the benzene derivatives fall into two distinct lattice structures. The benzene, toluene and chlorobenzene complexes have a 2:1 stoichiometry and similar lattice constants. The DMA and 1,2,4-trichlorobenzene complexes have a 4:1 stoichiometry and similar lattice constants, including a very short dimension of *ca.* 4.0 Å. A lattice constant of *ca.* 4.0 Å is reminiscent of that found in uniform segregated stack structures of ion-radical salts.[7,11] Attempts to get a complete crystal structure of one of the complexes with a simple aromatic molecule have not been successful to date. The contraction of volumes on complexation (Table II) and the spectral evidence presented below suggest that these complexes are most likely pi-complexes.

Spectral properties

In the absence of a complete crystal structure, the nature of these complexes can be discussed only on the basis of their spectral properties. From our investigation of the spectra of the complexes we have been able to classify the TNF, *p*-chloranil and DMA complexes of TCVDMA as Mulliken donor-acceptor complexes. In each of these three cases new absorption not characteristic of either component has been observed. Since the visible solution

TABLE II

Crystal data for TCVDMA and TCVDMA complexes

	TCVDMA[4]	2(TCVDMA)C_6H_6	2(TCVDMA)$C_6H_5CH_3$	2(TCVDMA)C_6H_5Cl	4(TCVDMA)·DMA	4(TCVDMA)·$C_6H_5Cl_3$	(TCVDMA)·TNF[1]
a	11.810Å	9.767(2)Å	9.771(2)Å	9.794(5)Å	3.992(6)Å	4.035(8)Å	7.467(1)Å
b	7.505	6.957(2)	6.980(2)	6.920(3)	16.315(10)	16.248(13)	11.992(1)
c	7.032	21.412(3)	21.711(4)	21.819(9)	20.562(11)	20.318(43)	14.405(1)
α	102.80°	90°	90°	90°	90°	90°	107.02(1)°
β	87.97	99.86(1)	97.14(1)	99.64(4)	90.27°	90.28(17)	102.49(1)°
γ	82.19°	90°	90°	90°	90°	90°	91.38(1)°
V_{mc}	600.7Å	1433.4Å^3	1469Å^3	1458Å^3	1339Å^3	1332Å^3	1198.9Å^3
V_{add}	—	1496.Å^3	1554Å^3	1539Å^3	1411Å^3	1408.6Å^3	1229.6Å^3
Z	2	2	2	2	1	1	2
ρ_{calc}	—	1.209	1.211	1.229	1.214	1.293	1.487
$\rho_{obs.}$	—	1.19(1)	1.20(1)	1.23(1)	1.22(1)	1.28(1)	1.49(1)

spectrum of TCVDMA is very sensitive to the solvent,[2] and we have observed that TCVDMA forms solid complexes with many solvents which red-shift its spectrum *vs.* the non-polar solvent isooctane, we first discuss the solvent effect on the spectrum of TCVDMA itself before discussing spectral evidence for donor-acceptor complex formation.

We further preface our discussion of the solution spectrum of TCVDMA by noting that in isooctane, the spectrum exhibits a maximum at 478 nm ($\varepsilon = 5.2 \times 10^4$) and a shoulder at 450 nm ($\varepsilon = 2.9 \times 10^4$.) It is not known at present whether the shoulder at 450 nm represents fine structure of the transition with a maximum of 478 nm or a separate transition. There has been no attempt at an assignment of the states associated with the spectral transitions of TCVDMA itself to date.

The absorption maximum of TCVDMA in isooctane at 478 nm is observed to progressively shift toward the maximum of 505 nm in benzene from study of the spectrum in isooctane-benzene mixtures; the shoulder at 450 nm in isooctane also shifts to lower energies and is not easily observable in benzene. These observations suggest that the spectral shift of TCVDMA is a solvent effect since new absorption to be associated with a complex is not observed.

Since TCVDMA is a solvatochromic molecule,[2] we initially sought correlations of the solvent shift of its visible maximum with empirical solvent polarity functions such as E_T* and Kosower's Z.[12] Our results for data both previously reported[2] and obtained in the present work were decidedly inferior to such correlations observed with other solvatochromics.[13] We then sought to correlate the data with several functions involving the refractive index or the dielectric constant of the solvent. The most quantitative correlation we found is shown in Figure 1 where we plot the shift ($\Delta\nu$) in the absorption maximum of TCVDMA in a given solvent from that in isooctane in cm^{-1} *vs.* $n^2 - 1/2n^2 + 1$, where n is the refractive index of the solvent at 20°, for the solvents benzene, toluene, and chlorobenzene, and observe a reasonable straight line. The abscissa of Figure 1 is from

$$\Delta\nu = 10.71 \times 10^9 \left(\frac{f}{\nu a^3}\right)\left(\frac{n^2 - 1}{2n^2 + 1}\right)$$

where f is the oscillator strength, ν the frequency, and a the radius of the solvent cavity. This expression is a result of the Bayliss–McRae[14] treatment of solvent shifts on absorption spectra which has been extended by others.[15]

The correlation of Figure 1 is surprising for several reasons and may be fortuitous given the relatively narrow range of abscissa involved.[15b] Also, the above expression was derived only for dispersion forces and initially[14] applied to non-polar solutes in non-polar solvents, while TCVDMA has a

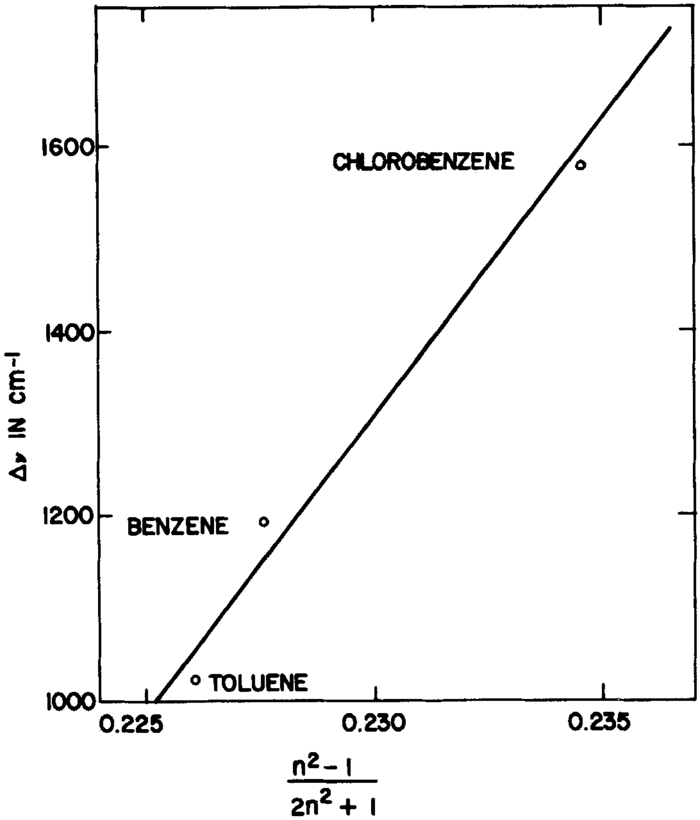


FIGURE 1 Plot of spectral shift in cm^{-1} of the absorption maximum of TCVDMA relative to isooctane for benzene, toluene, and chlorobenzene solvents *vs.* $n^2 - 1/2n^2 + 1$ where n is the solvent refractive index at 20°.

very large dipole moment,[3] 10.7–10.9D. The limitations of correlations such as the present one for polar solutes and the potential importance of specific associations have been previously discussed.[15b] Since we have noted above that the complexes of TCVDMA with these three aromatic solvents have similar lattice constants, the correlation of Figure 1 may imply a solvation structure of TCVDMA which is analogous for these three solvents.

In any Mulliken donor-acceptor complex there will be new absorption not characteristic of either complexing partner whose energy is related to the difference between the ionization energy of the donor (I_g) and the electron affinity of the acceptor (A_A).[16]

Distinct charge-transfer maxima separated from the absorption of the components are not observed for any of the TCVDMA complexes, a situation also seen with TCVPDM,[1,17] due to the intense visible absorption of those species. However, for the TCVDMA complexes of TNF and chloranil, spectra in ethanol solution and in KBr pellets (Figure 2) reveal absorption at wavelengths greater than 750 nm not due to either component of the complex and assigned to the tail of a charge-transfer absorption band. In chloroform solution, 10^{-3} M in TCVDMA, a "window" in the absorption spectrum is apparent between 350 and 400 nm. Portionwise addition of DMA up to a concentration of 10^{-2} M in this solution reveals new absorption with increasing absorbance from 0.04 at 390 nm to 0.44 at 350 nm; however, no maximum was observed in this region. A further attempt to observe a charge-transfer maximum in TCVDMA · TNF was made. In 0.5 mm path length cells, 10^{-3} M solution of TCVDMA in ethanol or chloroform gave a level baseline. Portionwise solution of TNF in the sample cell gave new absorbance in both cases between 500 and 530 nm, with maxima at 517 nm in ethanol and 502.5 and 527.5 nm in chloroform attributed to charge-transfer absorption. The new absorption, which we assign to charge-transfer absorption in DMA·4TCVDMA, TCVDMA·TNF, and the chloranil complex is at energies expected[16] for molecular species with the energy levels and redox potentials listed in Table III. Thus the complexes

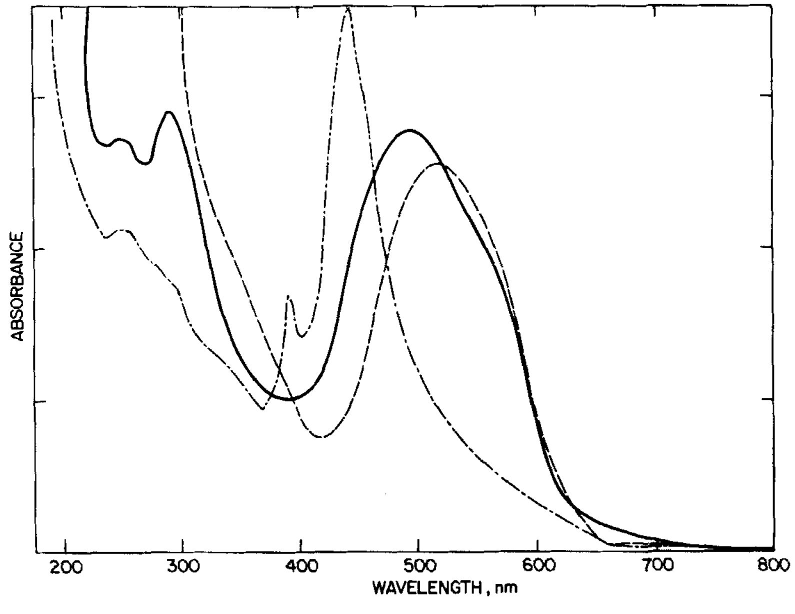


FIGURE 2 Solid state (KBr) absorption spectra of TCVDMA (–·–·), and its complex with TNF (– – – –) and *p*-chloranil (——).

TABLE III

Molecule	I_G,eV	A_A,eV	$E_{1/2}^{ox^a}$	$E_{1/2}^{red^a}$
DMA	7.45[b]	−1.24[c]	+0.71[d]	< −1.10[e]
TCVDMA	> 7.94[f]	—	+0.96[g]	−0.70[g]
C_6H_6	9.26[h]	−1.15[c]	+2.30[i]	
$C_6H_5CH_3$	8.82[h]	−1.11[c]	+1.98[i]	
C_6H_5Cl	9.00[h]	−0.75[c]	+2.07[i]	< −1.10[e]
$C_6H_3Cl_3$	~9.3[j]	—	> +2.0[e]	< −1.0[e]
TNF	—	+2.1[k]	> +1.6[e]	−0.42[l]
p-chloranil	≥ 10.11[h]	+2.8[m]	—	+0.02[n]

[a] Measured in acetonitrile solution vs. a saturated calomel electrode (SCE) unless otherwise specified.

[b] R. Egdell, J. C. Green and C. N. R. Rao, *Chem. Phys. Lett.*, **33**, 600 (1975).

[c] K. D. Jordan and P. D. Barrow, *Acc. Chem. Research*, **11**, 341 (1978).

[d] E. T. Sao, *et al. J. Am. Chem. Soc.*, **88**, 3498 (1966). This value is the potential at half-peak height for an irreversible anodic wave.

[e] Present work.

[f] This value reported in ref. b for *p*-nitrodimethylaniline.

[g] Reference 3.

[h] D. W. Turner, C. Baker, A. D. Baker, C. R. Brundle, "Molecular Photoelectron Spectroscopy," John Wiley, New York, N.Y. (1970), value listed for *p*-chloranil is that of *p*-benzoquinone which will be less than that of *p*-chloranil.

[i] C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, Inc., New York, New York, 1970, Chapter 3.

[j] D. G. Streets, G. P. Ceasar, *Mol. Phys.*, **26**, 1037 (1973). Value estimated from I_g of 1,2,3-trichlorobenzene.

[k] E. M. C. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63**, 3183 (1975).

[l] J. E. Kuder, J. M. Pochan, S. R. Turner and D. F. Hinman, *J. Electrochem. Soc.*, **125**, 1750 (1978).

[m] C. D. Cooper, W. F. Frey, R. N. Compton, *J. Chem. Phys.*, **69**, 2372 (1978).

[n] L. R. Melby in reference 5, p. 646.

of TCVDMA with DMA, TNF, and *p*-chloranil are Mulliken donor-acceptor complexes. We designate TCVDMA as the donor in its TNF and chloranil complexes and as the acceptor in its complex with DMA, in accord with the available data, summarized in Table III, concerning ionization energies, electron affinities, and redox potentials of these molecules. From Table III, TCVDMA is more easily oxidized and less readily reduced than TNF and chloranil and it is less easily oxidized and more easily reduced than DMA. Thus, TCVDMA is the first example of a molecule to form solid complexes in which it behaves as a donor with one molecule and as an acceptor with another.

The nature of the complexes of TCVDMA with benzene, toluene, chlorobenzene, and 1,2,4-trichlorobenzene and the role of these molecules in the complex is uncertain at present. When the experiment discussed above for spectral detection of complexation of DMA to TCVDMA in $CHCl_3$ solution was repeated using toluene and 1,2,4-trichlorobenzene instead of DMA, no new absorption was observed. If these complexes are typical donor-acceptor complexes, charge-transfer absorption between TCVDMA and any of these molecules would occur[16] at higher energies than those observed for DMA in this work, based on the data in Table III. However, from Table III, charge-transfer absorption from one TCVDMA molecule to another should occur[16] at lower energy than charge-transfer absorption involving TCVDMA and any of these molecules functioning either as a donor or as an acceptor. The possible occurence of intermolecular charge-transfer absorption in solid TCVDMA has been discussed.[6] Further discussion along these lines must await a crystal structure determination and other experimental work as well.

Solid state spectra of TCVDMA were studied using films evaporated onto quartz substrates. These spectra reveal absorption maxima at *ca.* 390 and 480 nm and a shoulder at longer wavelength as shown in Figure 3, in general agreement with solid state spectra of TCVDMA reported earlier.[6] However, the relative intensities of the maxima at *ca.* 390 and 480 nm vary

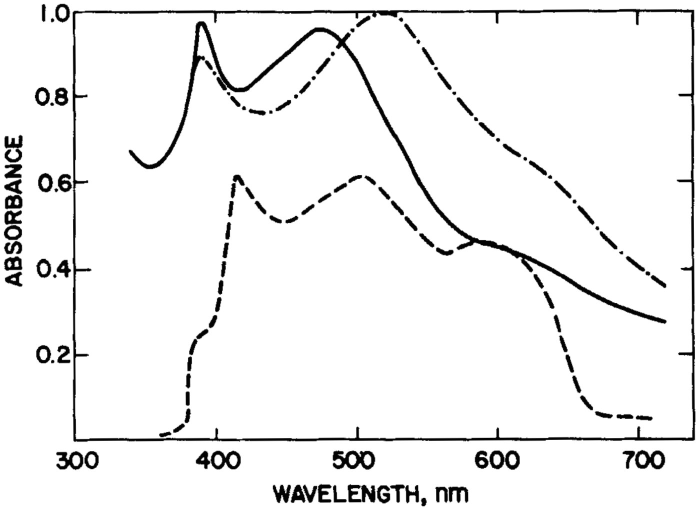


FIGURE 3 Solid state spectra of TCVDMA evaporated onto quartz discs: representative spectrum of evaporated film (——); spectrum of evaporated film saturated with benzene vapor (- - - -); spectrum of evaporated film heated at 110° for twenty minutes (—·—).

with different films. As displayed in Figure 3, heating of these films for *ca.* 20 minutes at 110° results in a decrease in the intensity at 390 nm and a shift of the maximum at 480 nm to 500 nm with modest intensity increase at 500 nm and longer wavelengths. Microscopic examination of relatively "thin" TCVDMA films suggests largely amorphous character while "thicker" films are clearly crystalline. No decomposition products could be detected by thin layer chromatographic analysis of those films which were heated. Solid state spectral behavior analogous to that observed in the present work by heating of TCVDMA films was reported earlier by Monahan and collaborators for arylazonaphthols[18] and indigo.[19] Also shown in Figure 3 is the dramatic consequence of exposing a TCVDMA film to benzene vapor at room temperature. The maxima shown in Figure 3 at 418, 505, and 583 nm are observed in both "thin" and "thick" films of TCVDMA. In view of the lack of detailed assignments of the transitions of TCVDMA and of a complete crystal structure noted above as well as the known[2] sensitivity of the spectrum of TCVDMA to is environment, a more detailed discussion of the results shown in Figure 3 is not appropriate at this time.

Given the large number of tricyanovinyl compounds which have been reported,[5] one would not expect, based on the relatively simple discussions herein, that the behavior reported for the simple aromatic solvents with TCVDMA would be unique. We have briefly explored several other molecules. From both benzene and DMA, we find that 4-(tricyanovinyl)-2,6-dimethylphenol[20] crystallizes unchanged. From DMA, we find that 3-(tricyanovinyl)-indole[20] does not crystallize with solvent. Cyclic voltammetry (experimental conditions as in Table III) of 4-tricyanovinyl)-2,6-dimethylphenol reveals the peak of an irreversible cathodic wave at -0.50 volts and no oxidation wave at potentials less than $+2.0$ volts. Also, analogous experiments on 3-(tricyanovinyl)-indole reveal the peak of an irreversible cathodic wave at -0.60 volts and no oxidation at potentials less than $+1.5$ volts.

Recently, it was reported,[21] in a publication devoid of experimental detail, that *p*-dimethylaminobenzylidenemalonitrile, (2,2-dicyanovinyl-DMA, DCVDMA) a molecular structure similar to TCVDMA, was dimorphic in that it crystallized as a yellow crystal from benzene and as an orange crystal from methanol. Since we had a sample of DCVDMA available, we decided to examine the detailed nature of the crystals reported[21] in light of our findings with TCVDMA. We found that DCVDMA crystallized from both benzene and methanol as yellow-orange crystals, with those from methanol slightly more intense in color. However, we found that the X-ray powder diffraction patterns of the crystals of DCVDMA isolated from methanol and benzene were indistinguishable. Thus, we were unable to reproduce the report[21] of dimorphic crystals for DCVDMA.

4 CONCLUSIONS

We have described above the first isolation of solid complexes of TCVDMA and noted several novel features. TCVDMA is the first example of a molecule to yield well-defined solid pi-complexes in which it behaves as donor with some molecules (TNF, *p*-chloranil) and as an acceptor with another (DMA). TCVDMA may thus be termed pi-amphoteric.[1b] A potential use of such pi-amphoteric molecules might be in the formation of new classes of complexes with three interacting components. Our attempts to use TCVDMA to form three component complexes with DMA and TNF have led only to the isolation of mixtures of the two-component complexes of these compounds to date.

TCVDMA has a very large molecular dipole moment, 10.7–10.9D.[3] The interactions of this dipole of a complexing partner, such as chlorobenzene, or with a centrosymmetric complexing partner, such as benzene, and the quantitative role of such interactions in the formation of the TCVDMA complexes with simple aromatics are uncertain at present. Additionally, the quantitative assessment of the contribution of such dipole-dipole or dipole-induced dipole interactions to the lattice energies of these complexes must await further experimental and theoretical study.

As we noted above, benzene is not a strong pi-donor or -acceptor, yet it easily complexes TCVDMA; its role in the crystalline complex is uncertain at present. While the crystal structure of the 1 : 1 pi-complex between benzene and decachloropyrene has been reported,[22] studies to probe the nature of the interaction between these molecules have not been reported to date. Another molecule with both donor and acceptor groups in conjugation, 4 - dicyanomethylene - 2 - methyl - 6 - *p* - dimethylaminostyryl - 4H - pyran, was recently reported[23] to crystallize from benzene as a 1:1 complex of unspecified nature.

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