Charge Transfer and Addition Products between Alkylated Phenazine Donors and Ethanetetracarbonitrile (TCNE): Crystal and Molecular Structure of the Dye 2,2'-(2,3,5,10-Tetrahydro-5,10-dimethylphenazine-2,3-diylidene)bis(propanedinitrile) (TMPP)

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Abstract: Mixing solutions of 5,10-dimethyl-5,10-dihydrophenazine (M_2P) and TCNE yields different solid reaction products with nearly 1:1 donor:acceptor stoichiometry: Without excluding air the reaction leads to an oxygen-containing intermediate of stoichiometry $C_{19}H_{15}N_5O$ (**1**). The dark green to black crystals are twinned having cell dimensions a = 14.34 Å, b = 30.10 Å, c = 4.17 Å, β = 90.1° and crystallizing in the monoclinic space group $P2_1/n$. Violet needles of the 1:1 salt, M_2P^+ $TCNE^-$ (**2**), are obtained only by excluding moisture and oxygen. They crystallize in always twinned specimens in a tetragonal space group, the unit cell along the needle axis being 7.46 (3) Å. Lustrous (brass-like) crystals of TMPP (**3**) (formula $C_{20}H_{12}N_6$, M_r = 336.358, d_c = 1.35 Mg·m^{-3}) are obtained under air and in moist solvents. They crystallize in the monoclinic space group $C2/c$ with a = 9.674 (3) Å, b = 19.411 (8) Å, c = 9.603 (3) Å, V = 1657.4 (9) Å^3, β = 113.20 (2)°, and Z = 4. The structure determination yielded in the final refinement an R_w index of 0.076. **3** is a condensation product of M_2P and TCNE under loss of 1 mol of H_2. Two rings of the former M_2P molecule are planar. The ring with the two "condensed" $>C{=}(CN)_2$ groups is twisted. The $>C{=}(CN)_2$ groups are also twisted with respect to each other and out of the "molecular" plane because of sterical hindrance. The molecules form regular stacks along the z axis with interplanar distances of 4.75 (2) Å. The linearly polarized strong optical reflection which causes the metallic luster is polarized perpendicular to the molecular planes, indicating appreciable intermolecular CT interactions. Corresponding products are obtained with the donors 5,10-dihydro-5,10-diethylphenazine (E_2P) and 5-methylphenazinium hexafluorophosphate ($MP^+PF_6^-$), thus representing a new class of thermally and chemically highly stable dyes with strong electron-donating and -withdrawing centers on one molecule.

We currently are investigating the physical properties–structure relations in solid donor:acceptor (DA) complexes of phenazine and its derivatives as donors with acceptors typically like 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile) (TCNQ) and ethanetetracarbonitrile (TCNE).[1,2] One of the most capable donors in this series is 5,10-dimethyl-5,10-dihydrophenazine, M_2P.[3] Reacting neutral M_2P with neutral TCNE yields—depending on the experimental conditions—three different solid compounds with an analytical composition close to M_2P:TCNE = 1:1.

In contrast to other popular acceptors like, e.g., TCNQ or 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), TCNE is well-known since its discovery[4] to be a highly reactive species. It may act as a dienophile to give Diels-Alder adducts even with compounds like anthracene,[5] as a π acceptor to form charge-transfer complexes with aromatic π donors;[6,7] with primary or secondary aliphatic amines it yields *N*-(tricyanovinyl)amines under evolution of hydrogen cyanide,[8] and with tertiary and secondary aromatic amines intensely colored 4-(tricyanovinyl)arylamine dyes.[8–10] The special activity of TCNE in *moist* solvents has been noticed since the early experiments with this compound.[11] The donor M_2P for itself is quite sensitive to oxidation and degrades under illumination with light under loss of methyl groups rapidly to different partly unknown species.[12]

It was not surprising, therefore, that the reaction between the reactive molecules M_2P and TCNE in solvents of varying moisture content led to products other than the normally expected 1:1 adduct. Only one of the solids (consisting of violet needles) can obviously be ascribed to the expected 1:1 CT complex. Two other compounds (a dark green one and a deep blue species with a striking luster in solid state) are condensation products. Here we report the unusual molecular structure of the latter reaction product and the unit cell parameters of the former "adduct" together with some characteristic physical data like ESR and optical behavior. The analogous reactions of the M_2P homologue 5,10-diethyl-5,10-dihydrophenazine (E_2P) and of 5-methylphenazinium hexafluorophosphate ($MP^+PF_6^-$) with TCNE have been investigated to obtain additional hints concerning the reaction mechanism.

Preparation of Compounds

Starting Materials. M_2P and E_2P were prepared analogously to an earlier described procedure.[13] Phenazine was reduced to the dianion with metallic potassium and alkylated by addition of methyliodide and ethyliodide, respectively. $MP^+PF_6^-$ was obtained from the methosulfate by anion exchange with $NH_4^+PF_6^-$.

Paramagnetic (Green) Condensation Product of M_2P with TCNE $C_{19}H_{15}N_5O$ (1). M_2P (1 mmol) and *technical* TCNE 1 mmol were each dissolved in 30 mL of hot, *absolute* ethanol and the two solutions combined. The reaction flasks were fitted with $CaCl_2$ drying tubes. The mixture was allowed to cool down slowly. Black-green needles are obtained after leaving the flask in the freezing compartment of a refrigerator. The compound can also be obtained by the same procedure, using absolute acetone or absolute acetonitrile as solvents. Anal. Calcd for

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$C_{19}H_{15}N_5O$: C, 69.28; H, 4.56; N, 21.26; O, 4.86. Found: C, 69.33; H, 4.43; N, 21.52; O, 5.16.

$M_2P^+TCNE^-$ (2). M_2P (2 mmol) was dissolved under a dry nitrogen atmosphere in 60 mL of absolute toluene, heated, and mixed with a solution of 2 mmol of TCNE (freshly sublimed at 130 °C in a N_2 stream) in 60 mL of hot and absolute acetonitrile (EGA gold label, distilled over P_2O_5 then over BaO under N_2 atmosphere). The mixture was slowly cooled in an oil bath. After 3 h the *air-sensitive* precipitate was filtered and handled in an inert gas atmosphere. The black needles have a violet luster. Anal. Calcd for $C_{20}H_{14}N_6$: C, 70.99; H, 4.17; N, 24.84. Found: C, 70.60; H, 4.20; N, 26.00.

TMPP (3). M_2P (1 mmol) was dissolved in about 70 mL of *technical* acetone and mixed with a solution of 1 mmol of TCNE in about 20 mL of *technical* acetone. A deep green almost black solution results, from which upon standing at room temperature lustrous brass-like crystals separate slowly. The precipitate is filtered off after a few hours (yield = 22% from theory). The dichroic crystals are only slightly soluble in common organic solvents, in acetone and acetonitrile, with a *deep blue* color. They can be heated up to 300 °C without noticeable changes. Anal. Calcd for $C_{20}H_{12}N_6$: C, 70.99; H, 4.17; N, 24.83. Found: C, 71.10; H, 4.01; N, 24.91.

Preparation of Single Crystals. Single crystals of the investigated materials were obtained by slow diffusion. The solid neutral compounds were filled in the two compartments of an H-shaped glass tube.[14] By use of oxygen-free, absolute solvents with moderate polarity like methanol, ethanol, or acetone as diffusion medium, black-violet needles of **2** grow up to 5-mm length within 5 days. Nonpolar solvents produce only very thin fibers. Solvents with higher polarity are not recommended because of the high solubility of the complex.

By use of acetone, or even better a 1:1 mixture of acetonitrile and toluene (in each case technical moist quality), for the diffusion process, thick monoclinic prisms of **3** grow to 4-mm edge length within 1 week. These crystals appear greenish under polarized light. In certain crystal positions a remarkable brass-like luster which is linearly polarized appears. **3** is only slightly soluble in acetone, acetonitrile, or Me_2SO but with a deep *blue* color, whereas **2** is highly soluble in polar solvents, exhibiting the well-known intensive green color of the free dissociated radical ions.

TEPP. Starting with E_2P and TCNE, a procedure corresponding to that used for TMPP yields crystals of TEPP which behave very similar to **3** with respect to shape, size, and solubility. Anal. Calcd for $C_{22}H_{16}N_6$ (M_r = 364.42): C, 72.51; H, 4.42; N, 23.06. Found: C, 72.38; H, 4.83; N, 22.80.

Reaction between $MP^+PF_6^-$, TCNE, and Malonodinitrile (MDN). A blue dye (MPP) can also be obtained starting from $MP^+PF_6^-$ instead of R_2P. Reacting neutral TCNE in DMF or acetonitrile (both technical grade) with $MP^+PF_6^-$ a deep blue solution can be obtained. The precipitated crystals could be identified as 2-(10-(methylphenazine)-2-ylidene)propanedinitrile (MPP) (see final section of this paper). Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.41; H, 3.90; N, 21.69. Found C, 74.55; H, 3.99; N, 21.65.

Using MDN, $N{\equiv}C{-}CH_2{-}C{\equiv}N$ (a "hydrogenated half" of TCNE), instead of TCNE under the above mentioned conditions results in an immediate reaction between MDN and $MP^+PF_6^-$ yielding again MPP. MPP surprisingly, too, can be obtained by reaction of M_2P^+ with MDN. While neutral M_2P under anaerobic conditions does not react with MDN the cation yields MPP with MDN but *no* (3)! Without exclusion of air, neutral M_2P reacts slowly with MDN to MPP, certainly because of the primary oxidation of M_2P to M_2P^+ by oxygen.

X-ray Investigations

$C_{19}H_{15}N_5O$ (1). Rotation and Weissenberg photographs of the black needles of $C_{19}H_{15}N_5O$ showed that the crystals have twinned lattices. Thus no further structure determinations were made. The cell parameters, determined from the rotation and Weissenberg photographs, are a = 14.34 Å, b = 30.10 Å, c = 4.17 Å, and β = 90.1°. Systematic absences of Bragg reflections $h0l$ for $h + 1 = 2n + 1$ and $0kl$ for $k = 2n + 1$ suggest that the crystals belong to the monoclinic space group $P2_1/c$.

$M_2P^+TCNE^-$ (2). Rotation photographs of the violet crystals of **2** showed very weak layers with odd orders and strong layers with even orders. The unit cell along the rotation axis is 7.46 (3) Å. Weissenberg photographs showed a tetragonal symmetry in the 0 and 2 zones but with a strange kind of systematic absence of Bragg reflections. The Weissenberg photograph of the first layer (4-days exposure) showed a geometry of reflections with regard to the even layers which could not be explained unambigously. Perhaps these appearances are caused by a twinned crystal, but this is speculative.

Table I

scan	$\theta{-}2\theta$
2θ max, deg	59.59
scan width, deg	1.8 (2ϑ) (considering α_1/α_2 splitting for larger scattering angles)
scan rate, deg min^{-1}	variable, min 2 (ϑ) max 29.3 (ϑ)
background (BG)	measured at either side, one quarter of the scan line each, subtracted from integrated intensity
check reflectns	2 (measured after every 100 reflections)
emperical absorptn correctn	ψ scans (at 10° (ψ) steps)
LP correctn	were applied to the data
$\sigma(I)$ calculatn	$\sigma(I) = \left[\text{total scan count} + \frac{\text{sum of BG counts}}{(\text{BG to scan ratio})^2}\right]^{1/2}$ (scan rate)

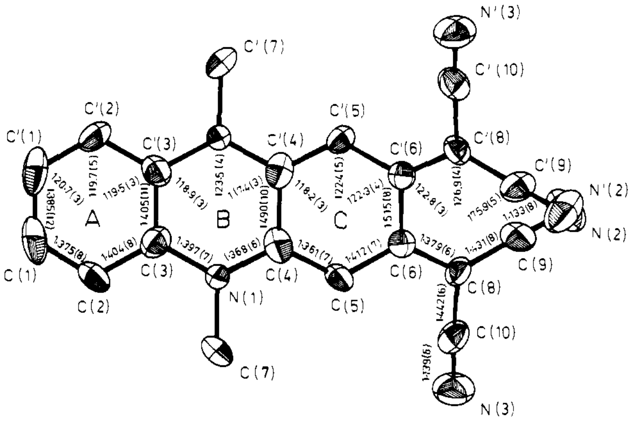

Figure 1. ORTEP plot of a molecule of + with bond angles and distances.

2,2'-(2,3,5,10-Tetrahydro-5,10-dimethyl-2,3-diylidene)bis(propanedinitrile) (3). Single-Crystal Structure Determination. Cell parameters (see Abstract) were first determined by rotation and Weissenberg photographs and then redetermined from an orientation matrix derived from 20 independent reflections on a Syntex R3 diffractometer (radiation Mo Kα graphite monochromator). The reflections showed systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Thus the space group is $C2/c$. Data collection was carried out on the diffractometer (according to Table I) yielding 1200 reflections with $I > 0$. No reflections were suppressed to get smaller standard deviations.

The structure was solved by direct methods. A refinement with all non-hydrogen atoms yielded an R value of 0.132 (isotropic temperature factors). A difference Fourier map showed the hydrogen atoms, and a refinement with all atoms and anisotropic temperature factors (H atoms with isotropic temperature factors) and weighted functions ($w = 1/\sigma^2(F)$ gave an R value of R_w = 0.076. Calculations were carried out with the SHELXTL program system[15] on a Nova 3 computer.

Description of the Structure. The atomic coordinates are shown in Table II. Bond distances and angles are shown in Figure 1. The distances between carbon and the hydrogen atoms are between 0.918 and 1.065 (±0.04) Å. The molecule lies on a 2-fold axis. Ring A and ring B of the molecule are planar. Ring C with the two "condensed" >C=(CN)$_2$ groups is significantly twisted. This is shown in Figures 2 and 3 with two, in c direction adjacent,

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Table II. Atomic Coordinates (×10^5)

	x/a	*y/b*	*z/c*	*U*
N(1)	15 267 (42)	18 486 (20)	28 653 (40)	285 (28)
C(1)	7 726 (63)	37 170 (28)	27 176 (72)	471 (43)
C(2)	15 531 (64)	31 080 (34)	29 140 (69)	498 (44)
C(3)	7 789 (58)	24 788 (27)	26 849 (63)	376 (36)
C(4)	8 325 (54)	12 244 (25)	27 423 (59)	304 (33)
C(5)	15 752 (55)	6 143 (25)	31 574 (48)	300 (33)
C(6)	8 170 (48)	−176 (24)	30 480 (46)	284 (32)
C(7)	31 415 (52)	18 337 (27)	31 009 (51)	503 (42)
C(8)	15 173 (53)	−5 894 (27)	38 793 (52)	324 (33)
C(9)	8 082 (62)	−12 048 (31)	40 907 (60)	391 (37)
C(10)	30 827 (55)	−5 555 (25)	48 856 (53)	366 (35)
N(2)	3 045 (55)	−16 912 (22)	43 458 (49)	558 (40)
N(3)	43 188 (45)	−5 556 (24)	56 868 (42)	549 (37)
H(1)	13 107 (514)	41 632 (215)	29 968 (456)	600
H(6)	37 584 (428)	20 580 (186)	41 805 (402)	600
H(7)	32 723 (470)	22 206 (191)	25 978 (450)	600
H(8)	34 843 (454)	14 030 (220)	30 017 (416)	600
H(2)	27 044 (450)	31 202 (272)	32 385 (425)	600
H(5)	27 261 (447)	5 912 (217)	38 585 (379)	600

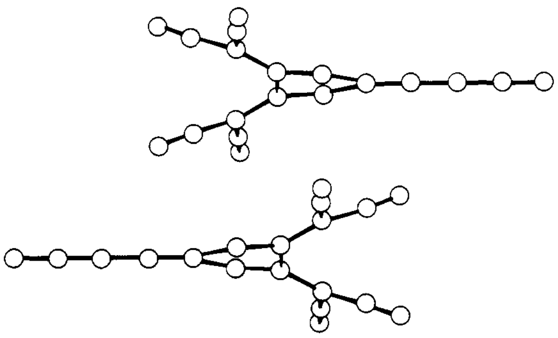
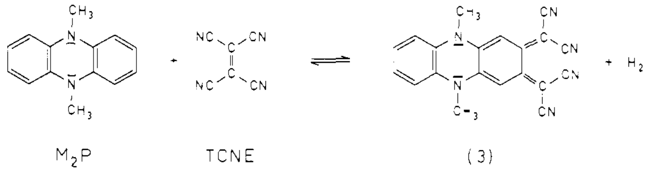


Figure 2. Projection of two TMPP molecules along the *ab* plane and parallel to the intramolecular N···N axis of ring B.

Scheme I



molecules. The >C=(CN)$_2$ groups are twisted with opposite orientation around the C(6)—C(8) and C′(6)—C′(8) bonds, respectively. Thus the different cyanonitrogen atoms N(2) and N′(2) of one molecule have a distance of 3.370 (8) Å (Figure 3). The molecules form regular stacks along the *c* axis with interplanar distances of 4.75 (2) Å with respect to the best least-squares planes through rings A and B. A perpendicular projection of two molecules of the stack is shown in Figure 4.

TMPP evidently is a product of a condensation reaction between M$_2$P and TCNE corresponding to Scheme I.

ESR Investigations of 1, 2, and 3

Experimental Conditions. EPR spectra were taken on a Bruker B-ER 418 spectrometer equipped with a Bruker NMR gaussmeter for field calibration and an EIP 351 D microwave frequency counter. EPR intensity was determined by double integration of the first derivative of the absorption line. The integration range was chosen at least 10 times the peak-to-peak line width.

Polycrystalline samples of **1**, **2**, and **3** show *g* values lying between 2.0031–2.0034. This is the range observed for several other CT complexes of TCNE with phenazine derivatives.[16]

Green Needles of $C_{19}H_{15}N_5O$ (1). Single crystals show a sharp, exchange narrowed Lorentz line. The line width increases linearly from 1 to 2.4 between 100 and 400 K (needle axis perpendicular to H_0). The line intensity is only weakly temperature dependent. While it is constant above 250 K it decreases continously by about 25% down to 100 K. In this respect **1** resembles very much other simple $M_2P^{+}\cdot$ salts like $M_2P^+Br^-$ or $M_2P^+BF_4^-$. The strong deviation from Curie behavior clearly shows the presence of intermolecular interactions.

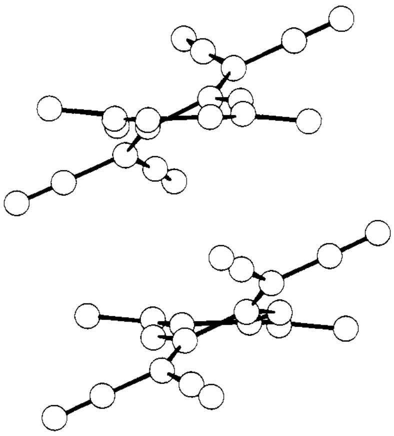


Figure 3. Projection of two TMPP molecules along the *ab* plane and perpendicular to the intramolecular N···N axis of ring B.

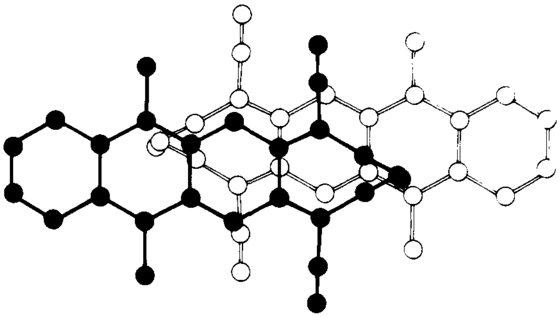


Figure 4. Projection of two TMPP molecules perpendicular to their *ab* planes.

CT Complex $M_2P^+TCNE^-$ (2). Single crystals show a symmetrical exchange narrowed line of peak-to-peak width of 3.7 G (long axis perpendicular to H_0) at room temperature. On lowering of the temperature the line becomes asymmetric. Below 240 K the line is symmetrical again with a width of 1.5 G. Yet far extending broad wings become visible. Below 140 K two rather broad fine structure lines with a line width of ca. 8–8.5 G are observed besides the central line. The fine structure splitting depends very much on the crystal orientation. In a special orientation—long crystal axis parallel to H_0—the splitting is 450 G. Between 140 and 100 K, the lowest accessible temperature, the intensity of the fine structure lines slightly increases with decreasing temperature (Figure 5). But as the same is true for the central line, it is probable that the unusual temperature behavior of the outer lines is simply due to some though small overlap of the lines.

The large fine structure splitting in **2** is to be compared with the zero-field parameters in the similar TCNQ compounds.[1,2,17] It is evident that the dipolar interaction between the unpaired electrons of neighboring radicals is much stronger in the TCNE than in the TCNQ salts. The reasons for this might be smaller intermolecular distances and/or a lower degree of delocalization of the unpaired electron in the TCNE compounds.

In contrast to this is the fact that the fine structure lines already merge at rather low temperature while in the corresponding phenazine TCNQ complexes this merging takes place at about room temperature or even higher.[1,2,17] If exciton–exciton collision is responsible for the line merging, then the exciton concentration

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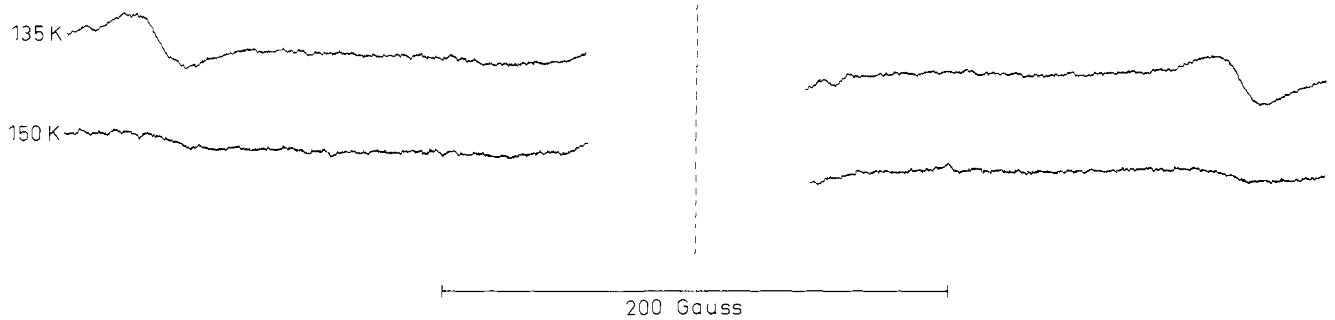


Figure 5. Single-crystal ESR spectra of $M_2P^+TCNE^-$ **2** in a special orientation at 135 and 150 K.

should be rather high already at about 140 K. This again would mean that the activation energy for the occupation of the triplet state should be rather small compared to the cases in phenazine TCNQ salts.[1,2,17]

TMPP (3). Single crystals of **3** give a single low-intensity absorption line of 20-G width. Solutions of **3** in Me_2SO show no EPR signal. This observation is reminiscent of the behavior of deeply colored solid dyes like for instance methylene blue, indigo, etc.[18]

The rather broad EPR line indicates only small intermolecular interactions. Effective exchange mechanism would lead to narrow lines as in **1** and **2**. This is in agreement with the low electrical conductivity in **3**.

Optical Investigations

Single Crystals of 3. Before taking the optical spectra, a correlation between the molecular structural parameters and certain crystal habit features (e.g. faces, edges) had to be established. We made oscillation photographs of a crystal of **3** in different orientations. It was possible to determine the *y* direction next to the *x* direction of the unit cell within the crystal. The TMPP molecules are nearly parallel to the crystallographic *ab* plane (angle between the TMPP plane and *ab* plane 14.7°), and the longer molecular axis lies parallel to *b*. For the optical investigations the crystal was mounted under a microscope on a device which could be rotated around different directions. Linearly polarized light was used to determine the directions in which the metallic "greenish" luster of the crystals could be observed or disappeared. The brass-like reflection disappeared for all orientations in which the directions of polarization and the planes of the TMPP molecules were parallel. Thus, it has to be concluded that the "metallic" reflection is polarized perpendicular to the molecular planes and, therefore, is caused not by intramolecular but by intermolecular charge-transfer interactions.

Solution and Polycrystalline Optical Spectra. Diluted solutions of **3**, TEPP, and MPP in acetonitrile reveal intense bands in the visible and prove the close similarity between **3** *and* TEPP and the different behavior of MPP. Wavelengths (in nm) and absorptivity are given in Table III.

The same intense absorptions can be observed in a polycrystalline sample of TMPP (KBr pellet) with an *additional* broad absorption in the near-IR (around 1150 nm = 1.15 μm) which might be caused by the intermolecular charge transfer and which might be responsible for the "metallic luster" of the solid compound. Single-crystal wavelength-dependent optical investigations have to be carried out to clarify this point. The recent interest in stable organic compounds absorbing in the near-IR makes this solid especially interesting.

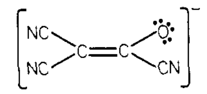
Conclusions. Its remarkable metallic reflection in the solid state and the blue color in solution are caused by strong intermolecular and intramolecular charge-transfer interactions, respectively. **3** and its derivatives are additional examples of compounds in which the strong absorption in solutions originates from the so-called intramolecular charge-transfer transition,[10] i.e., the transition between the donating phenazine part of the molecule and the accepting "cyano" part. The fact, that an additional long-wavelength intermolecular transition can be excited in the solid renders the photochemistry of the crystallized material especially interesting.

Table III. Wavelengths and Absorptivity (α) [$\ln (I/I_0) = -\alpha c d$] for 3, TEPP, and MPP in Acetonitrile Solutions

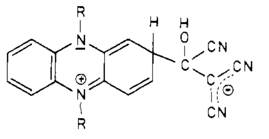
compd	λ, nm	α, mol/1000 cm²
3, $C_{20}H_{12}N_6$ concn = 3×10^{-5} M	λ_1 625	2.05×10^4
	λ_2 402	1.02×10^3
	λ_3 360	3.51×10^3
	λ_4 320	4.50×10^4
	λ_5 240	5.02×10^3
	λ_6 230	8.71×10^3
TEPP, $C_{22}H_{16}N_2$, concn = 6×10^{-6} M	λ_1 626	5.25×10^4
	λ_2 410	5.07×10^3
	λ_3 360	1.03×10^3
	λ_4 320	1.01×10^5
	λ_5 230	5.95×10^4
MPP, $C_{16}H_{10}N_4$, concn = 6×10^{-5} M	λ_1 670	1.26×10^4
	λ_2 615	1.84×10^4
	λ_3 580	9.96×10^3
	λ_4 415	2.70×10^3
	λ_5 392	2.32×10^3
	λ_6 338	2.45×10^4
	λ_7 238	2.60×10^4

Structural Relations

Solid Green Intermediate $C_{19}H_{15}N_5O$ (1). Elemental analysis, ESR, and X-ray data suggest that this compound is a CT complex between R_2P^+ cations and a paramagnetic negatively charged hydrolysis product of TCNE like a



anion. Alternatively, referring to the reaction of TCNE with thioenol ether[19] a paramagnetic intermediate zwitterion of the form



(1)

could be responsible for the type of ESR spectra and the elemental analysis.

CT Complex (2). Though detailed X-ray data could not be obtained from this compound (possibly because of twinning problems), the ESR results give good reason to assume that this is the 1:1 charge-transfer salt $M_2P^+TCNE^-$. The typical fine structure suggests rather strong interactions between different $TCNE^-\cdot$ or $M_2P^-\cdot$ and $TCNE^-\cdot$ radicals. The C≡N frequencies in the IR are split, suggesting a rather low site symmetry (dimerization!) of the $TCNE^-\cdot$ ions in the lattice.

TEPP and 3. Analytical, optical, ESR, and IR data leave no doubt that E_2P reacts with TCNE under moisture and air to the

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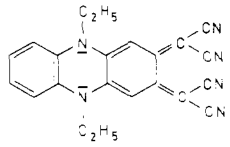
homologue of 3. This means that two ethyl groups on the B-ring nitrogens in TEPP replace the two methyl groups of 3. The strong correlations between physical and chemical properties ascertain the structure of TEPP as

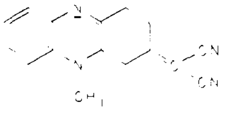


TEPP

The reaction path could be similar as the one proposed for the (2 + 2) cycloaddition of TCNE to cyclic thioenol ether,[19] with the final abstraction of H_2 per mole of adduct.

The structure and the physical properties of this new class of compounds are strongly related to the similar (tricyanovinyl)-amines.[8] (Tricyanovinyl)amines have found widespread interest because of their interesting optical[10] and dyeing[8] properties and because of their capability to yield charge-transfer complexes with donors *and* acceptors.[20] Since 3 and TEPP contain both π-donating and π-accepting groups in the molecule, a similar charge-transfer chemistry can be expected. The high chemical and thermal stability, the symmetry of the molecule, and the presence of two propanedinitrile groups make these dyes expecially interesting.

MPP. The reaction product between $MP^+PF_6^-$ and TCNE in acetonitrile is again a deep blue dye which is formulated as



MPP

It can be obtained additionally in an immediate reaction between $MP^+PF_6^-$ and malonodinitrile and from a solution of malonodinitrile with M_2P in DMF or acetonitrile which contains equimolar amounts of bromine as an oxidation agent. The latter reaction leads primarily to M_2P^+ and after partial degradation of M_2P^+ to NMP^+ which is involved in the above mentioned reaction. Similar "oxidative demethylations" of M_2P^+ species have been observed earlier.[12]

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Registry No. 1, 83720-86-9; **2**, 83720-87-0; **3**, 83720-88-1; M_2P, 15546-75-5; TCNE, 670-54-2; TEPP, 83720-89-2; E_2P, 62248-00-4; MDN, 109-77-3; $MP^+ \cdot PF_6^-$, 65149-30-6; MPP, 83720-90-5.

Supplementary Material Available: Listing of observed and calculated structure factors and a listing of the anisotropic temperature factors (9 pages). Ordering information is given on any current masthead page.

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Chemistry of Anthocyanin Pigments. 9.[1] UV-Visible Spectrophotometric Determination of the Acidity Constants of Apigeninidin and Three Related 3-Deoxyflavylium Salts

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Abstract: The equilibrium constants for the structural transformations of some 3-deoxyanthocyanidins in water at 25 °C have been measured by using the pH-jump method. This method has been described previously.[2] According to their particular substitution patterns, hydroxylated flavylium salts can exist in slightly acidic media in several neutral forms: the quinoidal bases A, the carbinol pseudobase B, and the chalcone pseudobase C. Two of the compounds investigated, namely 4′,5,7-trihydroxyflavylium (apigeninidin) and 4′-methoxy-4-methyl-5,7-dihydroxyflavylium chlorides, exist essentially as a mixture of the three neutral forms A, B, and C, the colored species A being the most abundant. As expected, 4′,7-dihydroxyflavylium chloride is stable in the open chalcone structure C. This result is in good agreement with the catalytic light effect generally observed for the ring-closure reaction of this species leading to the flavylium cation AH^+. Only for the monohydroxylated pigment 4′-methoxy-4-methyl-7-hydroxyflavylium chloride is the quinoidal base A perfectly stable, whatever the pH. In contrast to natural anthocyanins, the hydration of the pyrylium ring is less efficient and occurs, therefore, at much higher pH values (pH 5-6). Proton loss from the phenolic acidic hydroxyl groups of the flavylium cation takes place in the usual acidity range (pH 4-5), indicating that these groups are strongly hydrogen bonded to the surrounding water molecules. The chalcone content is much higher than for the anthocyanins, and for 4′,7-dihydroxyflavylium chloride for instance, the value for the equilibrium ratio of the chalcone to the carbinol is as high as 20.6.

Introduction

In a previous paper, a general method for measuring the equilibrium constants associated to the structural transformations of anthocyanins in aqueous solutions was described.[2] Anthocyanins are glycosylated polyhydroxy and polymethoxy derivatives of 2-phenylbenzopyrylium (flavylium) salts. This method is based on pH-jump experiments, where the position of the system, initially

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(1) Part 8: Brouillard, R. In "Anthocyanins as Food Colors"; Markakis, P., Ed.; Academic Press: New York, 1982; p 1.

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