REACTION OF TETRACYANOQUINODIMETHANE WITH AZOLES*

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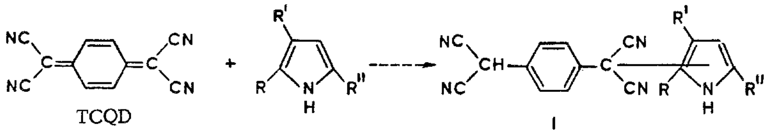
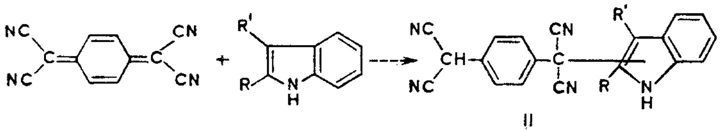
The reaction of tetracyanoquinodimethane (TCQD) with azoles was studied. It was found that products of 1,6 addition to the quinoid system of TCQD are formed with pyrrole, indole, and their methyl derivatives. The addition products split out HCN under the influence of UV light to give deeply colored products of replacement of one nitrile group in TCQD by a heterocyclic grouping. Data on the UV and NMR spectra of the compounds obtained are presented.

7,7,8,8-Tetracyanoquinodimethane (TCQD) is a strong organic acid, and reactions involving nucleophilic addition to the quinoid system are characteristic for it. It reacts readily with nucleophiles such as aromatic amines [1-3] and azulene [4] to give 1,6-addition products. We have observed that TCQD reacts readily with N-heterocyclic compounds containing one nitrogen atom in a five-membered ring to give addition products.



R and R' = H, CH$_3$ or a single bond, R'' = H or CH$_3$

Pyrrole and its methyl derivatives in polar solvents (for example, alcohol and acetonitrile) react with TCQD at 80° after a few minutes to give addition products (I). It follows from the NMR spectra of these compounds that the reaction with pyrrole and 2,4-dimethylpyrrole takes place in the 2 position of the heteroring, whereas the reaction takes place in the 3 position in the case of 2,5-dimethylpyrrole.



R and R' = H, CH$_3$ or a single bond

The reaction proceeds just as readily with indole and 2-methyl indole, but, in contrast to pyrrole, as one should have expected, the 3 position undergoes attack to give II. If the 3 position of the indole is occupied (for example, skatole), addition product II is formed only under more severe conditions [in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) at 150°], and the reaction takes place in the 2 position of the heteroring. In the case of skatole, addition product II was not isolated in pure form because of its rapid oxidation, but the NMR spectrum of a sample clearly showed that the reaction occurred in the 2 position of the heteroring.

Tetracyanoquinodimethane does not form an addition product with 2,3-dimethylindole; in this case the reaction stops at the step involving the formation of the molecular complex. Thus the reaction of TCQD with azoles is similar (with respect to the direction of the reaction to certain sites of the heteroring) to mild electrophilic substitution in azoles. This is explained by the similarity of the TCQD molecule and the molecules of typical electrophilic agents: On one hand, they are all strong electron acceptors, and on the other, the carbon atom in the TCQD molecule containing two nitrile groups can be considered to be a strong electrophilic center that attacks the donor molecule.

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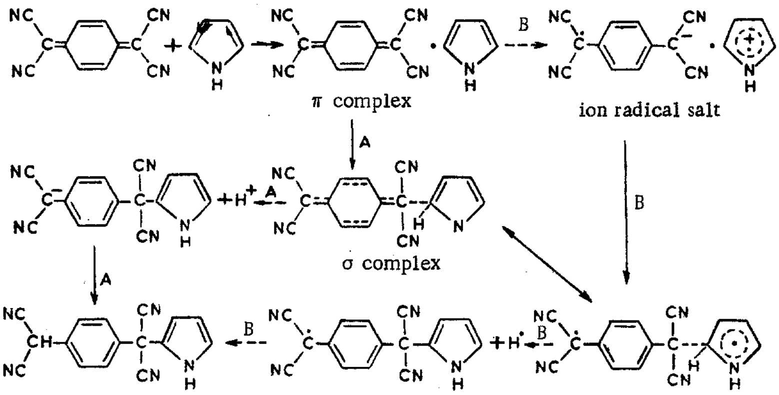
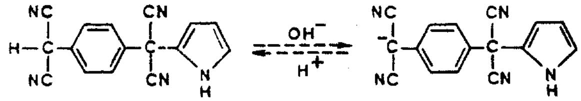


Two mechanisms for the reaction of TCQD with azoles can be assumed. The first mechanism involves direct replacement of the hydrogen in the heteroring by the attacking electrophilic center of the TCQD molecule to give a classical σ transition complex (path A). The second mechanism involves initial one-electron oxidation of the donor TCQD molecule to give an intermediate ion radical salt with subsequent nucleophilic substitution in the azole cation (path B). It should be noted that the σ complex (path A) and the product of conversion of the ion-radical salt (path B) are in point of fact resonance structures, and the difference in the subsequent transformations of these substrates consists in the fact that a proton is split out in the first case, whereas a hydrogen atom is split out in the second. We presently do not have data that make it possible to choose between these two mechanisms, although indirect proof, for example, the explicit decrease in the reaction rate as the ionization potential of the donor increases, constitutes evidence in favor of the second reaction pathway, since in this case the step involving the formation of the ion-radical salt is slowed down.

Compounds I and II are white crystalline substances; their physical constants are presented in Table 1. The UV spectra of I and II in nonpolar solvents are almost the same as the spectra of the corresponding starting heterocycles (Fig. 1, curves 1 and 2). In protic solvents these compounds readily dissociate with splitting out of the malononitrile proton to give a carbanion, for which an intense absorption band at λ_{max} 320 nm ($\varepsilon = 3 \cdot 10^4$, alcohol), the position of which is independent of the heterocycle used for the reaction (Fig. 1, curve 3), is characteristic. We have previously assigned this band to carbanion III on the basis of a study of the absorption spectra of p-phenylenedimalononitrile in various solvents [2]. The dissociation of I and II is reversible and the equilibrium is readily shifted when acids and alkalis are added.



III

The IR spectra of I and II contain bands of vibrations of aromatic and heterocyclic rings. The band of vibrations of nitrile groups is absent or appears as a very weak band at 2260 cm^{-1}, as observed for the products of the reaction of TCQD with aromatic amines [1].

TABLE 1. Physical Constants of α-Azolyl-p-phenylenedimalononitriles I and II

Compound	mp, °C (crystallization solvent)	Empirical formula	Found, %			Calculated, %			λmax, nm, chloroform (alcohol)	Synthetic method	Yield, %
			C	H	N	C	H	N			
α-(2-Pyrrolyl)-p-phenylenedimalononitrile	116—118 (80% alcohol)	$C_{16}H_9N_5$	70,6	3,3	26,1	70,8	3,3	25,8	265,270 (320)	A	72
α-(2,4-Dimethyl-5-pyrrolyl)-p-phenylenedimalononitrile	120—121,5 (alcohol)	$C_{18}H_{13}N_5$	72,4	4,5	23,6	72,2	4,4	23,4	266,272 (320)	A	82
α-(2,5-Dimethyl-3-pyrrolyl)-p-phenylenedimalononitrile	68—70 (alcohol)	$C_{18}H_{13}N_5$	72,1	4,8	23,3	72,2	4,4	23,4	266,272 (320)	B	92
α-(3-Indolyl)-p-phenylenedimalononitrile	164—165 (alcohol)	$C_{20}H_{11}N_5$	74,7	3,9	21,9	74,8	3,5	21,8	270,280 288(320	A	93
α-(2-Methyl-3-indolyl)-p-phenylenedi-lononitrile	167—167,5 (alcohol)	$C_{21}H_{13}N_5$	74,9	3,9	20,9	75,2	3,9	20,9	271,279 288(320)	A	70

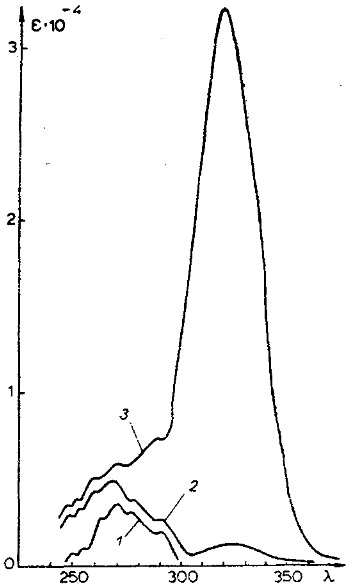


Fig. 1

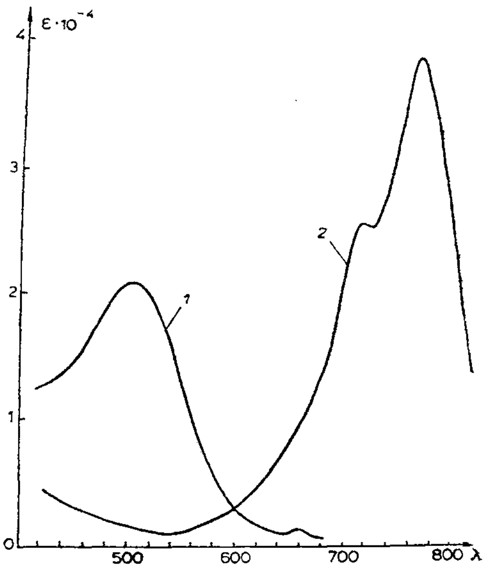
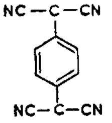
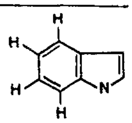


Fig. 2

Fig. 1. Electronic absorption spectra of indole in chloroform (1) and of α-(3-indolyl)-p-phenylenedimalononitrile in chloroform (2) and in alcohol (3).

Fig. 2. Electronic absorption spectra of 7-(2-cyano-3-indolyl)-7,8,8-tricyanoquinodimethane (VI) in acetonitrile (1) and in acetonitrile when alkali is added (2).

TABLE 2. Chemical Shifts of the Protons in Azoles and Corresponding Compounds I and II (on the δ scale, acetonitrile)

Compound	CN C—H CN		Heterocycle			
			N—H	C—H(α)	C—H(β)	
Pyrrole	—	—	9,03[a]	6,75	6,17	—
α-(2-Pyrrolyl)-p-phenylenedimalononitrile	5,60	7,66	9,63[b]	6,86	6,29, t J=2Hz 6,13, t J=2Hz	—
2,4-Dimethylpyrrole	—	—	8,23[b]	6,38	5,74	—
α-(2,4-Dimethyl-5-pyrrolyl)-p-phenylenedimalononitrile	5,61	7,72	8,68[b]	—	5,69	—
2,5-Dimethylpyrrole	—	—	8,42[b]	—	5,70, d J=2 Hz	—
α-(2,5-Dimethyl-3-pyrrolyl)-p-phenylenedimalononitrile	5,58	7,62	9,05[b]	—	5,58	—
Indole	—	—	9,17[b]	7,08[d]	6,48	6,94—7,65, m
α-(3-Indolyl)-p-phenylenedimalononitrile	5,58	7,70[c]	9,77[b]	7,15	—	6,95—7,84, m
3-Methylindole	—	—	8,85[b]	6,45	—	6,38—7,11, m
α-(3-Methyl-2-indolyl)-p-phenylenedimalononitrile	5,62	7,61	9,57[b]	—	—	7,15—7,80, m
2-Methylindole	—	—	9,00[b]	—	6,11	6,86—7,46, m
α-(2-Methyl-3-indolyl)-p-phenylenedimalononitrile	5,58	7,68	9,84[b]	—	—	6,83—7,56, m

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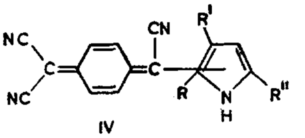
[a] Broad triplet, J = 64 Hz.

[b] Broad singlet.

[c] Doublet, J = 2 Hz.

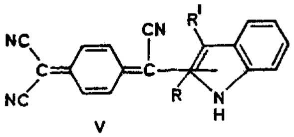
[d] Triplet, J = 4 Hz.

Data from the NMR spectra of I and II are presented in Table 2. The position of the substituent entering the heterocyclic ring was determined on the basis of these data. We note that the chemical shifts of the malononitrile proton in I and II, within the limits of the error in the measurements, do not change as a function of the heterocyclic grouping, whereas the signal itself vanishes completely when D_2O is added to the solution of the compound in acetonitrile due to hydrogen exchange by deuterium. Thus in the case of the product of reaction of TCQD with 2,5-dimethylpyrrole the 4-H signal of pyrrole was superimposed on the signal of the malononitrile proton, and a singlet at δ 5.58 ppm, corresponding to two protons, was observed in the spectrum. The intensity of the signal is halved when D_2O is added.



IV

R and R' = H, CH_3 or a single bond



V

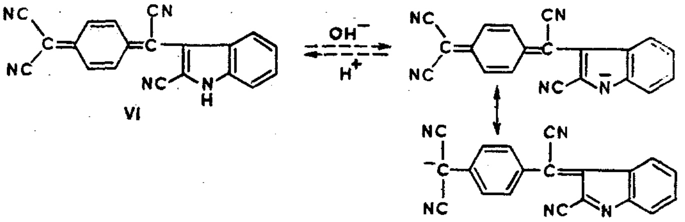
where R and R' = H, CH_3 or a single bond

When they are irradiated with UV light, all I and II split out hydrogen cyanide to give deeply colored blue products of replacement of one nitrile group in the TCQD molecule by a heterocyclic grouping (IV and V, respectively). The physical constants of IV and V are presented in Table 3. A photochemical reaction may also occur when solid I and II are irradiated and when solutions of them in polar and nonpolar solvents are irradiated. We note that dye IV, obtained from TCQD and pyrrole, is unstable, and only λ_{max} is presented for it.

When II, obtained from indole, is irradiated, a second red dye, isolated from the reaction mixture by chromatography, is formed in addition to the corresponding blue V. Elementary analysis showed the presence in this dye of yet another nitrile group as compared with the corresponding V. The mass spectrum of this substance contains a molecular peak with m/e 319 and peaks of fragments corresponding to splitting out of CN and $C(CN)_2$ groups. The IR spectrum contains the following vibrational bands: $\nu_{C=C}$ 1440, 1460, and 1500 cm^{-1}; $\nu_{C\equiv N}$ 2220 cm^{-1} (nitrile groups conjugated with a quinoid system: $\nu_{C\equiv N}$ 2210 cm^{-1} for V, as compared with $\nu_{C\equiv N}$ 2260 cm^{-1} for II); ν_{N-H} 3350 cm^{-1}. The electronic spectrum of the red substance contains a broad structureless band, but, in contrast to the corresponding V, it is found in the shorter-wave region of the spectrum [λ_{max} 507 nm (benzene)]. On the basis of these data and with allowance for the fact that this product is formed only in unsubstituted indole, it was assigned structure VI.

When VI is treated with alkali its color changes reversibly, probably due to facile splitting out of the proton attached to the nitrogen in the α position relative to the nitrile group and the formation of an anion (VII), depicted in the form of two resonance structures. Whereas the long-wave band of VI is found at λ_{max} 513 nm (acetonitrile) it is shifted to 780 nm when alkali is added (Fig. 2, curves 1 and 2, respectively).

A dye analogous to VI is formed when I, obtained by reaction of TCQD with pyrrole, is irradiated, but this dye was not isolated, 2,4- and 2,5-Dimethylpyrroles do not form dyes of this type. Compounds of the VI type are probably formed through reaction of molecules of dye V with nitrile anions or radicals evolved during the photodecomposition of II.



VI

VII

The electronic spectra of all IV and V contain the absorption of a broad structureless band at 550-650 nm, which was assigned to an intramolecular charge transfer band. The position of this band depends linearly on the ionization potential adopted for the reaction of the azole [5].

EXPERIMENTAL

Pyrrole and its methyl derivatives, as well as methyl derivatives of indole, were synthesized by literature methods. Pure-grade TCQD was used. LSL 5-40 μ silica gel was used for chromatographic purification of the compounds. A PRK-2 UV lamp was used for the photochemical reactions. The UV spectra of the compounds were recorded with a Hitache MSP-50L spectrophotometer. The NMR spectra were recorded with a Tesla BS-487B spectrometer (80 MHz). The IR spectra were recorded with a UR-20 spectrometer. The mass spectra were recorded with an MKh-1303 mass spectrometer.

α-Azolyl-p-phenylenedimalononitriles I and II. A) A mixture of 0.5 mmole of TCQD and 0.6 mmole of the azole in 30 ml of acetonitrile was refluxed until the TCQD vanished (verified by TLC) (from 5 to 40 min). The solvent was then removed by vacuum distillation to a volume of 5 ml, and the residual mixture was poured into 100 ml of ice water. The solid or semiliquid mass was separated and dried in vacuo at 50° for ~10 h. The solid product was recrystallized twice from alcohol to give the product in 70-92% yield.

B) A mixture of 0.5 mmole of TCQD and 0.6 mmole of the azole in 30 ml of ethanol was refluxed until the TCQD vanished (15 min, verified by means of TLC), after which the solvent was removed by vacuum dis-

TABLE 3. Physical Constants of 7-Azolyl-7,8,8-tricyanoquinodimethanes IV and V

Compound	mp, °C (crystallization solvent)	Empirical formula	Found, %			Calc., %			λmax, nm, acetonitrile (benzene)	Synthetic method	Yield, %
			C	H	N	C	H	N			
7-(2-Pyrrolyl)-7,8,8-tricyanoquinodimethane									552 (564)	A	
7-(2,4-Dimethyl-5-pyrrolyl)-7,8,8-tricyanoquinodimethane	216 (dec., acetone)	$C_{17}H_{12}N_4$	75,0	4,6	20,8	75,0	4,4	20,6	642 (608)	A	25
7-(2,5-Dimethyl-3-pyrrolyl)-7,8,8-tricyanoquinodimethane	260 (dec., acetone–benzene)	$C_{17}H_{12}N_4$	74,8	4,4	20,3	75,0	4,4	20,6	615 (578)	A	19
7-(3-Indolyl)-7,8,8-tricyanoquinodimethane	280 (dec., benzene)	$C_{19}H_{10}N_4$	77,4	3,9	19,0	77,5	3,4	19,0	584 (560)	B	37
7-(2-Methyl-3-indolyl)-7,8,8-tricyanoquinodimethane	266 (dec., acetone)	$C_{20}H_{12}N_4$	77,8	4,1	18,2	77,9	3,9	18,2	608 (582)	A	47
7-(3-Methyl-2-indolyl)-7,8,8-tricyanoquinodimethane	235 (dec., acetone–benzene)	$C_{20}H_{12}N_4$	78,3	4,5	18,1	77,9	3,9	18,2	595 (602)	C	26

tillation to a volume of 2 ml, and the residual solution was allowed to stand overnight at −5°. The yield of crystalline product was 93%. It was recrystallized in the minimum amount of alcohol.

7-Azolyl-7,8,8-tricyanoquinodimethanes IV and V. A) A mixture of 0.5 mmole of TCQD and 0.6 mmole of the azole was refluxed in 50 ml of acetonitrile until the TCQD vanished, and the resulting solution was irradiated in a 100-ml beaker from above with the complete light of a UV lamp, which was located at a distance of 15 cm from the surface of the solution. The dye, which precipitated as a finely crystalline substance, was removed periodically by filtration and recrystallized from acetonitrile, benzene, and acetonitrile–benzene. Irradiation was carried out for 16-48 h until the conversion of I and II was complete; this was verified by means of thin-layer chromatography. The dyes were obtained in 19-47% yields.

B) A solution of 0.5 mmole of the appropriate II in 50 ml of acetonitrile was irradiated with UV light as described in method A. The dye was obtained in 37% yield after recrystallization from benzene.

C) A mixture of 0.5 mmole of TCQD and 0.6 mmole of the azole in 30 ml of DMSO was stirred at 150° until the TCQD vanished, after which the solution was poured into 200 ml of ice water. The aqueous mixture was treated with 5 g of NaCl, the resulting precipitate was removed by filtration and dissolved in 50 ml of acetonitrile, and the solution was irradiated as described above. The dye was obtained in 26% yield.

TCQD–2,3-Dimethylindole Molecular Complex. Boiling solutions of 0.25 mmole of TCQD in 40 ml of acetonitrile and 0.5 mmole of 2,3-dimethylindole in 10 ml of acetonitrile were mixed, and the resulting solution was allowed to cool slowly, after which it was filtered to give 0.85 g (62%) of a product with mp 230° (dec.). Found: C 75.6; H 4.4; N 20.2%. $C_{12}H_4N_4 \cdot C_{10}H_{11}N$. Calculated: C 75.6; H 4.3; N 20.1%.

7-(2-Cyano-3-indolyl)-7,8,8-tricyanoquinodimethanes (VI). A 0.5 mmole sample of α-(3-indolyl)-p-phenylenedimalononitrile in 50 ml of acetonitrile was irradiated as described above for the preparation of V. The precipitated 7-(3-indolyl)-7,8,8-tricyanoquinodimethane [0.17 g (37%)] was separated, and the mother liquor was evaporated and chromatographed on silica gel [elution with benzene–acetone (4 : 1)] to give 0.1 g (20%) of a product with mp 260° (dec.). IR spectrum: $\nu_{C=C}$ 1440, 1460, and 1500 cm^{-1}; $\nu_{C\equiv N}$ 2220 cm^{-1}. UV spectrum, λ_{max} 513 nm (acetonitrile). Found: C 75.0; H 3.3; N 21.9%. $C_{20}H_9N_5$. Calculated: C 75.2; H 2.9; N 21.9%.

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