solution of the acid in water, and **barium 2-bromo-1,1,3,3-tetracyanopropenide** precipitated.

Tetraethylammonium 2-Chloro-1,1,3,3-tetracyanopropenide.—A solution of 6.9 g. (0.1 mole) of sodium nitrite in 25 ml. of water was added dropwise with stirring to a solution of 14.2 g. (0.05 mole) of tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide in 500 ml. of water and 25 ml. of hydrochloric acid. The resulting solution was heated to boiling, treated with carbon-black, and filtered. The precipitate that formed when the filtrate was cooled was collected on a filter, washed with water and dried (10.2 g.). This material was recrystallized from water to give 6.3 g. of orange needles of tetraethylammonium 2-chloro-1,1,3,3-tetracyanopropenide. **N-Methylquinolinium 2-chloro-1,1,3,3-tetracyanopropenide** was prepared by a similar procedure from N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide.

Tetramethylammonium 2-Chloro-1,1,3,3-tetracyanopropenide.—A solution of 5.0 g. of N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide in 50 ml. of hot water was passed through an acidic ion-exchange column (Amberlite IR-120-H). Concentrated hydrochloric acid, 10 ml., and then a solution of 5.0 g. of sodium nitrite in 25 ml. of water was added to the cooled percolate. The resulting solution was boiled for 5 minutes, cooled and then mixed with 10 ml. of aqueous 30% tetramethylammonium chloride solution. The precipitate that formed was collected on a filter, washed with water, and recrystallized from water. There was obtained 1.2 g. of tetramethylammonium 2-chloro-1,1,3,3-tetracyanopropenide as long colorless needles, m.p. 211–213°.

Barium Tricyanomethanide.—A hot aqueous solution (50 ml.) of barium chloride dihydrate was added with stirring to a hot solution of 33.9 g. of sodium tricyanomethanide in 50 ml. of water. The resulting solution was stored in a cold room at 4° for one week. The large crystals that formed were collected on a filter and recrystallized from water. There was obtained 17.5 g. of barium tricyanomethanide as colorless crystals, m.p. >300°.

Anal. Calcd. for BaC_8N_6: C, 30.26; N, 26.47. Found: C, 29.80; N, 26.30.

1-Amino-1-chloro-2,2-dicyanoethylene.[17]—Dry hydrogen chloride was passed into a solution of 6.4 g. of potassium tricyanomethanide in 200 ml. of acetone for 10 minutes. The precipitate of potassium chloride (3.5 g.) was separated by filtration, and the filtrate was allowed to stand at solid carbon dioxide temperature overnight and was then poured into *n*-heptane. The oil that separated was extracted with ethyl ether. On evaporation, the ether extract yielded 4 g. (63% yield) of 1-amino-1-chloro-2,2-dicyanoethylene as a light yellow solid.

Anal. Calcd. for $C_4H_2ClN_3$: C, 37.67; H, 1.57; Cl, 27.80; N, 32.95. Found: C, 37.99; H, 1.73; Cl, 27.46; N, 32.89.

1-Amino-2-bromo-2,2-dicyanoethylene was obtained as a sublimable white solid in a similar manner by the reaction of dry hydrogen bromide with potassium tricyanomethanide.

Anal. Calcd. for $C_4H_2BrN_3$: N, 24.43. Found: N, 24.82.

1-Amino-2-bromo-2,2-dicyanoethylene reacted at 20–30° with ethyl alcohol to form 1-amino-1-ethoxy-2,2-dicyanoethylene (m.p. 218–219°) and with methyl alcohol to yield 1-amino-1-methoxy-2,2-dicyanoethylene (m.p. 213–214°).

Ultraviolet Spectra.—The ultraviolet absorption spectra of a number of free cyanocarbon acids and their salts were determined. The absorption maxima and extinction coefficients for a given free acid and any of its salts were essentially identical, so only the anions are listed in Table II.

(17) E. L. Little, U. S. Patent 2,773,892 (1956).

Wilmington, Delaware

[Contribution No. 440 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co.]

Cyanocarbon Chemistry. VI.[1] Tricyanovinylamines

By B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower

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Tetracyanoethylene reacts with primary amines and some secondary amines to give N-tricyanovinylamines (I). It generally reacts with secondary and tertiary arylamines by attacking the aromatic ring to give 4-tricyanovinylarylamines such as II. The 4-tricyanovinylarylamines are a new class of dyes with strong affinity for hydrophobic fibers. Some of their analogs have similar dyeing characteristics.

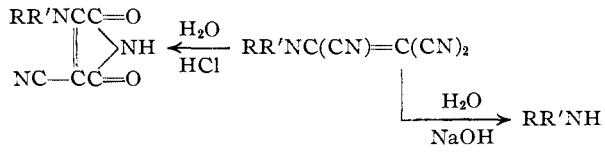
Tetracyanoethylene reacts with ammonia and hydrazine with elimination of hydrogen cyanide to give, respectively, bis-(tricyanovinyl)-amine and 1,2-bis-(tricyanovinyl)-hydrazine.[1] The present paper describes the related reactions of tetracyanoethylene with amines.

N-Tricyanovinylamines.—Tetracyanoethylene reacts readily with primary or secondary aliphatic amines and with most primary and some secondary aromatic amines to give N-tricyanovinylamines (I) and hydrogen cyanide.

$$RR'NH + C(CN)_2{=}C(CN)_2 \longrightarrow RR'NC(CN){=}C(CN)_2 + HCN$$

I

Sixteen such N-tricyanovinylamines, all solids ranging in color from white to yellow, have been prepared (Table I). The N-tricyanovinylamine structure is assigned partly on the basis of absorption spectra. Thus, N-tricyanovinyl derivatives of primary amines (*e.g.*, aniline, *n*-butylamine) absorb strongly in the N–H stretching region of the infrared, whereas N-tricyanovinyl derivatives of secondary amines (*e.g.*, N-methyl-*p*-toluidine, piperidine) do not. The compounds are hydrolyzed by base to give the parent amine in good yield, which is evidence that the tricyanovinyl group is attached to nitrogen rather than carbon. Acid hydrolysis of N-tricyanovinyl-*n*-butylamine gave *α*-*n*-butylamino-*β*-cyanomaleimide.

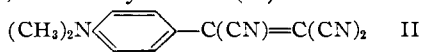


N-Tricyanovinylamines can react with a second molecule of amine to give 1,1-diamino-2,2-dicyanoethylenes.

$$BuNHC(CN){=}C(CN)_2 + Me_2NH \longrightarrow BuNHC(NMe_2){=}C(CN)_2$$

(1) Paper V, W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, This Journal, 80, 2795 (1958).

4-Tricyanovinylarylamines.—Tetracyanoethylene does not react with tertiary aliphatic amines like triethylamine, but it readily reacts with both tertiary and secondary aromatic amines, attacking the ring to give 4-tricyanovinylarylamines. For example, N,N-dimethylaniline gives 4-tricyanovinyl-N,N-dimethylaniline (II).[2]



$(CH_3)_2N$—$C(CN)=C(CN)_2$ II

The 4-tricyanovinylarylamines absorb visible light very strongly (ϵ_{max} 37,000–47,000) and comprise a new class of brilliant red and blue dyes that often have great affinity for hydrophobic fibers. The strong absorption of visible light is consistent with the highly conjugated structure assigned, and infrared spectra confirm the structure; thus, the product from tetracyanoethylene and N-methylaniline, 4-tricyanovinyl-N-methylaniline, absorbs strongly in the N–H stretching region of the infrared. Chemical evidence for the 4-tricyanovinylarylamine structure was supplied by stepwise hydrolysis of 4-tricyanovinyl-N,N-dimethylaniline (II) to ethyl 4-dimethylaminobenzoate *via* 4-(1-hydroxy-2,2-dicyanovinyl)-N,N-dimethylaniline (III).

$$\text{II} \xrightarrow{\text{NaOH}} \underset{\text{III}}{4\text{-}Me_2\overset{+}{N}HC_6H_4(\overset{-}{O})=C(CN)_2} \xrightarrow[\text{HCl}]{\text{EtOH}} 4\text{-}Me_2NC_6H_4CO_2Et$$

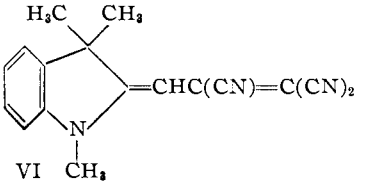
The intermediate vinyl alcohol III is a strong acid (pK_a 2.3); it is formulated as a zwitterion on the basis of its infrared spectrum. Three other 4-tricyanovinylanilines were similarly converted to vinyl alcohols by mild alkaline hydrolysis. The vinyl alcohols are assigned a 1-hydroxyvinyl rather than a 2-hydroxyvinyl structure because it has been shown in the analogous reaction of tricyanovinylbenzene with alkoxide ion that 1-alkoxy-2,2-dicyanovinylbenzene is formed.[3]

The structure of 4-tricyanovinyl-N,N-dimethylaniline (II) was established definitely by an unequivocal synthesis. Hydrogen cyanide was added to 4-dimethylaminobenzalmalononitrile (IV), and the adduct V was oxidized to 4-tricyanovinyl-N,N-dimethylaniline (II) by lead tetraacetate. Several other 4-tricyanovinylarylamines were made in the same way.

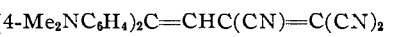
$$\underset{\text{IV}}{4\text{-}Me_2NC_6H_4CH=C(CN)_2} \xrightarrow[2,\ HOAc]{1,\ NaCN} \underset{\text{V}}{4\text{-}Me_2NC_6H_4CH(CN)CH(CN)_2} \xrightarrow{Pb(OAc)_4} \text{II}$$

The bulkiness of the tricyanovinyl group makes steric factors of great importance in determining the course of reaction of an arylamine with tetracyanoethylene. Thus, with aniline or N-methyl-*p*-toluidine only an N-tricyanovinyl derivative was isolated; with N-methylaniline only a *p*-tricyanovinyl derivative was isolated; with 2,6-dimethylaniline both an N-tricyanovinyl derivative and a *p*-tricyanovinyl derivative were formed; and with N,N-dimethyl-*p*-toluidine no tricyanovinylation at all was detected. These and other results (Tables I and II) indicate that *o*-tricyanovinylation of arylamines cannot easily occur, that one N-substituent generally prevents N-tricyanovinylation unless the *para* position is filled, and that substituents *ortho* to the amine group promote *p*-tricyanovinylation at the expense of N-tricyanovinylation.

1,3,3-Trimethyl-2-methyleneindoline and 1,1-bis-(4-dimethylaminophenyl)-ethylene reacted with tetracyanoethylene to give the tricyanovinyl derivatives VI and VII, respectively. Evidently some vinylamines and *p*-aminoarylethylenes can react with tetracyanoethylene in the same manner as arylamines.



VI

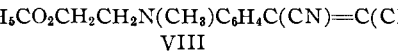


$(4\text{-}Me_2NC_6H_4)_2C=CHC(CN)=C(CN)_2$

VII

A few derivatives of the 4-tricyanovinylarylamines have been prepared (Table II). 4-Tricyanovinyl-N,N-dimethylaniline (II) reacts with nitric acid under mild conditions to give a mononitro derivative in which the nitro group is probably *ortho* to the amino group. 4-Tricyanovinylaniline has been N-acylated, and both it and 4-tricyanovinyl-2,6-dimethylaniline have been diazotized and coupled to give azo compounds.

Dyeing Properties of 4-Tricyanovinylarylamines.—Many of the 4-tricyanovinylarylamines give brilliant dyeings, most often red, on hydrophobic fibers such as polyethylene terephthalate and polyacrylonitrile. The dyeings have good wash-fastness. Over fifty 4-tricyanovinylarylamines (Table II) have been prepared. All things considered, 4-tricyanovinyl-N-methyl-N-(2-benzoxyethyl)-aniline (VIII) is the best of these dyes yet

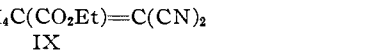


$4\text{-}C_6H_5CO_2CH_2CH_2N(CH_3)C_6H_4C(CN)=C(CN)_2$

VIII

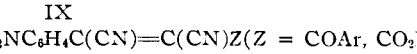
prepared. Its wash-fastness, sublimation-fastness, light-fastness and affinity for hydrophobic fibers are all good. It can be applied from a moderately acidic bath (*p*H 3–6) without serious decomposition, but, like other simple tricyanovinylarylamine dyes, it is rapidly decomposed in basic dye baths. The decomposition by base involves replacement of the α-cyano group by hydroxyl, as in the conversion of II to III.

Analogs of 4-Tricyanovinylarylamines.—A number of analogs of tricyanovinylarylamines (Table II) were prepared in efforts to get dyes of other shades and better properties. One analog (IX) had a carbethoxy group instead of a cyano group in the α-position of the vinyl group; it was prepared by condensation of ethyl 4-dimethylaminoglyoxylate with malononitrile. The other analogs (X) had a chromophore other than cyano at the β-position of the vinyl group.



$4\text{-}Me_2NC_6H_4C(CO_2Et)=C(CN)_2$

IX



$4\text{-}R_2NC_6H_4C(CN)=C(CN)Z$ (Z = COAr, CO_2R, etc.)

X

(2) This reaction is the basis of a semi-quantitative determination of tetracyanoethylene.

(3) Paper VII, G. N. Sausen, V. A. Engelhardt and B. S. Fisher, THIS JOURNAL, 80, 2815 (1958).

Table 1

Properties of N-Tricyanovinylamines, $RR'NC(CN)=C(CN)_2$

N-Tricyanovinylamine	Yield, %	M.p., °C.	Crystn. solvent	EtOH λ_{max}, mμ	EtOH $\epsilon_{max} \times 10^{-2}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
n-$C_4H_9NHC_2(CN)_3$	67	58	Et_2O/petr. ether	325	127	$C_9H_{10}N_4$	62.0	62.1	5.8	5.9	32.2	32.3
$(CH_2)_5NC_2(CN)_3$	37	86–87	C_6H_6/petr. ether	334	154	$C_{10}H_{10}N_4$	64.5	64.5	5.4	5.4	30.1	29.6
Cyclo-$C_6H_{11}NHC_2(CN)_3$	51	147–148	$CHCl_3/CCl_4$	325	136	$C_{11}H_{12}N_4$	66.0	66.1	6.0	6.2	28.0	28.3
n-$C_{18}H_{37}NHC_2(CN)_3$	41	83	HOAc/H_2O	326	125	$C_{23}H_{38}N_4$	74.5	73.7	10.3	10.0	15.1	15.0
$C_6H_5CH_2NHC_2(CN)_3$	67	121–122	$CHCl_3/CCl_4$	327	141	$C_{12}H_8N_4$	69.2	69.2	3.9	3.9	26.9	26.8
$C_6H_5NHC_2(CN)_3$	59	176	Benzene	345	147	$C_{11}H_6N_4$[c]	68.0	68.3	3.1	3.2	28.9	28.5
o-$CH_3C_6H_4NHC_2(CN)_3$[a]	25	129–130	50% HOAc	330	119	$C_{12}H_8N_4$	69.2	69.5	3.9	4.1	26.9	27.0
p-$CH_3C_6H_4NHC_2(CN)_3$	49	174	HOAc/H_2O	350	135	$C_{12}H_8N_4$	69.2	69.3	3.9	4.0	26.9	27.0
p-$CH_3C_6H_4N(CH_3)C_2(CN)_3$	80	174–176	EtOH	335	119	$C_{13}H_{10}N_4$[d]	70.3	70.2	4.5	4.6	25.2	25.1
p-$ClC_6H_4NHC_2(CN)_3$	84	160	80% EtOH	346	149	$C_{11}H_5N_4Cl$	57.8	57.8	2.2	2.2	24.5	24.3
m-$O_2NC_6H_4NHC_2(CN)_3$	55	171	50% MeOH	345	159	$C_{11}H_5N_5O_2$	55.2	55.4	2.1	2.3	29.3	29.0
p-$O_2NC_6H_4NHC_2(CN)_3$	46	170	50% EtOH	332	155	$C_{11}H_5N_5O_2$	55.2	55.4	2.1	2.1	29.3	29.0
o-$HOC_6H_4NHC_2(CN)_3$	91	>300	Acetone[b]	341	195	$C_{11}H_6N_4O$	62.8	63.0	2.9	3.0		
p-$CH_3OCOC_6H_4NHC_2(CN)_3$	53	180	EtOH	360	172	$C_{13}H_8N_4O_2$	61.9	61.8	3.2	3.5	22.2	22.5
p-$C_6H_4[NHC_2(CN)_3]_2$	78	>300	Acetone	375	223	$C_{16}H_8N_8$	61.9	62.1	2.0	2.0	36.2	36.3
1-$C_{10}H_7NHC_2(CN)_3$	45	179	HOAc/H_2O	330	106	$C_{16}H_9N_4$	73.8	73.8	3.3	3.5	22.9	23.4

[a] Contaminated with 7% 4-tricyanovinyl-*o*-toludine. [b] No good solvent found; purification by slurrying. [c] Calcd.: mol. wt., 194. Found: mol. wt. (in boiling acetone), 198. [d] Calcd.: mol. wt., 222. Found: mol. wt. (in boiling acetone), 217.

The latter analogs (X) were prepared as in the conversion of IV to II, by condensing a 4-aminobenzaldehyde with a compound having an active methylene group, adding hydrogen cyanide to the product, and oxidizing. The same method was used to prepare 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile (XI), a deep blue dye vinylogous to the 4-tricyanovinylarylamines. Its structure was established by two-step hydrolysis to methyl 4-dimethylaminocinnamate. The blue color of an alcohol solution of the trinitrile XI is instantly destroyed by base, but acid regenerates it, and the ability of the basic solution to give back color on acidification is only gradually lost over a period of hours. These observations suggest that base reversibly converts XI to the colorless intermediate XII which gradually and irreversibly breaks down to XIII. Intermediates like XII are probably formed during the far faster basic hydrolysis of the 4-tricyanovinylarylamines.

$$\underset{\text{XI}}{4\text{-}Me_2NC_6H_4CH{=}CHC(CN){=}C(CN)_2} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}}$$

$$\underset{\text{XII}}{4\text{-}Me_2NC_6H_4CH{=}CHC(CN)(OH)C^-(CN)_2} \longrightarrow$$

$$\underset{\text{XIII}}{4\text{-}Me_2NC_6H_4CH{=}CHC(OH){=}C(CN)_2} + CN^-$$

The analogs of 4-tricyanovinylarylamines share their virtues and defects as dyes. None was prepared that was the equal of the best 4-tricyanovinylarylamines in dyeing properties.

Acknowledgments.—We are indebted to Drs. D. R. Baer, S. N. Boyd and H. P. Landerl of the Organic Chemicals Department, E. I. du Pont de Nemours & Co., for supplying intermediates and giving valuable advice.

Experimental

N-Tricyanovinylamines[4] (Table 1).—The N-tricyanovinylamines generally were made by the interaction of tetracyanoethylene with primary or secondary amines in boiling tetrahydrofuran. No more than a slight excess of amine was used to avoid formation of 1,1-diamino-2,2-dicyanoethylenes. In a typical experiment, 20.0 g. (0.157 mole) of *p*-chloroaniline was added over a period of about 20 minutes to a stirred solution of 20.0 g. (0.156 mole) of tetracyanoethylene in 200 ml. of tetrahydrofuran held at 20–30°. The mixture was stirred and refluxed for three hours. Distillation of solvent at a pressure of 30 mm. (bath temperature 40°) left a crystalline residue. This on crystallization from 80% ethanol gave 30.0 g. (84% yield) of *p*-chloro-N-tricyanovinylaniline in the form of yellow crystals, m.p. 160°.

Dimethylformamide was used as a reaction medium in place of tetrahydrofuran with similar results. Conditions were as described later in this paper for the synthesis of 4-tricyanovinylarylamines from arylamines and tetracyanoethylene, but with equivalent quantities of reactants.

Hydrolysis of N-Tricyanovinylaniline to Aniline.—A mixture of 1.00 g. of N-tricyanovinylaniline and 50 ml. of 10% potassium hydroxide was refluxed for three hours and steam distilled. The distillate, which contained oily drops, was extracted with ether. The dried extract was saturated with hydrogen chloride to precipitate 0.44 g. (66% yield) of aniline hydrochloride, m.p. 194–196°. The hydrochloride was treated with 5 ml. of 20% sodium hydroxide, and the liberated aniline was taken up in ether. Addition of 1 ml. of pyridine and 0.5 ml. of acetyl chloride to the dried ether solution gave acetanilide, m.p. 113–114° alone or mixed with an authentic sample.

Similarly, 2.00 g. of N-methyl-N-tricyanovinyl-*p*-toluidine gave 0.50 g. (34% yield) of N-acetyl-N-methyl-*p*-toluidine, m.p. 81–81.5° alone or mixed with authentic material.

Hydrolysis of N-Tricyanovinyl-*n*-butylamine to α-*n*-Butylamino-β-cyanomaleimide.—A solution of 8.7 g. of N-tricyanovinyl-*n*-butylamine in a mixture of 25 ml. of acetone, 6 ml. of water and 40 ml. of 12 *N* hydrochloric acid was kept at 25° for six hours. α-*n*-Butylamino-β-cyanomaleimide precipitated as pale yellow crystals. It weighed 5.6 g. (80% yield) after recrystallization from water; m.p. 180–181°. Its infrared spectrum had an N–H band at 3.05 μ and succinimide-type C=O bands at 5.6 and 5.8 μ.

Anal. Calcd. for $C_9H_{11}N_3O_2$: C, 56.0; H, 5.7; N, 21.8; mol. wt., 193. Found: C, 56.2; H, 5.8; N, 22.0; mol. wt., in boiling acetone, 189.

1-Dimethylamino-1-*n*-butylamino-2,2-dicyanoethylene.—Dimethylamine (5.0 ml., 0.10 mole) was added over a period of five minutes to a stirred solution of 5.25 g. (0.031 mole) of N-tricyanovinyl-*n*-butylamine in 50 ml. of pyridine. The mixture was heated slowly to boiling, cooled, and then allowed to stand at room temperature for 48 hours. The reaction mixture was poured over 500 g. of ice, and a white precipitate of 1-dimethylamino-1-*n*-butylamino-2,2-dicyanoethylene was collected by filtration. After recrystallization from 80% ethanol, it weighed 4.30 g. (74% yield) and melted at 95°.

Anal. Calcd. for $C_{10}H_{16}N_4$: C, 62.5; H, 8.4; N, 29.1; mol. wt., 192. Found: C, 62.6; H, 8.5; N, 29.3; mol. wt. in boiling ethanol, 189.

1-Dimethylamino-1-(*p*-chlorophenylamino)-2,2-dicyanoethylene.—*p*-Chloro-N-tricyanovinylaniline was treated with dimethylamine as in the preceding experiment. A

(4) R. E. Heckert, U. S. Patent 2,762,832 (1956).

brick-red solid that gradually precipitated was separated by filtration, and the filtrate was worked up as in the preceding experiment to give colorless 1-dimethylamino-1-(*p*-chlorophenylamino)-2,2-dicyanoethylene in 40% yield, m.p. 224–226°.

Anal. Calcd. for $C_{12}H_{11}N_4Cl$: C, 58.5; H, 4.5; N, 22.8; Cl, 14.4; mol. wt., 247. Found: C, 58.6; H, 4.4; N, 22.8; Cl, 14.4; mol. wt. in boiling ethanol, 243.

The brick-red solid had the composition of **N,N-dimethyl-α,β-dicyano-β-(*p*-chlorophenylamino)-acrylamidine**. It was isolated in 40% yield, m.p. 280°.

Anal. Calcd. for $C_{13}H_{12}N_5Cl$: C, 57.0; H, 4.4; N, 25.6; Cl, 13.0. Found: C, 57.2; H, 4.4; N, 25.0; Cl, 13.1.

One gram of the acrylamidine was heated for a few minutes in 15 ml. of 6 *N* hydrochloric acid at 60°. The initially red solution rapidly lost its color, and pale yellow **α-(*p*-chlorophenylamino)-β-cyanomaleimide** precipitated. It weighed 0.80 g. (91% yield) after being dissolved in dimethylformamide and reprecipitated with water; m.p. 263° It was weakly acidic. Its infrared spectrum had an N–H band at 3.1 μ and C=O bands at 5.6 and 5.8 μ.

Anal. Calcd. for $C_{11}H_6ClN_3O_2$: C, 53.3; H, 2.4; N, 17.0; Cl, 14.3; mol. wt., 248. Found: C, 53.3; H, 2.6; N, 17.0; Cl, 14.3; mol. wt. in boiling acetone, 250.

Complex mixtures were obtained when 1-dimethylamino-1-(*p*-chlorophenylamino)-2,2-dicyanoethylene was submitted to acid hydrolysis under various conditions. Failure to isolate a maleic acid derivative is evidence against a 1,2-dicyanoethylene structure.

Preparation of 4-Tricyanovinylarylamines (Table II) by Condensation of Tetracyanoethylene with Arylamines.[5] **A. Arylamines.**—Previously known arylamines were obtained from commercial sources or prepared according to directions in the literature. Three new amines were prepared in 70–80% yield by acylation of N-2-hydroxyethylanilines in pyridine at 40–70°. The reaction mixtures were diluted with water, and the products were separated by filtration or extraction with ether. Benzoyl chloride and N-2-hydroxyethyl-N-methylaniline gave **N-2-benzoxyethyl-N-methylaniline**, b.p. 184–186° (33 mm.), $n^{25}D$ 1.5834.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.2; H, 6.7; N, 5.5. Found: C, 75.4; H, 6.8; N, 5.4.

Terephthaloyl chloride and N-2-hydroxyethyl-N-methylaniline gave **bis-(N-methyl-N-phenyl-2-aminoethyl) terephthalate**, m.p. 132–133° after crystallization from acetone.

Anal. Calcd. for $C_{26}H_{28}N_2O_4$: C, 72.2; H, 6.5; N, 6.5. Found: C, 71.8; H, 6.6; N, 6.7.

Benzoyl chloride and N,N-bis-(2-hydroxyethyl)-aniline gave **N,N-bis-(2-benzoxyethyl)-aniline**, m.p. 77° after crystallization from methanol.

Anal. Calcd. for $C_{24}H_{23}NO_4$: C, 74.0; H, 6.0; N, 3.6. Found: C, 73.9; H, 5.9; N, 3.6.

B. Condensation in Dimethylformamide.—Tetracyanoethylene gradually was added to a stirred solution of the amine in 2–3.5 times its weight of dimethylformamide. The rate of addition and the cooling of the reaction vessel were such as to maintain a temperature of 25–40°. Up to a 30% excess of the more accessible reactant was used. The mixture was stirred at 50–60° for ten minutes and cooled to 0°. If the 4-tricyanovinylarylamine crystallized out, it was removed by filtration and recrystallized. Otherwise, the mixture was poured into four to six volumes of ice and water. If a solid separated from the aqueous mixture, it was removed by filtration and recrystallized. If a gummy product separated, it often could be induced to crystallize by trituration with acetic acid or methanol.

For example, 5.8 g. (0.045 mole) of tetracyanoethylene was added to a stirred solution of 7.5 g. (0.062 mole) of N,N-dimethylaniline in 15 ml. of dimethylformamide at 25–40°. The mixture was stirred at 50–60° for ten minutes, cooled to 0°, and filtered to separate 4-tricyanovinyl-N,N-dimethylaniline, wt. 7.75 g. after being washed with acetic acid and methanol. A second crop weighing 2.0 g. was obtained by pouring the combined filtrates into 150 ml. of a well-stirred mixture of ice and water. The two crops were recrystallized separately from acetic acid (6.5 ml./g.) to give a total of 8.3 g. (83% yield) of pure 4-tricyanovinyl-N,N-dimethylaniline (Table II).

(5) R. E. Heckert, U. S. Patent 2,762,810 (1956).

C. Condensation in Pyridine.—Pyridine is nearly as good a medium for the reaction as dimethylformamide. The same procedure was followed as with dimethylformamide except that the reaction mixture was acidified with an equal volume of acetic acid before being poured into ice-water. Pyridine was especially useful when 4-tricyanovinyl derivatives of N-(2-acyloxyethyl)-anilines were to be prepared; the N-(2-hydroxyethyl)-anilines could be successively treated with an acyl halide and tetracyanoethylene without the necessity of isolating the acyloxyethyl intermediate.

In a typical example, 6.1 g. (5% excess) of *m*-chlorobenzoyl chloride was added dropwise to a solution of 5.0 g. (0.033 mole) of N-2-hydroxyethyl-N-methylaniline in 15 ml. of pyridine at 50–60°. The mixture was stirred at 80° for five minutes and cooled to 25°. Tetracyanoethylene (4.4 g., 5% excess) was added at 25–35°, and the mixture was stirred at 55° for five minutes. The mixture was cooled to 5°, 25 ml. of acetic acid was added, and the cold solution was poured into 250 ml. of ice and water with good stirring. The water was decanted from a gum that subsequently crystallized on trituration with methanol. The solid was recrystallized from acetic acid to give 6.4 g. (50% yield) of 4-tricyanovinyl-N-(2-*m*-chlorobenzoxyethyl)-N-methylaniline (Table II) in the form of glistening black crystals.

Conversion of 4-Dimethylaminobenzalmalononitrile (IV) to 4-Tricyanovinyl-N,N-dimethylaniline (II).—A mixture of 2.0 g. (10 mmoles) of 4-dimethylaminobenzalmalononitrile[6] and 1.3 g. (20 mmoles) of potassium cyanide in 20 ml. of 50% ethanol was stirred on the steam-bath until a homogeneous solution was obtained (four minutes). The solution was filtered and diluted with 20 ml. of water containing 2 ml. of acetic acid. This caused the precipitation of **4-(1,2,-2-tricyanoethyl)-N,N-dimethylaniline** (V), which was separated by filtration, washed with water and dried; wt. 2.1 g. (92% yield), m.p. 125–130°. A portion crystallized twice from 50% ethanol was colorless and melted at 138–139°.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.6; H, 5.4; N, 25.0. Found: C, 69.6; H, 5.6; N, 24.9.

Lead tetraacetate (4.4 g., 9.9 mmoles) was added to a solution of 2.0 g. (8.9 mmoles) of 4-(1,2,2-tricyanoethyl)-N,N-dimethylaniline in 20 ml. of acetic acid. The solution was stirred on a steam-bath for two hours and cooled to 25°. 4-Tricyanovinyl-N,N-dimethylaniline (Table II) crystallized out as dark blue needles, wt. 0.78 g. (39% yield). Its infrared and visible spectra were identical with those of 4-tricyanovinyl-N,N-dimethylaniline prepared by the condensation of tetracyanoethylene with N,N-dimethylaniline.

Properties of 4-Tricyanovinyl-N,N-dimethylaniline (II).—4-Tricyanovinyl-N,N-dimethylaniline, a typical 4-tricyanovinylarylamine, is a very weak base, for it cannot be titrated by perchloric acid in acetic acid. Furthermore, it does not quaternize readily with methyl iodide, in which it dissolves to give a deep red solution (λ_{max} 519 mμ, ε 45,000) that shows no change in absorption maximum or intensity even after standing at 25° for two days. However, its amine group is protonated by 96% sulfuric acid, in which it dissolves to give colorless solutions from which it can be regenerated by dilution with water. The absorption maximum of 4-tricyanovinyl-N,N-dimethylaniline varies considerably with the solvent, as the following values show: in isooctane, λ_{max} 478 mμ; in ether, 498; benzene, 507; acetic acid, 509; ethanol or acetone, 514; acetonitrile, 517; methyl iodide, ethyl benzoate or N,N-dimethylaniline, 519; dimethylformamide, 525; pyridine, 527; *m*-cresol, 545. These values correspond to a color range of orange to purple. The maximum molecular extinction coefficient is always high (39,000–45,000). Other properties are listed in Table II, along with properties of many other 4-tricyanovinylarylamines.

Aminobenzalmalononitriles and their analogs (Table III) were prepared by condensation of aminobenzaldehydes with malononitrile and other compounds having an active methylene group. The aminobenzaldehydes, all but two of which are described in the literature, were purchased or prepared by standard methods. The two new aldehydes were prepared in 70–80% yield by the procedure of Campaigne and Archer[7] from an amine, dimethylformamide and phosphorus

(6) F. Sachs and W. Lewin, *Ber.*, **35**, 3569 (1902).

(7) E. Campaigne and W. L. Archer, *Org. Syntheses*, **33**, 27 (1953).

TABLE II

PROPERTIES OF 4-TRICYANOVINYLANILINES, THEIR VINYLOGS, THEIR ANALOGS, AND RELATED COMPOUNDS

Compound[a]	Prepn. method[b]	Yield, %	M.p., °C.	Crystn. solvent	$\lambda_{max}^{Acetone}$, mμ	$\epsilon_{max} \times 10^{-2}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
4-$H_2NC_6H_4C_2(CN)_3$	C	69	197–198	HOAc	480	372	$C_{11}H_6N_4$	68.0	67.7	3.1	3.2	28.9	28.7
4-$AcNHC_6H_4C_2(CN)_3$	C,[h] D	20	183–186	EtOH	411	238	$C_{13}H_8N_4O$	66.1	66.5	3.4	3.6	23.7	23.7
4-*n*-$C_{15}H_{31}CONHC_6H_4C_2(CN)_3$	D	35	105–106	EtOH	413	246	$C_{27}H_{36}N_4O$	75.0	74.9	8.4	8.3	13.0	12.7
4-H_2N-3,5-$Me_2C_6H_2C_2(CN)_3$	A	52	288–289	$MeNO_2$	500	369	$C_{13}H_{10}N_4$	70.3	70.3	4.5	4.7	25.2	25.7
4-$MeNHC_6H_4C_2(CN)_3$	A	70	178–179	MeOH	498	414	$C_{12}H_8N_4$	69.2	69.3	3.9	3.9	26.9	26.9
4-$PrNHC_6H_4C_2(CN)_3$	A	45	181–182	HOAc	504	430	$C_{14}H_{12}N_4$	71.2	71.1	5.1	5.1	23.7	23.7
4-$BuNHC_6H_4C_2(CN)_3$	A	42	117–118	HOAc	504	440	$C_{15}H_{14}N_4$	72.0	71.4	5.6	5.3	22.4	22.3
4-isoAmNHC$_6$H$_4$C$_2$(CN)$_3$	A	29	120–121	HOAc	503	444	$C_{16}H_{16}N_4$	72.7	72.9	6.1	6.1	21.2	21.0
4-isobornyl-$NHC_6H_4C_2(CN)_3$	A	70	210–211	HOAc	511	472	$C_{21}H_{22}N_4$	76.3	76.7	6.7	6.8	17.0	17.1
4-$HOCH_2CH_2NHC_6H_4C_2(CN)_3$	A	47	183–184	HOAc	503	440	$C_{13}H_{10}N_4O$	65.5	65.3	4.2	4.4	23.5	23.2
4-$NCCH_2CH_2NH$-3-$MeC_6H_3C_2(CN)_3$	A	51	198–199	HOAc	491	376	$C_{15}H_{11}N_5$	69.0	69.4	4.2	4.6	26.8	27.0
4-$HO_2CCH_2NHC_6H_4C_2(CN)_3$	A	21	235–237	HOAc	488	371	$C_{12}H_8N_4O_2$	61.9	62.1	3.2	3.4	22.2	22.2
4-$C_6H_5CH_2NHC_6H_4C_2(CN)_3$	A	28	150–151	HOAc	498	418	$C_{18}H_{12}N_4$	76.0	75.6	4.3	4.5	19.7	19.9
4-$C_6H_5NHC_6H_4C_2(CN)_3$	A	59	187–188	Benzene	512	370	$C_{17}H_{10}N_4$	75.5	75.0	3.7	3.6	20.7	21.1
4-(1-$C_{10}H_7$)$NHC_6H_4C_2(CN)_3$	A	30	210–212	HOAc	498	368	$C_{21}H_{12}N_4$	78.7	78.8	3.8	4.0	17.5	17.6
4-(9-Anthryl)$NHC_6H_4C_2(CN)_3$	A	72	250–255	BuOH	493	370	$C_{25}H_{14}N_4$	81.1	80.7	3.8	3.9	15.1	15.2
9-Piperidinoanthracene-$C_2(CN)_4$[i]	A	90	151	EtOH[e]	509[j]	20	$C_{15}H_{19}N_5$	77.1	77.1	4.9	5.0	18.0	17.9
4-(*o*-$HO_2CC_6H_4$)$NHC_6H_4C_2(CN)_3$	A	34	215–216	HOAc	483	274	$C_{18}H_{10}N_4O_2$	68.8	68.9	3.2	3.9	17.8	17.4
6-$C_2(CN)_3$-tetrahydroquinoline	A	37	194–195	HOAc	519	438	$C_{14}H_{10}N_4$	71.8	72.3	4.3	4.4	23.9	24.0
4-$Me_2NC_6H_4C_2(CN)_3$	A,[h] C	83	173–175	HOAc	514	415	$C_{13}H_{10}N_4$	70.3	70.3	4.5	4.5	25.2	25.1
4-$Et_2NC_6H_4C_2(CN)_3$	A	80	164	HOAc	521	465	$C_{15}H_{14}N_4$	72.0	71.8	5.6	5.4	22.4	22.3
4-$Pr_2NC_6H_4C_2(CN)_3$	A	79	138–139	HOAc	524	473	$C_{17}H_{18}N_4$	73.4	72.7	6.5	6.6	20.1	19.7
4-$Bu_2NC_6H_4C_2(CN)_3$	A	60	126–127	HOAc	525	471	$C_{19}H_{22}N_4$	74.5	74.5	7.2	6.7	18.3	18.2
4-Me_2N-3-$MeC_6H_3C_2(CN)_3$	A	39	161–162	HOAc[c]	515	260	$C_{14}H_{12}N_4$					23.7	24.4
4-Me_2N-2-$MeC_6H_3C_2(CN)_3$	A, C[h]	25	129–130	HOAc[c]	529	215	$C_{14}H_{12}N_4$	71.2	70.1	5.1	5.2	23.7	23.3
4-Me_2N-2-$ClC_6H_3C_2(CN)_3$	A,[h] C	46	140–142	HOAc	512	188	$C_{13}H_9ClN_4$	60.8	59.6	3.5	3.5	21.8	22.7
4-Me_2N-3-$O_2NC_6H_3C_2(CN)_3$	E	77	162–163	EtOH	479	300	$C_{13}H_9N_5O_2$	58.4	57.8	3.4	3.3	26.2	26.4
4-$O(CH_2CH_2)_2NC_6H_4C_2(CN)_3$	A	63	188–189	HOAc	507	359	$C_{15}H_{12}N_4O$	68.2	68.2	4.6	4.7	21.2	21.1
4-$ClCH_2CH_2N(Et)C_6H_4C_2(CN)_3$	A	55	152–153	HOAc	507	433	$C_{15}H_{13}ClN_4$	63.2	63.6	4.6	4.6	19.7	20.0
4-$NCCH_2CH_2N(Me)C_6H_4C_2(CN)_3$	A	86	174–175	HOAc	502	400	$C_{15}H_{11}N_5$	69.0	69.5	4.2	4.2	26.8	26.9
4-$NCCH_2CH_2N(Et)C_6H_4C_2(CN)_3$	A	63	159–160	HOAc	507	423	$C_{16}H_{13}N_5$	69.8	70.0	4.8	4.8	25.4	25.7
4-$(NCCH_2CH_2)_2NC_6H_4C_2(CN)_3$	A	50	156	HOAc	488	372	$C_{17}H_{12}N_6$	68.0	67.8	4.0	4.1	28.0	28.3
4-$C_6H_5CH_2N(Et)C_6H_4C_2(CN)_3$	A	37	146–147	HOAc	515	435	$C_{20}H_{16}N_4$	76.9	76.6	5.2	5.1	17.9	17.8

TABLE II (*Continued*)

Compound[a]	Prepn. method[b]	Yield, %	M.p., °C.	Crystn. solvent	$\lambda_{max}^{Acetone}$ mμ	$\epsilon_{max} \times 10^{-2}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
4-$(C_6H_5CH_2)_2NC_6H_4C_2(CN)_3$	A	75	167–168	HOAc	507	445	$C_{25}H_{18}N_4$	80.2	79.2	4.9	4.8	15.0	15.0
4-$C_6H_5N(Me)C_6H_4C_2(CN)_3$	A	65	108–109	HOAc	509	409	$C_{18}H_{12}N_4$	76.0	76.1	4.3	4.4	19.7	19.6
4-$C_6H_5N(Et)C_6H_4C_2(CN)_3$	A	57	147–148	HOAc	511	435	$C_{19}H_{14}N_4$	76.5	76.7	4.7	4.9	18.8	18.7
4-$C_6H_5N(n\text{-}C_6H_{13})C_6H_4C_2(CN)_3$	A	71	88–89	HOAc	513	439	$C_{23}H_{22}N_4$	77.9	78.2	6.3	6.3	15.8	15.9
4-$C_6H_5N(n\text{-}C_{12}H_{25})C_6H_4C_2(CN)_3$	A	77	77–78	MeOH/HOAc	513	434	$C_{29}H_{34}N_4$	79.4	79.0	7.8	7.8	12.8	13.0
4-$(C_6H_5)_2NC_6H_4C_2(CN)_3$	A	46	174–175	HOAc	513	346	$C_{23}H_{14}N_4$	79.8	79.8	4.1	4.1	16.2	16.2
4-iso-$BuCO_2CH_2CH_2N(Me)C_6H_4C_2(CN)_3$	B	32	122–125	BuOH	510	434	$C_{19}H_{20}N_4O_2$	67.8	67.8	6.0	5.9	16.7	16.8
4-$Et_2CHCO_2CH_2CH_2N(Me)C_6H_4C_2(CN)_3$	B	18	94–101	BuOH	510	426	$C_{20}H_{22}N_4O_2$	68.6	68.7	6.3	6.0	16.0	16.4
4-$EtOCO(CH_2)_4CO_2CH_2CH_2N(Me)C_6H_4C_2(CN)_3$	B	40	80–82	BuOH	510	416	$C_{22}H_{24}N_4O_4$	64.7	65.1	5.9	6.0	13.7	14.0
4-$C_6H_5CO_2CH_2CH_2N(Me)C_6H_4C_2(CN)_3$	A, B[h]	43	141–142	HOAc	510	406	$C_{21}H_{16}N_4O_2$	70.8	70.7	4.5	4.6	15.7	16.0
4-[*p*-$MeC_6H_4CO_2CH_2CH_2N(Me)]C_6H_4C_2(CN)_3$	B	54	144–145	HOAc	511	416	$C_{22}H_{18}N_4O_2$	71.3	71.5	4.9	5.1	15.1	14.9
4-[*m*-$ClC_6H_4CO_2CH_2CH_2N(Me)]C_6H_4C_2(CN)_3$	B	50	131–136	HOAc	510	402	$C_{21}H_{15}ClN_4O_2$	64.5	63.9	3.9	4.0	9.1[e]	9.0
4-[4-Me-3-$O_2NC_6H_3CO_2CH_2CH_2N(Me)]$-$C_6H_4C_2(CN)_3$	B	22	153–154	HOAc	510	406	$C_{22}H_{17}N_5O_4$	63.6	63.7	4.1	4.2	16.9	16.8
4-[1-$C_{10}H_7CO_2CH_2CH_2N(Me)]C_6H_4C_2(CN)_3$	B	39	179–185	HOAc	512	382	$C_{25}H_{18}N_4O_2$	73.9	72.9	4.5	4.6	13.8	13.6
4-$C_6H_5CO_2CH_2CH_2N(CH_2CH_2CN)C_6H_4C_2(CN)_3$	A	43	157–158	HOAc	493	403	$C_{23}H_{17}N_5O_2$	69.9	69.8	4.3	4.4	17.7	18.1
4-$(C_6H_5CO_2CH_2CH_2)_2NC_6H_4C_2(CN)_3$	A	79	185	HOAc	505	417	$C_{29}H_{22}N_4O_4$	71.0	71.0	4.5	4.6	11.4	11.4
p-C_6H_4=[4-$CO_2CH_2CH_2N(CH_3)C_6H_4C_2(CN)_3]_2$	A	89	284–285	HOAc	519[g]	691	$C_{36}H_{26}N_8O_4$	68.1	68.7	4.1	4.5	17.7	17.2
p-$C_2(CN)_3$-julolidine	A	59	265–266	Me_2CO/HOAc	555	472	$C_{17}H_{14}N_4$	74.4	74.8	5.1	5.5	20.4	20.3
4-$Me_2NC_{10}H_6C_2(CN)_3$-1	A	44	166–167	HOAc[c]	550	142	$C_{17}H_{12}N_4$					20.6	20.9
4-$Me_2NC_6H_4CH$=$CHC_2(CN)_3$	C	47	235–238	Xylene	582	639	$C_{15}H_{12}N_4$	72.6	72.4	4.9	4.7	22.6	22.6
(4-$Me_2NC_6H_4)_2C$=$CHC_2(CN)_3$	A	68	155–167	BuOH	591	264	$C_{23}H_{21}N_5$	75.2	73.8	5.8	5.9	19.1	18.8
1,3,3-Me_2-2-[$C_2(CN)_3CH$=]indoline	A	26	248–250	HOAc	500	471	$C_{17}H_{14}N_4$	74.4	74.2	5.1	5.3	20.4	20.5
4-$Me_2NC_6H_4C(CN)$=$C(CN)CO_2CH_2C_6H_5$	C	52	143–144	PrOH	500	316	$C_{20}H_{17}N_3O_2$	72.5	72.7	5.2	5.2		
4-$Me_2NC_6H_4C(CN)$=$C(CN)CO_2CH_2CH_2C_6H_5$	C	55	135–136	PrOH	498	310	$C_{21}H_{19}N_3O_2$	73.0	73.0	5.6	5.4		
4-$(NCCH_2CH_2)_2NC_6H_4C(CN)$=$C(CN)CO_2Bu$[d]	C	58	139–140	BuOH	463	251	$C_{21}H_{21}N_5O_2$	67.2	66.9	5.6	5.5	18.7	18.6
4-$Me_2NC_6H_4C(CO_2Et)$=$C(CN)_2$	G	63	129–130	EtOH	453	428	$C_{15}H_{15}N_3O_2$	66.9	66.9	5.6	5.8	15.6	16.1
4-Me_2N-3-$O_2NC_6H_3C(CN)$=$C(CN)CONH_2$	E	7	144–145	EtOH	423		$C_{13}H_{11}N_5O_3$	54.7	55.0	3.9	4.0	24.6	24.6
4-$Me_2NC_6H_4C(CN)$=$C(CN)CO$-2-C_4H_3S	C	67	160–161	EtOH	500	218	$C_{17}H_{13}N_3OS$	66.4	66.3	4.3	4.3		
2-[4-$Me_2NC_6H_4C(CN)$=]-1,3-diketohydrindene	C	48	178–181	BuOH	559	329	$C_{19}H_{14}N_2O_2$	75.5	74.6	4.7	4.8	9.3	9.0
4-(2-HO-1-$C_{10}H_6N$=N)-$C_6H_4C_2(CN)_3$	F	53	275–278	HOAc	539[f]	366	$C_{21}H_{11}N_5O$	72.2	71.8	3.2	3.3	20.0	21.1
4-(4-Me_2N-1-$C_{10}H_6N$=N)-3,5-$Me_2C_6H_2C_2(CN)_3$	F	55		EtOH	438[g]	145	$C_{25}H_{20}N_6$					20.8	20.5

[a] $C_2(CN)_3$ = tricyanovinyl; $C_{10}H_6$ = naphthylene; C_4H_3S = 2-thienyl; Pr = *n*-C_3H_7; Bu = *n*-C_4H_9. [b] A, condensation of an amine with tetracyanoethylene; B, acylation of an amine followed by condensation with tetracyanoethylene; C, successive treatment of a benzal compound with sodium cyanide, acetic acid and lead tetraacetate; D, acylation; E, nitration; F, coupling to a diazotized 4-tricyanovinylaniline; G, condensation of malononitrile and the glyoxylate. [c] Purification by slurrying, not recrystallization. [d] Formed by transesterification during crystallization of corresponding methyl ester (crude, m.p. 180–195°) from butanol. [e] Chlorine analysis. [f] In 2-methoxyethanol. [g] In dimethylformamide. [h] Preferred procedure. [i] This π-complex rather than a condensation product precipitated from a dimethylformamide solution of the components at 45°. [j] In methylene chloride.

TABLE III

PROPERTIES OF AMINOBENZALMALONONITRILES AND THEIR ANALOGS

Compound[a]	Yield, %	M.p., °C.	Crystn. solvent	$\lambda_{max}^{Acetone}$, mμ	$\epsilon_{max} \times 10^{-2}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2-$H_2NC_6H_4CH$=$C(CN)_2$[b]	30	166–167	EtOH	447	103	$C_{10}H_7N_3$	71.0	70.7	4.2	4.3	24.8	24.8
4-$H_2NC_6H_4CH$=$C(CN)_2$	78	213–214	EtOH	405	438	$C_{10}H_7N_3$	71.0	71.0	4.2	4.1	24.8	24.9
4-$AcNHC_6H_4CH$=$C(CN)_2$[f]	67	228–229	HOAc	360	340	$C_{12}H_9N_3O$	68.2	68.0	4.3	4.5	19.9	19.9
4-Me_2N-2-MeC_6H_3CH=$C(CN)_2$	62	201–202	Acetone	439	494	$C_{13}H_{13}N_3$	73.9	73.8	6.2	6.4	19.9	19.8
4-Me_2N-2-ClC_6H_3CH=$C(CN)_2$	90	202–203	EtOH	432	476	$C_{12}H_{10}ClN_3$	62.2	62.2	4.4	4.6	18.1	18.2
4-Et_2N-2-ClC_6H_3CH=$C(CN)_2$	89	117	EtOH	437	546	$C_{14}H_{14}ClN_3$	64.8	64.9	5.4	5.4	13.6[c]	14.1
4-$NCCH_2CH_2N(Et)C_6H_4CH$=$C(CN)_2$	79	122–123	EtOH	422	538	$C_{15}H_{14}N_4$	72.0	72.2	5.6	5.7	22.4	22.5
4-$(NCCH_2CH_2)_2NC_6H_4CH$=$C(CN)_2$	85	218–220	Acetone	410	479	$C_{16}H_{13}N_5$	69.8	69.9	4.8	4.8	25.4	25.5
4-$(C_6H_5CH_2)_2NC_6H_4CH$=$C(CN)_2$	86	187–189	EtOH	425	552	$C_{24}H_{19}N_3$	82.5	81.8	5.5	5.6	12.0	12.0
p-$(NC)_2C$=CH-julolidine	83	163–165	EtOH	456	618	$C_{16}H_{15}N_3$	77.1	76.6	6.1	5.9	16.9	16.6
1,3,3-Me_3-2-$[C(CN)_2$=CHCH=]indoline	40	244–245	Acetone	433	652	$C_{16}H_{15}N_3$	77.1	77.5	6.1	6.1	16.9	16.9
1,3,3-Me_3-2-$[C(CN)_2$=C(SMe)CH=]indoline[g]	30	155–157	C_6H_6/C_6H_{12}	439	290	$C_{15}H_{17}N_3S$	69.1	68.4	5.8	5.9	10.8[d]	10.9
4-$Me_2NC_6H_4CH$=$C(CN)CO_2Me$[e,h]	48	141–142	MeOH	421	424	$C_{13}H_{14}N_2O_2$	67.8	68.0	6.1	6.1		
4-$Me_2NC_6H_4CH$=$C(CN)CO_2CH_2C_6H_5$	80	133–134	EtOH	423	474	$C_{19}H_{18}N_2O_2$	74.5	74.2	5.9	5.9		
4-$Me_2NC_6H_4CH$=$C(CN)CO_2CH_2CH_2C_6H_5$	83	142–143	EtOH	420	464	$C_{20}H_{20}N_2O_2$	75.0	74.8	6.3	6.3		
4-$NCCH_2CH_2N(Me)C_6H_4CH$=$C(CN)CO_2CH_3$	81	171–172	BuOH	410	439	$C_{15}H_{15}N_3O_2$	66.9	66.9	5.6	5.5		
4-Me_2N-2-MeC_6H_3CH=$C(CN)CO_2Et$[e]	66	118–120	EtOH	430	405	$C_{15}H_{18}N_2O_2$	69.7	69.1	7.0	7.2		
4-$NCCH_2CH_2N(Me)C_6H_4CH$=$C(CN)CO_2CH_2C_6H_5$[e]	78	135–136	EtOH	412	458	$C_{21}H_{19}N_3O_2$	73.0	72.7	5.6	5.4		
4-$NCCH_2CH_2N(Me)C_6H_4CH$=$C(CN)CO_2CH_2CH_2C_6H_5$[e]	78	90–91	MeOH	409	448	$C_{22}H_{21}N_3O_2$	73.5	73.4	5.9	5.9		
4-$(NCCH_2CH_2)_2NC_6H_4CH$=$C(CN)CO_2Me$	65	185–186	BuOH	400	413	$C_{17}H_{16}N_4O_2$	66.2	66.2	5.2	5.4		
4-$(NCCH_2CH_2)_2NC_6H_4CH$=$C(CN)CO_2CH_2C_6H_5$[e]	83	168–169	BuOH	402	430	$C_{23}H_{20}N_4O_2$	71.9	72.0	5.2	5.5		
4-$Me_2NC_6H_4CH$=$C(CN)CONH_2$[e]	79	194–195	EtOH	403	364	$C_{12}H_{13}N_3O$	67.0	66.8	6.1	5.9		
4-$Me_2NC_6H_4CH$=$C(CN)CO$-2-C_4H_3S	80	171–172	EtOH	450	426	$C_{16}H_{14}N_2OS$	68.1	67.6	5.0	5.2		
4-$Me_2NC_6H_4CH$=$C(CN)SO_2C_6H_5$	77	196–197	BuOH	425	528	$C_{17}H_{16}N_2O_2S$	65.4	65.4	5.2	5.3	9.0	9.0
4-(4-$Me_2NC_6H_4CH$=)-1-C_6H_5-3-(2-C_4H_3S)-5-pyrazolone[c]	83	175–176	EtOH	459	466	$C_{22}H_{19}N_3OS$	70.8	71.0	5.1	5.4		
4-[4-$NCCH_2CH_2N(Me)C_6H_4CH$=]-3-Me-1-C_6H_5-5-pyrazolone[e]	85	151–152	BuOH	425	406	$C_{21}H_{20}N_4O$	73.2	73.0	5.9	5.9		
4-[4-$(NCCH_2CH_2)_2NC_6H_4CH$=]-3-Me-1-C_6H_5-5-pyrazolone[e]	80	177–178	BuOH	416	421	$C_{23}H_{21}N_5O$	72.0	72.1	5.5	5.6		
4-(4-$Me_2NC_6H_4CH$=$CHCH$=)-3-Me-1-C_6H_5-5-pyrazolone[e]	85	161–162	Toluene	483	434	$C_{21}H_{21}N_3O$	76.1	75.3	6.4	6.5	12.7	13.4
3-Pyridine-CH=$C(CN)CO_2CH_2C_6H_5$	77	124–125	EtOH	298	166	$C_{16}H_{12}N_2O_2$	72.7	72.1	4.6	4.7	10.6	10.7
4-Pyridine-CH=$C(CN)CO_2CH_2C_6H_5$	62	96–97	EtOH	273	140	$C_{16}H_{12}N_2O_2$	72.7	73.0	4.6	4.7	10.6	10.6

[a] $C_{10}H_6$ = naphthylene; $C_4H_{10}S$ = 2-thienyl; Pr = *n*-C_3H_7; Bu = *n*-C_4H_9. [b] Roughly an equal quantity of a cyclization product, 2-amino-3-cyanoquinoline, was formed simultaneously, m.p. 225–226° (from ethanol), $\lambda_{max}^{Acetone}$ 371 mμ (ε 4300). Calcd. for $C_{10}H_7N_3$: C, 71.0; H, 4.2; N, 24.8. Found: C, 70.8; H, 4.4; N, 25.0. [c] Chlorine analysis. [d] Sulfur analysis. [e] Successive treatment with sodium cyanide and lead tetraacetate gave the corresponding α-cyanovinyl compound, λ_{max} 40–100 mμ greater than that of this compound; product not obtained analytically pure. [f] Prepared from 4-$H_2NC_6H_4CH$=$C(CN)_2$ and acetic anhydride. [g] Prepared by refluxing 1,1,3-trimethyl-2-methyleneindoline and $(MeS)_2$-C=$C(CN)_2$ in ethanol containing triethylamine by procedure of H. D. Edwards and J. D. Kendall, U. S. Patent 2,533,233 (1950). [h] Sodium cyanide in methanol gave 4-$Me_2NC_6H_4CH(CN)CH(CN)Co_2Me$, 89% yield, m.p. 120–121°. *Anal.* Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.4; H, 5.9; N, 16.3. Found: C, 65.3; H, 5.8; N, 16.4.

oxychloride. 4-(**Dibenzylamino**)-**benzaldehyde**, m.p. 91–92°, was purified by crystallization from aqueous methanol.

Anal. Calcd. for $C_{21}H_{21}NO$: N, 4.7. Found: N, 4.7.

4-Bis-(2-cyanoethyl)-aminobenzaldehyde melted at 118–119° after crystallization from ethanol.

Anal. Calcd. for $C_{13}H_{13}N_3O$: C, 68.7; H, 5.8. Found: C, 68.6; H, 5.6.

Of the compounds having an active methylene group, all save one were known and were either purchased or prepared as described in the literature. The new one, **2-phenylethyl cyanoacetate**, b.p. 102° (0.1 mm.), $n^{25}D$ 1.5125, was prepared in 71% yield by slowly distilling a mixture of benzene and ethanol from a mixture of 50 g. of ethyl cyanoacetate, 75 g. of 2-phenethyl alcohol, 75 ml. of benzene and 0.5 g. of sodium hydride.

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.8; H, 5.9. Found: C, 70.3; H, 5.8.

The benzal compounds were prepared by adding a little piperidine in excess acetic acid to equimolar amounts of aldehyde and methylene compound dissolved in slightly more refluxing absolute ethanol than needed for solution. Refluxing was continued for two hours unless crystallization began sooner. Thus, 61.4 g. (0.35 mole) of *p*-dimethylaminobenzaldehyde and 52.2 g. (0.35 mole) of benzyl cyanoacetate were dissolved in 350 ml. of refluxing ethanol. To the solution was added 5.0 ml. of a catalyst mixture made by dissolving 10 ml. (0.10 mole) of piperidine in 29 ml. (0.50 mole) of acetic acid. The solution was refluxed two hours, cooled to 0°, and filtered in order to separate 94.5 g. of benzyl 4-dimethylamino-α-cyanocinnamate. After recrystallization from a mixture of 2 l. of 95% ethanol and 250 ml. of benzene, the benzyl ester weighed 85.4 g. (80% yield). Its physical properties are listed in Table III, together with those of the other new aminobenzal compounds.

In a few cases the piperidine–acetic acid catalyst was replaced by the same volume of a solution of 0.5 g. of sodium in 10 ml. of methanol, with equally good results.

Preparation of 4-Tricyanovinylarylamines and Related α-Cyanovinyl Compounds[8] of Table II from 4-Aminobenzalmalononitriles and Similar Compounds.—The general procedure was to add hydrogen cyanide to the double bond of a 4-aminobenzal compound and to oxidize the adduct with lead tetraacetate, much as described above for the conversion of 4-dimethylaminobenzalmalononitrile to 4-tricyanovinyl-N,N-dimethylaniline. However, the preferred procedure differed in that the hydrogen cyanide adduct was usually not isolated, the adduct was prepared by addition of aqueous sodium cyanide to a dimethylformamide solution of the benzal compound, and no more than the calculated amount of lead tetraacetate was used in order to avoid oxidation of the final product. The 4-aminobenzal compounds used as starting materials were purchased or prepared as described in an earlier section of this paper. The procedure is illustrated by the following example.

A mixture of 4.47 g. (0.020 mole) of 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1-dicarbonitrile[9] and 50 ml. of dimethylformamide was stirred and warmed in a 250-ml. flask under an atmosphere of nitrogen until the dinitrile was in solution. The solution was cooled to 25°, 6.5 ml. (30% excess) of 4 *N* aqueous sodium cyanide was added dropwise during one minute, and the solution was stirred four minutes longer. The solution warmed up to about 35° during the addition, and the color of the solution turned from deep red to light pink. Acetic acid (75 ml.) and 8.87 g. (0.020 mole) of recrystallized lead tetraacetate were successively added during a period of two minutes, causing the temperature to rise to about 50°. The mixture was stirred ten minutes, cooled to 0°, and filtered to separate 2.45 g. of 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile (Table II). After recrystallization from 140 ml. of xylene, the trinitrile weighed 2.35 g. (47% yield).

If the α-cyanovinyl product did not crystallize from the reaction mixture, it was isolated by diluting the reaction mixture with water. For example, the above experiment was repeated except that the warm reaction mixture was not cooled to cause crystallization of the product, but was poured into 500 ml. of a well-stirred mixture of ice and water. The cold aqueous suspension of product was stirred ten minutes and filtered to give 3.82 g. of 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile. It was 88% pure, to judge from its visible absorption spectrum. Two recrystallizations from xylene gave 2.1 g. (42% yield) of pure trinitrile.

The physical properties and analytical data of α-cyanovinyl compounds prepared by this procedure are included in Table II. By comparing light absorption data of Tables II and III, it is seen that the absorption maximum of an α-cyanovinyl compound is commonly 40–100 mμ greater than that of the corresponding 4-aminobenzal compound, showing that the α-cyano group exerts a remarkably strong bathochromic effect. Five analogous instances of a strong bathochromic effect by a cyano group have been reported for other classes of dyes.[10]

Hydrolysis of 4-Tricyanovinylanilines to 4-(1-Hydroxy-2,2-dicyanovinyl)-anilines.[11]—4-Tricyanovinylaniline (9.66 g.) was added to 50 ml. of boiling 10% sodium hydroxide, and the refluxing mixture was stirred for three minutes. The resultant solution was cooled rapidly to 0°, which caused the sodium salt of 4-(1-hydroxy-2,2-dicyanovinyl)-aniline to precipitate. The salt was separated by filtration, washed with cold 10% sodium hydroxide, and air-dried; wt. 8.6 g. The filtrate was diluted with 250 ml. of water, acidified with sulfuric acid, and distilled until 150 ml. of distillate had been collected; a prussian blue test and potentiometric titration with silver nitrate showed that the distillate contained 0.79 g. (59% yield) of hydrogen cyanide. The sodium salt was dissolved in 20 ml. of boiling water, 3.8 ml. of 12 *N* hydrochloric acid was added, and the solution was cooled quickly to 0°, causing the precipitation of 4-(1-hydroxy-2,2-dicyanovinyl)-aniline. This substance was separated by filtration, recrystallized from 70% ethanol, and air-dried to give 5.13 g. (47% yield) of the dihydrate. Anhydrous **4-(1-hydroxy-2,2-dicyanovinyl)-aniline** was obtained by drying the product of two additional recrystallizations at 100° (0.4 mm.) for three hours; yellow needles, m.p. >300°, λ_{max}^{water} 307 mμ (ε 14,800), pK_a (water) 4.28.

Anal. Calcd. for $C_{10}H_7N_3O$: C, 64.9; H, 3.8; N, 22.7; neut. equiv., 185. Found: C, 65.5; H, 4.0; N, 22.6; neut. equiv., 194.

Similar procedures were used to obtain three 4-(1-hydroxy-2,2-dicyanovinyl)-anilines[12] from the corresponding 4-tricyanovinylanilines. All were recrystallized from ethanol.

4-(1-Hydroxy-2,2-dicyanovinyl)-N-methylaniline m.p. 228–230°, pK_a (95% ethanol) 3.35. *Anal.* Calcd. for $C_{11}H_9N_3O$: C, 66.3; H, 4.6; N, 21.0. Found: C, 66.4; H, 4.6; N, 21.0.

4-(1-Hydroxy-2,2-dicyanovinyl)-2,6-dimethylaniline: 71% yield, m.p. >300°, pK_a (95% ethanol) 3.05. *Anal.* Calcd. for $C_{12}H_{11}N_3O$: C, 67.6; H, 5.2; N, 19.7. Found: C, 67.6; H, 5.4; N, 19.5.

4-(1-Hydroxy-2,2-dicyanovinyl)-N,N-dimethylaniline (III): m.p. 202–204° *in vacuo*, λ_{max}^{EtOH} 330 mμ (ε 16,000), pK_a (95% ethanol) 2.26. *Anal.* Calcd. for $C_{12}H_{11}N_3O$: C, 67.6; H, 5.2; N, 19.7. Found: C, 67.6; H, 5.5; N, 20.2.

The last compound was obtained as a **monohydrate** if air-dried instead of being dried at 100° (0.4 mm.). Its ultraviolet absorption spectrum was identical with that of the anhydrous sample.

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.3; H, 5.7; N, 18.2. Found: C, 62.4; H, 5.2; N, 18.5.

The infrared spectrum of 4-(1-hydroxy-2,2-dicyanovinyl)-N-methylaniline has no absorption band in the 2.7–3.2 μ region, where enolic O–H and amino N–H groups absorb. Neither is there absorption in the 5.8–6.0 μ region, where absorption by carbonyl would be expected if the compound had a ketone structure. There are absorption bands at 3.7 and 4.1 μ that resemble bands shown by salts of amines with strong acids. The spectra of the other three 1-hydroxy-2,2-dicyanovinyl compounds are similar to this one.

Ethanolysis of 4-(1-Hydroxy-2,2-dicyanovinyl)-N,N-dimethylaniline (III) **to Ethyl 4-Dimethylaminobenzoate.**—A solution of 2.0 g. of 4-(1-hydroxy-2,2-dicyanovinyl)-N,N-dimethylaniline in 75 ml. of ethanol saturated with hydrogen

(8) R. E. Heckert, U. S. Patent 2,803,640 (1957); D. R. Baer and R. E. Heckert, U. S. Patent 2,798,881 (1957).

(9) E. Hertel and K. A. Hoffmann, *Z. physik. Chem.*, **50B**, 382 (1941).

(10) P. Erhlich and L. Benda, *Ber.*, **46**, 1931 (1913); M. Bathegay and G. Hugel, *Bull. soc. chim.*, [4] **31**, 441 (1922); K. Albrecht, *Ber.*, **27**, 3294 (1894).

(11) W. J. Middleton, U. S. Patent 2,726,249 (1955).

(12) These compounds were prepared by Dr. A. S. Hay.

chloride was refluxed for five hours. The mixture was cooled to 0°, filtered to remove ammonium chloride, concentrated to a volume of 20 ml. on a steam-bath, and poured into excess cold 10% sodium hydroxide. This caused the precipitation of 1.8 g. of ethyl 4-dimethylaminobenzoate, m.p. 62–63°. After recrystallization from aqueous ethanol, it melted at 64–64.5°.[13]

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.4; H, 7.8; N, 7.3. Found: C, 68.5; H, 7.9; N, 7.2.

A solution of 2.0 g. of the ester in 1.8 ml. of acetic acid, 0.6 ml. of 96% sulfuric acid and 1.2 ml. of water was refluxed four hours and poured over ice. Neutralization with 10% aqueous sodium hydroxide gave a precipitate of 4-dimethylaminobenzoic acid. After recrystallization from a mixture of ethanol and hexane, it had the same melting point (244–245°) and infrared spectrum as an authentic sample.[14]

Condensation of Tetracyanoethylene with 2,6-Dimethylaniline and *o*-Toluidine.—2,6-Dimethylaniline (10.0 g.) was added slowly to a solution of 10.0 g. of tetracyanoethylene in 75 ml. of tetrahydrofuran. The mixture was stirred and refluxed 16 hours. Cooling to 25° caused the precipitation of 13.0 g. of dark blue solid. The solid was separated and washed with boiling acetic acid to give 9.0 g. (52% yield) of nearly pure 4-tricyanovinyl-2,6-dimethylaniline, $\lambda_{max}^{acetone}$ 500 mμ (ε 28,000), after recrystallization from nitromethane. Evaporating the tetrahydrofuran filtrate to dryness left 6.0 g. of a blue solid; $\lambda_{max}^{acetone}$ 341 mμ (*k* 33), 511 mμ (*k* 54). Assuming that these maxima are due, respectively, to N-tricyanovinyl-2,6-dimethylaniline and 4-tricyanovinyl-2,6-dimethylaniline and that the N-tricyanovinylaniline has a molecular extinction coefficient of 14,000, it can be estimated that the 6.0-g. residue contained about 1.9 g. (11% yield) of N-tricyanovinyl-2,6-dimethylaniline and 3.0 g. (17% yield) of 4-tricyanovinyl-2,6-dimethylaniline.

Similarly, 5.0 g. of *o*-toluidine and 5.0 g. of tetracyanoethylene were refluxed in 30 ml. of tetrahydrofuran, the solvent was evaporated at reduced pressure, and the residue was recrystallized twice from 50% aqueous acetic acid to give 2.0 g. (25% yield) of red-brown tricyanovinyl derivative, $\lambda_{max}^{acetone}$ 330 mμ (*k* 57) and 497 mμ (*k* 8.7). These spectral data indicate that the recrystallized solid was about 93% N-tricyanovinyl-*o*-toluidine and 7% 4-tricyanovinyl-*o*-toluidine.

4-Tricyanovinylacetanilide.—4-Acetamidobenzalmalononitrile (Table III) was prepared by refluxing a solution of 3.00 g. of 4-aminobenzalmalononitrile in 20 ml. of acetic anhydride for 30 minutes. Cooling caused the precipitation of 2.52 g. (67% yield) of 4-acetamidobenzalmalononitrile, m.p. 228–229° after recrystallization from acetic acid.

A solution of 394 mg. of 4-acetamidobenzalmalononitrile in 5 ml. of dimethylformamide was treated successively with 0.6 ml. (28% excess) of 4 *N* sodium cyanide, 7.5 ml. of acetic acid and 0.91 g. (10% excess) of lead tetraacetate. The mixture was poured into 50 ml. of ice and water. Crude 4-tricyanovinylacetanilide (194 mg.) was separated by filtration. After two crystallizations from ethanol, the acetanilide (Table II) melted at 183–186°.

Refluxing a solution of 500 mg. of 4-tricyanovinylaniline in 5 ml. of acetic anhydride for 30 minutes also gave 4-tricyanovinylacetanilide, but spectral data on material twice crystallized from ethanol showed it to be only about 80% pure.

4-Tricyanovinyl-N-palmitoylaniline.—Palmitoyl chloride (0.74 g., 5% excess) and 0.22 g. of pyridine were added successively to 500 mg. of 4-tricyanovinylaniline in 10 ml. of dimethylformamide. The mixture was heated at 100° for 75 minutes and poured into 50 ml. of ice and water. The slightly gummy solid that precipitated was dissolved in acetone and reprecipitated in water. Crystallizing the resultant powder three times from ethanol gave 4-tricyanovinyl-N-palmitoylaniline as yellow crystals, m.p. 105–106° (Table II).

1-(4-Tricyanovinylphenylazo)-2-naphthol.—A solution of 0.4 g. (0.0058 mole) of sodium nitrite dissolved in about 1 ml. of water was added dropwise to a solution of 1.0 g. (0.005 mole) of 4-tricyanovinylaniline and 0.5 ml. of sulfuric acid in 10 ml. of glacial acetic acid at 25°. After the mixture had been stirred at 20–25° for five minutes, the excess nitrous acid was decomposed by the addition of 0.5 g. of sulfamic acid dissolved in 10 ml. of water. The solution of diazonium compound was added to 100 ml. of 95% ethanol containing 2.0 g. (0.021 mole) of β-naphthol. The azo dye began to form at once. The mixture was brought to *p*H 8–10 by addition of 10% aqueous sodium hydroxide and was stirred for 15 minutes at 20–40°. 1-(4-Tricyanovinylphenylazo)-2-naphthol (0.95 g.) was separated by filtration and washed with water and acetic acid. After recrystallization from 150 ml. of acetic acid, the azo compound (Table II) was in the form of blue-black plates; wt. 0.37 g. (21% yield).

4-(4-Tricyanovinyl-2,6-dimethylphenylazo)-1-dimethylaminonaphthalene (Table II) was prepared from 1.0 g. of 4-tricyanovinyl-2,6-dimethylaniline and 4 ml. of 1-dimethylaminonaphthalene by the same procedure except that the alcoholic solution of 1-dimethylaminonaphthalene contained 3.0 g. of sodium acetate and neutralization with sodium hydroxide was omitted.

2-Nitro-4-tricyanovinyl-N,N-dimethylaniline.—To a stirred suspension of 440 mg. of 4-tricyanovinyl-N,N-dimethylaniline in 25 ml. of acetic acid at 15° there was added 0.7 ml. of 90% nitric acid. The resultant solution was stirred ten minutes at 15° and poured into 200 ml. of ice and water. 2-Nitro-4-tricyanovinyl-N,N-dimethylaniline (Table II) was separated by filtration. It weighed 409 mg. (77% yield) after one crystallization from ethanol.

3-Nitro-α,β-dicyano-4-dimethylaminocinnamamide.—Ninety grams of α-cyano-4-dimethylaminocinnamamide (Table III) was dissolved in 500 ml. of dimethylformamide at 35°. Triethylamine (2.0 ml.) was added, the solution was cooled to 16°, and 65 ml. of liquid hydrogen cyanide was added. The temperature rose to 30°. The mixture was stirred two hours at 30–35°, cooled to 0°, and poured into 3 l. of a stirred mixture of ice and water. This gave an orange oil that gradually solidified. The solid was filtered and recrystallized from 1 l. of 95% ethanol to give 67 g. (66% yield) of **α,β-dicyano-β-(4-dimethylaminophenyl)-propionamide**, a pale yellow solid melting at 140–150° *in vacuo*. A sample for analysis melted at 146–153° *in vacuo* after three recrystallizations from ethanol. The wide melting-point range suggests that the product is a mixture of stereoisomers.

Anal. Calcd. for $C_{13}H_{14}N_4O$: C, 64.4; H, 5.8; N, 23.1. Found: C, 64.4; H, 6.0; N, 23.3.

A solution of 121 mg. of the propionamide in 5 ml. of 1 *N* nitric acid was heated to about 90° with swirling, at which temperature the solution suddenly became deeply colored. The mixture was cooled in ice, diluted with 5 ml. of water, and filtered to separate 56 mg. of crude 3-nitro-α,β-dicyano-4-dimethylaminocinnamamide, an orange solid. After recrystallization from ethanol, the nitrocinnamamide (Table II) weighed 16 mg.

Oxidation of α,β-dicyano-β-(4-dimethylaminophenyl)-propionamide with the calculated amount of lead tetraacetate in acetic acid gave crude α,β-dicyano-4-dimethylaminocinnamamide, $\lambda_{max}^{acetone}$ 467 mμ (*k* 45). No suitable recrystallization solvent was found.

4-(1-Carbethoxy-2,2-dicyanovinyl)-N,N-dimethylaniline (IX).—A solution of 4.42 g. (0.02 mole) of ethyl 4-dimethylaminophenylglyoxylate,[15] 5.82 g. (0.08 mole) of malononitrile and 0.3 ml. of piperidine in 7 ml. of ethanol was refluxed for 17 hours. The reaction mixture was taken up in benzene, and the benzene solution was washed with water, dried and evaporated to dryness at 25°. The residue was recrystallized from ethanol to give 3.4 g. (63% yield) of 4-(1-carbethoxy-2,2-dicyanovinyl)-N,N-dimethylaniline in the form of orange needles, m.p. 129–130° (Table II).

Degradation of 4-(4-Dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile (XI) to Methyl 4-Dimethylaminocinnamate (XIII).—A slurry of 1.24 g. of the tricarbonitrile in 75 ml. of ethanol was boiled and stirred while 7.5 ml. of 2.5 *N* sodium hydroxide was added rapidly. After 12 minutes of refluxing, the resulting brown solution was cooled to 5°, acidified with 15 ml. of 2 *N* hydrochloric acid, diluted with 50 ml. of water, and filtered to separate 0.67 g. of a blue solid. Spectral and analytical data for the product of another run suggest that the solid was a mixture consisting mainly of α-cyano-β-hydroxy-4-dimethylaminocinnamamide. Since efforts to isolate a pure substance were unsuccessful, the blue solid was suspended in 35 ml. of boiling methanol, the mixture was saturated with hydrogen chlo-

(13) H. Rivier and C. Schneider, *Helv. Chim. Acta*, **2**, 717 (1919), report m.p. 67–68°.

(14) M. L. Rousset, *Bull. soc. chim.*, [3] 11, 318 (1894).

(15) M. A. Guyot, *Compt. rend.*, **144**, 1120 (1907).

ride, and the resultant solution was refluxed for 15 hours. The solution was then cooled, diluted with 100 ml. of ice-water, and neutralized with 10% aqueous sodium carbonate, which caused 310 mg. of gray solid to precipitate. Sublimation of the gray solid at 100–115° (0.5 mm.) followed by recrystallization of the sublimate from methanol gave 164 mg. (16% yield) of methyl 4-dimethylaminocinnamate. The ester had the same melting point (137–138°) and X-ray diffraction pattern as an authentic sample.[16]

Basic Hydrolysis of 4-(4-Dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile (XI).—A 0.000342 *M* solution of 4-(4-dimethylaminophenyl)-1,3-butadiene-1,1,2-tricarbonitrile in methanol was prepared; λ_{max} 582 mμ (*k* 258), 355 mμ (*k* 26). Fifty milliliters of this solution was mixed with 50 ml. of 0.12 *N* methanolic sodium hydroxide. The deep blue color of the tricarbonitrile was instantly replaced by a brownish-yellow color; λ_{max} 462 mμ (*k* 19). In the course of five hours, the maximum at 462 mμ gradually disappeared and a new one appeared at 400 mμ (*k* 31). At timed intervals a 5-ml. portion of the basic mixture was diluted to 25 ml. with a 0.21 *N* solution of acetic acid in methanol, and the spectrum of the acidic solution was determined. The tricarbonitrile was partially regenerated by the acid, as shown by reappearance of blue color and a corresponding absorption maximum at 582 mμ. Except for diminished absorption at 582 mμ, the treatment with base caused no marked spectral change. From the optical density at 582 mμ, it was possible to estimate the extent of hydrolysis of the tricarbonitrile for the following times in minutes. The percentages were: 1.5 min., 2.7%; 10, 9.3%; 20, 13.9%; 40, 25.2%; 80, 43%; 160, 67%; 320, 87%. These figures correspond to a rate of hydrolysis approximately first order in tricarbonitrile concentration.

Semi-quantitative Determination of Tetracyanoethylene.—A weighed 10-mg. sample of material believed to contain tetracyanoethylene is dissolved in 100 ml. of N,N-dimethylaniline by shaking the mixture at room temperature for a few minutes. The solution is allowed to stand for 15 to 20 hours at room temperature to ensure complete conversion of tetracyanoethylene to 4-tricyanovinyl-N,N-dimethylaniline. A 5-ml. portion is diluted to 100 ml. with acetone, and the visible absorption spectrum of the solution is determined. A maximum near 515 mμ indicates that the original material contains tetracyanoethylene. The percentage, *P*, of tetracyanoethylene can be estimated within a few per cent. from the corresponding specific extinction coefficient, k_{max}. With pure tetracyanoethylene the coefficient determined in this way is 246, so that $P = 100k_{max} \div 246$.

(16) P. Pfeiffer and G. Haefelin, *Ber.*, **55**, 1769 (1922).

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 441 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. VII.[1] Tricyanoethylenes

BY G. N. SAUSEN, V. A. ENGELHARDT AND W. J. MIDDLETON

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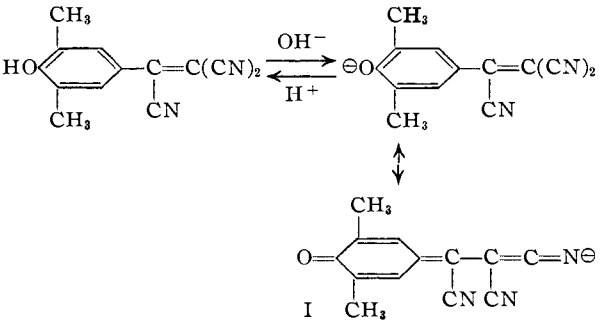
Routes to tricyanoethylenes include direct alkylation of an aromatic or heterocyclic nucleus with tetracyanoethylene, condensation of an aldehyde with malononitrile followed by the addition of hydrogen cyanide and subsequent dehydrogenation, and condensation of an acyl cyanide with malononitrile. The tricyanovinyl group undergoes a variety of chemical reactions including replacement of the 1-cyano group by reaction with nucleophilic reagents such as alcohols, hydroxide ion, amines and malononitrile anion. It serves as the dienophilic group in Diels–Alder reactions, and is converted to substituted pyrroles and substituted thiophenes by reaction with mercaptans and with hydrogen sulfide, respectively.

Tetracyanoethylene (TCNE) reacts with most primary and some secondary aromatic amines with elimination of hydrogen cyanide to give N-tricyanovinylamines, and it reacts readily with both tertiary and secondary aromatic amines to give the corresponding 4-tricyanovinylarylamines.[1] This paper describes the preparation and chemistry of tricyanovinyl hydrocarbons, tricyanovinyl phenols and tricyanovinyl heterocyclic compounds.

Syntheses of Tricyanoethylenes. A. Alkylation with Tetracyanoethylene.—Tetracyanoethylene reacts readily with selected aromatic and heterocyclic nucleii with elimination of the elements of hydrogen cyanide to give the corresponding C-tricyanovinyl compounds. For example, reaction with phenanthrene gives a mono-(tricyanovinyl)-phenanthrene, probably the 9-derivative, and reaction of TCNE with pyrrole and N-methylpyrrole gives the corresponding tricyanovinyl heterocycles, probably substituted in the 2-position. These reactions are carried out at room temperature in solvents such as acetone and tetrahydrofuran. Reaction of TCNE with 2,6-dimethylphenol occurs in the presence of pyridine, and 4-(tricyanovinyl)-2,6-dimethylphenol is obtained as an orange solid. In the absence of a basic catalyst lower yields of product are obtained. The phenol serves as an indicator becoming bright yellow in dilute acid solution and deep burgundy in alkaline solution (I).



B. Aldehyde Route.—An alternate route to tricyanovinyl compounds involves condensation of an aldehyde with malononitrile followed by the addition of hydrogen cyanide to give the 1,2,2-tricyanoethyl compound II. Dehydrogenation of II to the corresponding tricyanovinyl derivative III completes the synthesis.

$$RCHO \longrightarrow \underset{II}{RCH(CN)CH(CN)_2} \longrightarrow \underset{III}{RC(CN)=C(CN)_2}$$

The application of this route to the preparation of tricyanovinylarylamines was described in a previous paper.[1] In the present study tricyanovinyl-

(1) Paper VI, B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, THIS JOURNAL, **80**, 2806 (1958).