21. *The* cis- *and* trans-*αβ-Dicyanostilbenes. Part I. The Geometrical Configuration and Cyclisation of the* trans-*Isomer, the Previously Alleged Diphenylmaleidinitrile.*

By D. G. COE, M. M. GALE, R. P. LINSTEAD, and C. J. TIMMONS.

The chemical and physical properties of αβ-dicyanostilbene, as usually obtained, show that it is the *trans*- and not the *cis*-isomer as previously assumed. Cyclisation with concentrated sulphuric acid affords 3-cyano-2-phenylinden-1-one. The ultraviolet-light absorption of *trans*-dicyanostilbene indicates steric hindrance to complete conjugation.

αβ-DICYANOSTILBENE, m. p. 161°, results from the dehydrohalogenation of an α-halogenobenzyl cyanide and from related reactions:

$$(A)\quad 2\mathrm{Ph{\cdot}CHX{\cdot}CN} \longrightarrow \mathrm{NC{\cdot}CPh{:}CPh{\cdot}CN}\quad (B)$$
$$(\mathrm{A};\ \mathrm{X} = \mathrm{Br};^{1-6}\ \mathrm{Cl};^{7-9}\ \mathrm{I};^{10,11}\ \mathrm{NO_2};^{12,13}\ \mathrm{Ph{\cdot}SO_2};^{14}\ \mathrm{S{\cdot}CO{\cdot}NH_2}^{3}).$$

Since alkaline hydrolysis followed by acidification [2, 9, 15] or direct acid hydrolysis [16] converted the dinitrile into αβ-diphenylmaleic anhydride, the dinitrile was generally assumed to have the *cis*-configuration also, and it is usually referred to in the literature as

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[1] Doyer, Inaug. Diss., Leiden, 1878.
[2] Reimer, *Ber.*, 1880, **13**, 742; 1881, **14**, 1797.
[3] Davies and Maclaren, *J.*, 1951, 1434.
[4] (*a*) Banfield, Ph.D. Thesis, Melbourne, 1950; (*b*) Kinnear, *J. Soc. Chem. Ind.*, 1948, **67**, 35.
[5] Von Braun, *Ber.*, 1903, **36**, 2651.
[6] Ramart-Lucas and Hoch, *Ann. Chim.*, 1930, **13**, 385.
[7] Michaël and Jeanprêtre, *Ber.*, 1892, **25**, 1678.
[8] Anbar, Dostrovsky, Samuel, and Yoffe, *J.*, 1954, 3603.
[9] Korchak and Lisseenko, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 1329.
[10] Chalanay and Knoevenagel, *Ber.*, 1892, **25**, 285, 289.
[11] Cook and Linstead, *J.*, 1937, 929.
[12] Wislicenus and Endres, *Ber.*, 1902, **35**, 1755.
[13] Thurston and Shriner, *J. Org. Chem.*, 1937, **2**, 183.
[14] Dodson and Turner, *J. Amer. Chem. Soc.*, 1951, **73**, 4517.
[15] Rügheimer, *Ber.*, 1882, **15**, 1625.
[16] Heller, *Annalen*, 1908, **358**, 349.

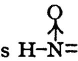
diphenylmaleidinitrile, although the possibility that inversion accompanied hydrolysis was realised by Chalanay and Knoevenagel.[10] *A priori*, it is difficult to explain the production of the *cis*-isomer, which is more sterically hindered and is less stable than the *trans*-isomer. Interest in the configuration of the dinitrile was renewed on its conversion into macrocyclic pigments such as octaphenyltetra-azaporphin.[11, 17] However, this reaction does not necessitate a *cis*-structure for the dinitrile, as the formation of pigments from dimethylfumarodinitrile has been demonstrated, inversion occurring under the conditions employed.[18] Further study of the physical and chemical properties of the dicyanostilbene has now shown it to have the *trans*-configuration of diphenylfurmarodinitrile.

The dinitrile was prepared in 35% yield in one step by the action of alcoholic ammonia on α-bromobenzyl cyanide.[4a] Because α-halogenobenzyl cyanides are lachrymatory alternative routes were investigated. The toluenesulphonyloxy-analogue (*A*; X $= p\text{-}\mathrm{Me{\cdot}C_6H_4{\cdot}SO_3}$) was readily obtained from benzaldehyde, potassium cyanide, and toluene-*p*-sulphonyl chloride and was converted by potassium thiocyanate into the thiocyanato-derivative, which on treatment with alkali gave the αβ-dicyanostilbene, m. p. 161°, in 27% overall yield from benzaldehyde. In contrast, Kretov and Panchenko[19] reported that brief hot alkaline hydrolysis of this thiocyanate yielded a "high-melting dicyanostilbene" with m. p. 243°. Direct hydrolysis of the toluenesulphonate gave *trans*-αβ-dicyanostilbene in low yield. Hydrolysis of the corresponding benzoyloxy- and acetoxy-derivative did not produce dicyanostilbene but, as also reported by earlier workers, gave benzoin,[7, 20] presumably because nucleophilic reagents attack the acyl–oxygen bond instead of the C–X bond, as in the other derivatives. Support for this explanation is given by the rough correlation of the acid dissociation constants (*K*) of the hydrogen acids, HX, and the yields of dicyanostilbene produced, as shown in Table 1, the overall reaction probably proceeding by the scheme:

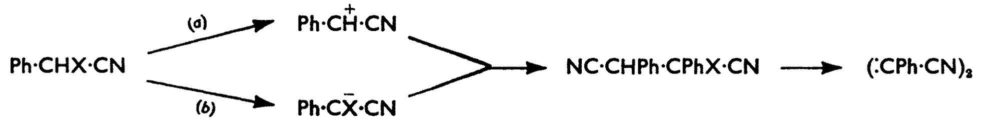
TABLE 1. *Yields of dicyanostilbene from various esters (A) and dissociation constants of* HX *in water.*

X	*K*	Yield (%)	X	*K*	Yield (%)
I	(*s*)	50	$\mathrm{Ph{\cdot}SO_3}$ [b]	2×10^{-1}	35
Br	(*s*)	>35	$\mathrm{NO_2}$	†	20
Cl	(*s*)	>27	$p\text{-}\mathrm{Me{\cdot}C_6H_4{\cdot}SO_3}$ [b]	1×10^{-1}	13
CNS [a]	(*s*)	60	$\mathrm{B_2O}$ [b]	7×10^{-5}	0
$\mathrm{S{\cdot}CO{\cdot}NH_2}$	*	66	AcO [b]	2×10^{-5}	0

(*s*), Strong acid: the first three are in order of acid strength in acetic acid.[c]
* Free acid unknown.


$\mathrm{H{-}\overset{\overset{O}{\uparrow}}{N}{=}O}$

† The hypothetical acid is H–N=O which is unknown (and is not nitrous acid).
[a] Gorman and Connell, *J. Amer. Chem. Soc.*, 1947, **69**, 2063. [b] Landolt–Börnstein, "Tabellen," 5th edn., Vol. II, p. 1123. [c] Kolthoff and Willman, *J. Amer. Chem. Soc.*, 1934, **56**, 1007.



Step (*a*) will proceed more readily the greater the stability of X^-, that is, the larger the dissociation constant of HX. The removal of the proton in step (*b*) will also be facilitated by a more highly electronegative group X, as well as by the cyano- and the phenyl groups, which will weaken the carbon–hydrogen bond towards nucleophilic attack. Combination of the oppositely charged ions leads to the dibenzyl derivative, which may then lose HX

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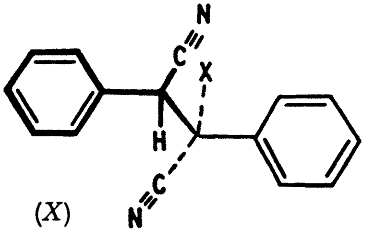
[17] Linstead, *J.*, 1953, 2873.
[18] Baguley, France, Linstead, and Whalley, *J.*, 1955, 3521.
[19] Kretov and Panchenko, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1975.
[20] Davis, *J.*, 1910, **97**, 949; Greene and Robinson, *J.*, 1922, **121**, 2182.

to give the dicyanostilbene. In an example of this reaction involving a *p*-bromobenzyl cyanide, the dibenzyl type intermediate has been isolated.[21] Consideration of possible conformations for the intermediate, which must necessarily be able to have the halogen and hydrogen atoms in the same plane as the central carbon atoms for ready elimination,[22] leads to the configuration shown (*X*) and its enantiomorph. Other conformations entail much greater steric interaction between non-bonded groups. Elimination of HX from this conformation will then be expected to give *trans*-dicyanostilbene. The latter reaction bears some similarities to the elimination reactions of β-acyloxy-esters, where it has been noted that there is a relation between the strengths of the acids eliminated and the yields of the unsaturated products, which also had the *trans*-configuration.[23]

TABLE 2. *Light absorption of cyanostilbenes.*

trans	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
Ph·CH:CHPh [a]	2280	16,000
	2950 *	29,000
NC·CPh:CHPh	2290	15,000
	3110	23,000
NC·CPh:CPh·CN	2360	12,000
	3240	19,000
cis	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
Ph·CH:CHPh [a]	2240	24,000
	2800	10,500
NC·CPh:CHPh [b]	2240	23,000
	2950	17,000

* Main band; there is also vibrational fine structure.
[a] Beale and Roe, *J.*, 1953, 2755. [b] Codington and Mosettig, *J. Org. Chem.*, 1952, **17**, 1027.



(*X*)

Dehydrogenation of diphenylsuccinodinitrile was not a practicable approach to dicyanostilbene.[24]

The ultraviolet-light absorption of the dicyanostilbene obtained is consistent with the *trans*-configuration, but not with the *cis*. A comparison with some related stilbenes is shown in Table 2. The introduction of one cyano-group into *trans*-stilbene has no appreciable effect on the 2280 Å band. This is in contrast to the introduction of alkyl groups,[25] the larger steric requirements of which cause complex variations. The long-wavelength (*K*) band characteristic of the conjugated system is displaced regularly towards longer wavelengths by the cyano-groups. This is in keeping with the conjugating properties of this substituent indicated in the spectra of various ethylenic nitriles,[26] which, in the absence of steric hindrance to coplanarity of the chromophore, absorb similarly to the corresponding acids, esters, and amides.*

In the *trans*-series the progressive decrease in intensity of the long-wavelength band on cyano-substitution is unexpected, as this band has been shown [28] to be an allowed even–odd transition, so that simple substitution would be expected to increase the band intensity. A decrease would, however, arise if the cyano-substituents prevent the

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* When this work was commenced, references [26] were not available, and the published spectra [27] for propenyl cyanide and cyano*cyclo*hexene were suspected (correctly) of being erroneous, so that *trans-trans*-sorbonitrile was prepared and shown to have similar absorption properties to the acid and amide (see Experimental section).

[21] Wislicenus and Elvert, *Ber.*, 1908, **41**, 4121.

[22] For summary see Klyne, " Progress in Stereochemistry," Butterworths, 1954, London, Vol. I, p. 64; cf. Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44; Cram, Greene, and Depuy, *J. Amer. Chem. Soc.*, 1956, **78**, 790.

[23] Linstead, Owen, and Webb, *J.*, 1953, 1211, 1218; Hein, *J. Amer. Chem. Soc.*, 1955, **77**, 2797.

[24] Bergdolt and Knoevenagel, *Ber.*, 1903, **36**, 2861; Braude, Linstead, *et al.*, *J.*, 1954, 2544 *et seq.*

[25] Braude, *J.*, 1949, 1902; Derkosch and Friedrich, *Monatsh.*, 1953, **84**, 1146.

[26] Herr and Heyl, *J. Amer. Chem. Soc.*, 1950, **72**, 1753; Wendler, Graber, Jones, and Tishler, *ibid.*, 1952, **74**, 3630; Cairns, Engelhardt, Jackson, Kalb, and Sauer, *ibid.*, p. 5636; Braude and Wheeler, *J.*, 1955, 320, 329.

[27] Braude, *Ann. Reports*, 1945, **47**, 114, 122.

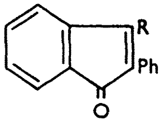
[28] Platt, *J. Amer. Chem. Soc.*, 1952, **74**, 2376.

molecule's taking up a planar conformation,[29] and detailed *X*-ray diffraction studies on the crystal show that the nitrile and phenyl groups are not coplanar.[30] The loss of vibrational fine structure in the *K*-band on cyano-substitution is probably an example of Calvin and Lewis's [31] " loose bolt " effect which also occurs in the *cis*-stilbene series.[32]

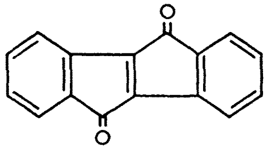
The infrared spectrum of the *trans*-dicyanostilbene in Nujol showed no bands in the 6 μ region, consistently with the presence of a symmetrically substituted carbon–carbon double bond.* The position (2240 cm.$^{-1}$) of the $C{\equiv}N$ stretching vibration indicates some conjugation of the nitrile group,[34] in agreement with the ultraviolet evidence.

The *trans*-configuration of the dicyanostilbene has been conclusively proved by recent *X*-ray diffraction studies,[35] and is in accord with the demonstration by Reimer [2, 36 (cf. 10)] that *meso*diphenylsuccinodinitrile was the main product of its reduction, as would be expected for *trans*-addition to a *trans*-double bond.[37] It is probable that various nuclear-substituted dicyanostilbenes claimed to have the *cis*-configuration are also *trans*-derivatives.[11, 16, 21, 38–40]

Whilst previous chemical reactions of *trans*-dicyanostilbene had usually been accompanied by inversion to derivatives with a *cis*-configuration (see p. 123), it is now shown that treatment with cold concentrated sulphuric acid converts it into the red 3-cyano-2-phenylinden-1-one (I; R = CN) in which the *trans*-arrangement of the phenyl groups is preserved. This is in contrast to Bartholdy's isolation [40] of diphenylmaleic anhydride apparently under these conditions. Interconversion of the nitrile (I; R = CN) and amide (I; R = $CO{\cdot}NH_2$) was readily accomplished with hot sulphuric acid and with phosphoric oxide in benzene respectively. Attempts to achieve further cyclisation to the unknown 3 : 6-dihydro-3 : 6-dioxodibenzopentalene (II) [41] with hot sulphuric acid, by analogy with the cyclisation of diphenylsuccinic acid to 3 : 6 : 7 : 8-tetrahydro-3 : 6-dioxodibenzopentalene,[42] were unsuccessful. Similarly numerous attempts to hydrolyse the nitrile or the amide to the known acid [6] (I; R = CO_2H) failed, as a result of the hindered location of the amide group. The indenones (I; R = CN and $CO{\cdot}NH_2$) were characterised as the 2 : 4-dinitrophenylhydrazones, which behaved differently from normal 2 : 4-dinitrophenylhydrazones in giving an intense blue colour with alkali. The implications of this observation, which are irrelevant to the present work, will be discussed elsewhere.[43] The structure of the indenone (I; R = CN) was confirmed by permanganate oxidation to benzoic and phthalic acid. The formation of the cyano-ketone (I; R = CN)



(I)



(II)

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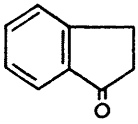
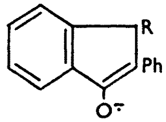
* Felton and Orr have recently reported a weak carbon–carbon double bond band at 1619 cm.$^{-1}$ in chloroform.[33]

[29] Braude and Sondheimer, *J.*, 1955, 3754.
[30] Wallwork, unpublished work.
[31] Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273.
[32] Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, 1940, **62**, 2973.
[33] Felton and Orr, *J.*, 1955, 2170.
[34] Kitson and Griffith, *Analyt. Chem.*, 1952, **24**, 334.
[35] Timmons and Wallwork, *Chem. and Ind.*, 1955, 62.
[36] Reimer, *Ber.*, 1881, **14**, 1797.
[37] Crombie, *Quart. Rev.*, 1952, **6**, 101.
[38] Wislicenus and Fischer, *Ber.*, 1910, **43**, 2234.
[39] Heller, *Annalen*, 1904, **332**, 247.
[40] Bartholdy, *Ber.*, 1907, **40**, 4400.
[41] Brand, Gabel, and Ott, *Ber.*, 1936, **69**, 2504.
[42] Roser, *Annalen*, 1888, **247**, 152; Blood and Linstead, *J.*, 1952, 2263.
[43] Timmons, unpublished work.

is analogous to the cyclisations of nuclear-substituted *trans*-monocyanostilbenes to substituted 2-phenylindenones studied by Pfeiffer and his co-workers.[44]

Catalytic hydrogenation of the indenones (I; R = CN and CO·NH$_2$) in the presence of palladium–charcoal afforded the corresponding indanones (III). In neutral or acid solution these existed in the colourless keto-form, as indicated by the similarity of their absorption spectra to that of acetophenone (see Table 3). The cyanoindanone (III; R = CN) in neutral or alkaline solution readily underwent dehydrogenation in air to the indenone (I; R = CN)—so rapidly in fact that it was necessary to protect the indanone (III; R = CN) from air during crystallisation. The carbamoylindanone (III; R = CO·NH$_2$) was stable in air, and with alkali gave a stable yellow colour, due to the formation of the enolate ion (IV; R = CO·NH$_2$), the light absorption of which is typical of a substituted *trans*-stilbene derivative (cf. Table 2).


(III)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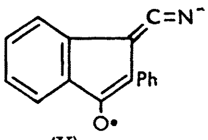
(V)

TABLE 3. *Light-absorption properties of some indenones and derived compounds.*

R = CN	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	R = CO·NH$_2$	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$
I	2630	28,500	I	2580	38,800
	4430	2,800		4220	1,800
I–dnp.†	4300	31,500	I–dnp.†	3870	26,500
III	2430	13,500	III	2450	12,500
	2830	2,100		2860 *	2,000
	2890	2,100		2930	2,200
	3150 *	1,000		3330 *	270
IV §	2600	>7,500	IV §	2630	4,500
	3400	>4,700		3540	19,000
V ‡	5350	>1,500	Cf. COPhMe [a]	2400	13,000
	7200	>430		2780	1,100
Cf. COPhMe dnp.† [b]	3800	27,500		3200	50

* Inflection. † dnp. = 2 : 4-dinitrophenylhydrazone in chloroform.
‡ By addition of alkali to solution of (V) containing ~1 g./l.
§ By addition of alkali to solution of (V) containing ~0·2 g./l.
[a] Ref. 27, p. 126. [b] Braude and Jones, *J.*, 1945, 498.

As it was shown above (p. 125) that conjugated amides and nitriles usually absorb similarly, the difference in the absorption of the amide and the nitrile (I; R = CO·NH$_2$ and CN) is unexpected: the amide shows less absorption at long wavelengths and more at short wavelengths. This may be attributed in part to the steric hindrance to coplanarity of the phenyl and the amide group, which can be shown from scale drawings, and in part to the greater conjugating power of the nitrile group. Similar but more marked effects are exhibited in the light absorption of the 2 : 4-dinitrophenylhydrazones, the main band shifting from 4300 Å in the nitrile to 3870 Å in the amide which shows conjugation only slightly greater than in acetophenone dinitrophenylhydrazone. These examples of steric hindrance in phenylindenones are similar to the numerous cases studied in detail in the diphenyl series, recently discussed by Braude and Forbes.[45]

In contrast to the carbamoylindanone (III; R = CO·NH$_2$), addition of alkali to dilute solutions of the cyanoindanone (III; R = CN) gave an unstable yellow colour, due to the enolate ion (IV; R = CN), which underwent aerial oxidation to the indenone (I; R = CN). However, with more concentrated solutions, addition of alkali gave other colours, purple in ethanol, and blue in dimethylformamide. It seems likely that these bands at longer

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[44] Pfeiffer, Behr, Kübler, and Ruping, *J. prakt. Chem.*, 1929, **121**, 85.
[45] Braude and Forbes, *J.*, 1955, 3776.

wavelengths are due to the presence of the semiquinone [46] (V), formed as an intermediate in the oxidation to the indenone (I; R = CN).

Preliminary experiments, which will be reported later, on irradiation of *trans*-dicyanostilbene indicate that a mixture of compounds is produced containing some *cis*-dicyanostilbene.

EXPERIMENTAL

Analytical data were determined in the microanalytical laboratory (Mr. F. H. Oliver and his staff). Ultraviolet light absorption data refer to EtOH solutions unless otherwise stated, and were determined with Hilger-Spekker and Unicam S.P. 500 instruments. All solutions of stilbene derivatives were kept in the dark to minimise isomerism, before determination of their light absorption.

*α-Cyanobenzyl Toluene-*p*-sulphonate* (with E. W. GARNISH).—A solution of potassium cyanide (16 g.) in water (50 ml.) was added dropwise with stirring to a cooled mixture of benzaldehyde (26·5 g.) and toluene-*p*-sulphonyl chloride (56 g.) at such a rate that the temperature did not rise above 20°. The mixture was set aside overnight at 0°. The solid formed was filtered off, washed with water, and dissolved in warm alcohol–acetone–ether (2 : 2 : 1; 120 ml.). After filtration, the solution was cooled and ice-water (100 ml.) added. After the mixture had been kept at 0° for two days, the oil that separated initially solidified almost completely, to give *α-cyanobenzyl toluene-*p*-sulphonate* (60 g., 90%), m. p. 54—56°, which, crystallised from ethanol, had m. p. 57—58° (Found: C, 62·5; H, 4·6; N, 5·1; S, 12·3. $C_{15}H_{13}O_3NS$ requires C, 62·7; H, 4·6; N, 4·9; S, 11·1%). As the material was slightly unstable at room temperature it was stored at 0°.

α-Cyanobenzyl Bromide.—Distillation of technical bromobenzyl cyanide (" B.B.C."),[4b] kindly supplied by the Chemical Defence Experimental Establishment, Porton, gave α-cyanobenzyl bromide as a nearly colourless oil, b. p. 111°/0·8 mm.

α-Cyanobenzyl Thiocyanate.—A warm solution of ammonium thiocyanate (65 g.) in alcohol (250 ml.) was added to α-cyanobenzyl bromide (150 g.) in alcohol (150 ml.). After a few minutes a precipitate was formed; the mixture was then heated to boiling and immediately filtered into cold water (1500 ml.). The resulting pasty solid was filtered off, washed with cold water, and drained. The product (92 g., 70%) was heated with charcoal in benzene–light petroleum (b. p. 80—100°; 1 : 1) and after filtration and crystallisation gave α-cyanobenzyl thiocyanate (65 g., 50%), m. p. 60—63°, sufficiently pure for further reactions. Repeated crystallisation from benzene–light petroleum (b. p. 40—60°; 1 : 1) gave colourless needles, m. p. 65° (Kretov and Panchenko [19] give m. p. 63—65°), which slowly became brown in air. Some decomposition was observed in hot solutions, making the crystallisations wasteful. Light absorption: Max. 2270 Å, infl. 2340 and 2540 Å; ε = 13,000, 10,700, and 2000 respectively. Attempted purification by chromatography on alumina caused decomposition to *trans*-dicyanostilbene, m. p. 160°. Alternative preparations employing potassium thiocyanate or acetone gave essentially similar results.

αβ-Diphenylsuccinodinitrile.—*trans*-α-Cyanostilbene (*cis*-α-phenylcinnamonitrile) was prepared by Wawzonek and Smolin's method.[47] Light absorption: see Table 2. It was converted into diphenylsuccinodinitrile [48] which by repeated crystallisation was separated into the *meso*-compound, m. p. 225° (Chalanay and Knoevenagel [10] give m. p. 240° for the *meso*-compound completely freed from the racemic form) ($\lambda_{max.}$ 2510, 2570, and 2640 Å, ε = 460, 550, and 370), and a small amount of the racemic form, m. p. 160°.

trans-*αβ-Dicyanostilbene* (*Diphenylfumarodinitrile*).—(*a*) The following method was developed from that indicated by Banfield.[4a] α-Cyanobenzyl bromide (75 g., 50 ml.) was added to a mixture of ethanol (300 ml.) and aqueous ammonia (300 ml.; *d* 0·880). The mixture was set aside for 5 days, then poured into water (1·5 l.). After 1½ hr., the *trans*-αβ-dicyanostilbene (30 g., 35%) was filtered off. Recrystallisation successively from benzene, ethanol, and carbon tetrachloride gave needles, m. p. 161° (von Braun [5] gives m. p. 160°) (Found: C, 83·7; H, 4·5; N, 12·1. Calc. for $C_{16}H_{10}N_2$: C, 83·5; H, 4·4; N, 12·2%). Light absorption: see Table 2. The *X*-ray crystal structure is described elsewhere.[30, 35] The infrared spectrum in Nujol

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[46] Wheland, " Resonance in Organic Chemistry," John Wiley, New York, 1955 p. 389.

[47] Wawzonek and Smolin, *Org. Synth.*, 1949, **29**, 83.

[48] Lapworth and MacRae, *J.*, 1922, **121**, 1699.

suspension showed bands at 2240 (w, C⋮N); 754 (s, Ph); 717 (vw, Ph) and 690 (s, Ph) cm.$^{-1}$, but no bands in the 6 μ region (C⁚C) (w = weak, s = strong, vw = very weak).

(*b*) To a solution of α-cyanobenzyl thiocyanate (40 g.) in ethanol (250 ml.) was added powdered potassium hydroxide (13 g.) or alternatively aqueous ammonia (105 ml.; *d* 0·880). Heat was evolved and the mixture was cooled to room temperature, stirred, and set aside for 0·5 hr. The green-blue precipitate was filtered off, washed with ice-cold ethanol, and on crystallisation from ethanol afforded *trans*-αβ-dicyanostilbene, (14 g., 52%), m. p. 160°. The use of crude α-cyanobenzyl thiocyanate gave material that required numerous crystallisations.

(*c*) A solution of α-cyanobenzyl toluene-*p*-sulphonate (10 g.) in acetone (30 ml) was added to aqueous ammonia (30 ml; *d* 0·880) and the mixture set aside for a week, then poured into water (300 ml.). The precipitate (0·5 g.) of dicyanostilbene was filtered off, crystallised from ethanol, and had m. p. and mixed m. p. 160°. Varying the conditions of the reaction or using potassium hydroxide or sodium hydrogen carbonate did not improve the yield.

(*d*) *meso*-Diphenylsuccinodinitrile (10 g.) was heated with palladium black [49] (0·5 g.) at 250°/100 mm. for 4 hr. in a slow stream of carbon dioxide. Some liquid (*ca.* 2 ml.) distilled. Fractional crystallisation of the residue from acetic acid (charcoal) gave dicyanostilbene (0·5 g., 5%) and unchanged diphenylsuccinodinitrile (7·6 g., 76%). Bergdolt and Knoevenagel [24] reported a 20% yield of dicyanostilbene. Attempts to increase the yield by the addition of a hydrogen acceptor (cf. Braude, Linstead, *et al.*[24]) such as *p*-nitrotoluene, or *o*-, *m*-, and *p*-nitrobenzoic acid were unsuccessful.

3-*Cyano*-2-*phenylindenone* (I; R = CN).—(*a*) *trans*-αβ-Dicyanostilbene (0·95 g.) was dissolved in cold concentrated sulphuric acid (60 ml.), set aside for 18 hr., then poured into water (500 ml.) and stirred for a few minutes. The red precipitate was filtered off, washed with water, and heated with 2N-sodium hydroxide on the steam-bath for 10 min. The solid was filtered off, washed with water, dried, and chromatographed on alumina in benzene solution. The main product, 3-*cyano*-2-*phenylindenone* (I; R = CN) (0·93 g., 97%), after rechromatography, crystallised from ethanol, benzene, acetic acid, or dioxan in red needles, m. p. 145° (Found: C, 82·7; H, 4·3; N, 6·1. $C_{16}H_9ON$ requires C, 83·1; H, 3·9; N, 6·1%). Light absorption: see Table 3. The material is unstable if kept for several weeks. A small amount of 3-carbamoyl-2-phenylindenone (0·03 g., 3%) was also obtained. In some preparations it was difficult to free the products from traces of unchanged *trans*-αβ-dicyanostilbene; but this could be obviated by heating the sulphuric acid solution on the steam-bath for 15 min. before dilution: both 3-cyano-2-phenylindenone (50%) and 3-carbamoyl-2-phenylindenone (46%) were then separated by chromatography.

The 2 : 4-*dinitrophenylhydrazone* crystallised from dioxan in small orange prisms, m. p. 277—279° (Found: C, 64·1; H, 3·3; N, 16·9. $C_{22}H_{13}O_4N_5$ requires C, 64·1; H, 3·2; N, 17·0%). Light absorption: see Table 3. It gave an intense blue colour with alcoholic alkali.

(*b*) 3-Carbamoyl-2-phenylindenone (I; R = CO·NH$_2$) (2·5 g.) was heated in benzene (500 ml.) with phosphoric oxide (16 g.) for 7 hr. with occasional shaking. After cooling, the phosphoric oxide was filtered off and digested with hot benzene and chloroform. The combined filtrates were chromatographed on alumina and 3-cyano-2-phenylindenone (1·7 g., 72%) was obtained.

3-*Carbamoyl*-2-*phenylindenone* (I; R = CO·NH$_2$).—(*a*) *trans*-αβ-Dicyanostilbene (1 g.) was dissolved in concentrated sulphuric acid (60 ml.) and, after 24 hr., was heated on the steam-bath for 25 min. The mixture was allowed to cool to room temperature before being poured into water (500 ml.). The precipitate was filtered off and washed with 2N-sodium hydroxide and with water. 3-*Carbamoyl*-2-*phenylindenone* (1 g., 92%) was obtained as orange needles (from ethanol, acetic acid, or ethanol–dioxan), m. p. 225—227° (Found: C, 77·2; H, 4·6; N, 5·7. $C_{16}H_{11}O_2N$ requires C, 77·1; H, 4·5; N, 5·6%). Light absorption: see Table 3. The 2 : 4-*dinitrophenylhydrazone*, prepared in dioxan–ethanol containing sulphuric acid, crystallised from acetic acid or dioxan in red hexagonal plates, m. p. 281—283° (Found: C, 61·8; H, 3·5; N, 16·2. $C_{22}H_{15}O_5N_5$ requires C, 61·5; H, 3·5; N, 16·3%). Light absorption: see Table 3. It gave an intense purple colour with alcoholic alkali.

(*b*) Hydrolysis of 3-cyano-2-phenylindenone under the conditions described under (*a*) also gave 3-carbamoyl-2-phenylindenone (92%).

Attempts to hydrolyse the amide to the corresponding acid with alcoholic potassium hydroxide, constant-boiling hydrochloric acid, or nitrous acid were unsuccessful.

3-*Cyano*-2-*phenylindanone* (III; R = CN).—3-Cyano-2-phenylindenone (I; R = CN)

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[49] Wieland, *Ber.*, 1912, **45**, 484.

(0·5 g.) in ethyl acetate (60 ml.) absorbed 1·1 mols. of hydrogen when shaken with palladium–charcoal (5%). The hydrogen was replaced by oxygen-free nitrogen and the catalyst removed. After distillation of the ethyl acetate, the residue was crystallised as rapidly as possible from ether–methanol under nitrogen several times and afforded *3-cyano-2-phenylindanone* (*ca.* 70 mg.) as colourless needles, m. p. 81—83° (Found: C, 81·8; H, 4·9; N, 6·1. $C_{16}H_{11}ON$ requires C, 82·4; H, 4·8; N, 6·0%). Light absorption: see Table 3. When a solution in ethanol was exposed to air for 3 hr., complete oxidation occurred to 3-cyano-2-phenylindenone, m. p. and mixed m. p. 143°. A colourless solution of 3-cyano-2-phenylindanone in methanol, on addition of 2N-sodium hydroxide, gave a purple colour, which was discharged by the further addition of acetic acid.

3-Carbamoyl-2-phenylindanone (III; R = CO·NH$_2$).—3-Carbamoyl-2-phenylindenone (1 g.) in ethyl acetate (200 ml.) absorbed 1 mole of hydrogen when shaken with palladium–charcoal (5%). The product, after crystallisation from aqueous methanol containing acetic acid (0·5%), was *3-carbamoyl-2-phenylindanone*, colourless needles, m. p. 165° (Found: C, 75·9; H, 5·2; N, 5·6. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2; N, 5·6%). Light absorption: see Table 3. No coloration was observed on drawing air through a neutral ethanolic solution of 3-carbamoyl-2-phenylindanone for 24 hr.

Oxidation of 3-Carbamido-2-phenylindenone (I; R = CO·NH$_2$).—An aqueous solution (600 ml.) of potassium permanganate (25 g.) was added in 5 portions during 2 hr. to a stirred suspension of 3-carbamoyl-2-phenylindenone (6·5 g.) in 5% aqueous potassium hydroxide (100 ml.) at 100°. Heating was continued for a further hour. After cooling and passage of sulphur dioxide into the mixture the solution was acidified with concentrated hydrochloric acid and was extracted with ether continuously for 2 days. On concentration of the ether solution to 150 ml., phthalic acid (2·02 g.; m. p. 180°) crystallised. This on recrystallisation from water had m. p. and mixed m. p. 210—214° (2 g., 52%), and was converted by heat into the anhydride, m. p. and mixed m. p. 130° after vacuum sublimation and crystallisation from benzene. Evaporation of the residual ether solution gave benzoic acid (3·21 g., 98%), m. p. and mixed m. p. 121° (from water).

trans-trans-*Sorbonitrile.*—This was prepared by the method of Doebner and Wolff[50] in 20% overall yield from sorbic acid ($\lambda_{\max.}$ 2540 Å., ε 27,000) *via* the amide (m. p. 167—170°; $\lambda_{\max.}$ 2540 Å, ε = 27,000) and had b. p. 72—74°/16 mm., n_D^{20} 1·5152 (Bruylants and Rowies[51] give b. p. 78°/20 mm., n_D^{20} 1·5137). Light absorption: Max. 2540 Å, ε 30,000.

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[50] Doebner and Wolff, *Ber.*, 1901, **34**, 2221.

[51] Bruylants and Rowies, *Bull. Soc. chim. Belges*, 1950, **59**, 244.