

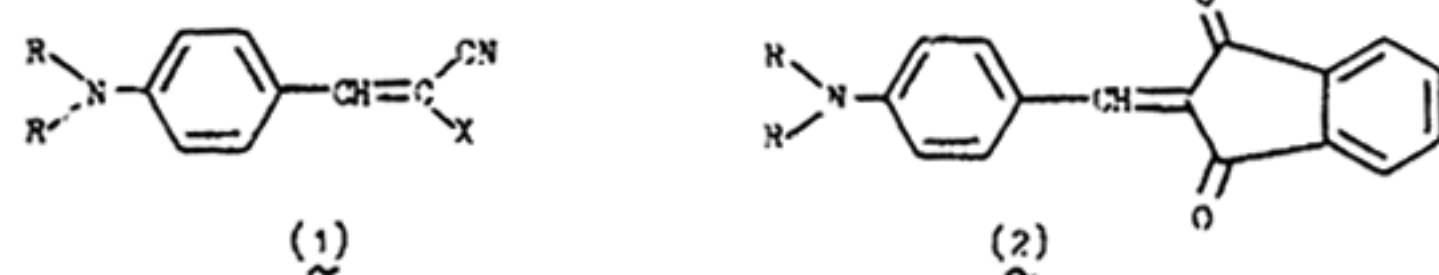
Light Absorption and Emission Properties of Cyanovinyl-substituted Dimethoxybenzenes

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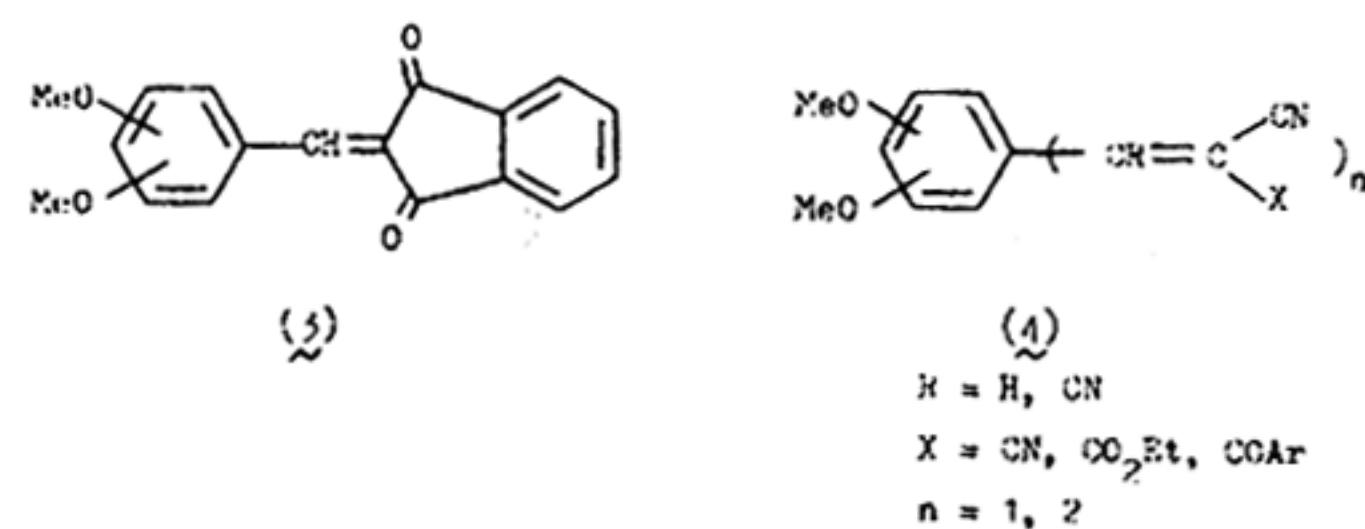
Synthetic routes to a range of dyes based on cyanovinyl-substituted dimethoxybenzenes are described. The light absorption and fluorescence properties of these compounds in fluid solution at room temperature are discussed.

Dyes based on cyanovinyl-substituted aromatic systems containing amino auxochromes (e.g. 1, X = CN, CO₂Et) are well known, and are of technological value as textile dyes.¹ Recently it was shown that replacement of the amino group in related benzylideneindan-1,3-dione dyes (2) by two methoxy groups, as in (3), leads to dyes with enhanced fluorescence properties and improved resistance to photochemical fading.² It was thus of interest to examine related cyanovinyl-substituted dimethoxybenzenes (4).



¹ J.M. Straley, 'Chemistry of the Synthetic Dyes,' Vol. 3, ed. K. Venkataraman, Academic Press, New York, 1970, pp. 449 - 454.

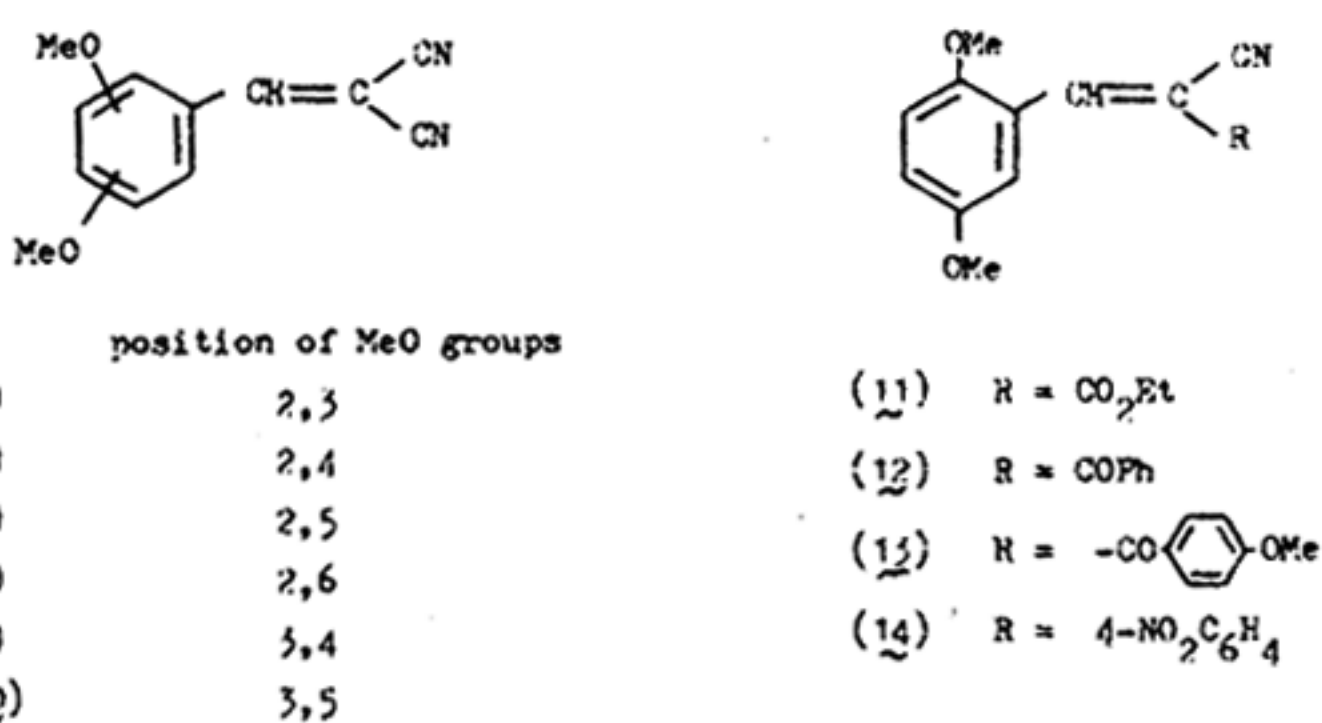
² K.Y. Chu and J. Griffiths, *J. Appl. Chem. Biotech.*, 1978, 28, 144.



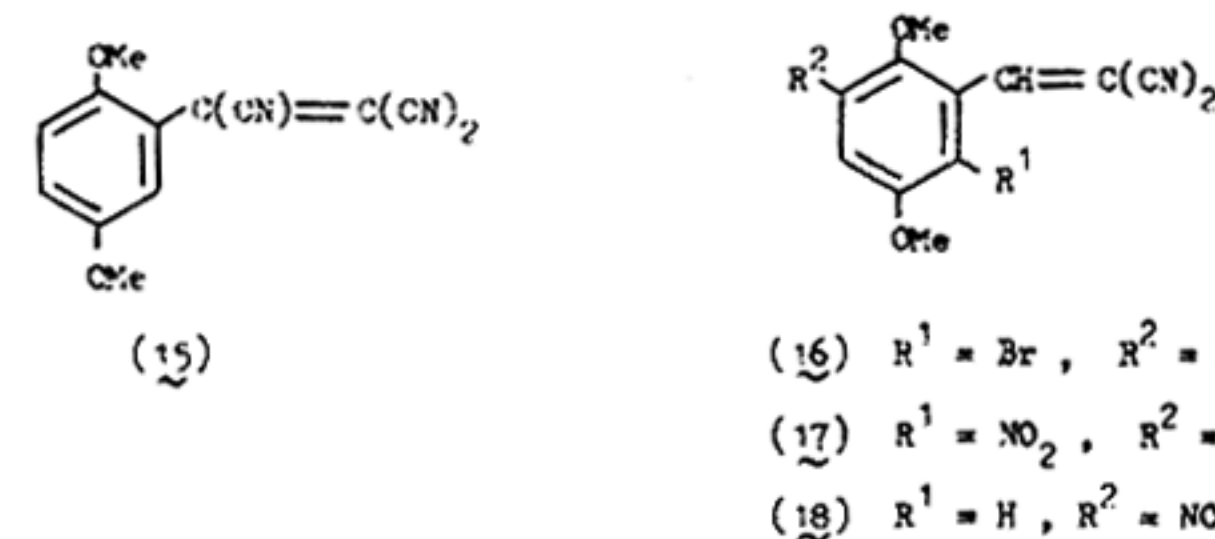
Discussion

Synthesis of Cyanovinyl-substituted Dimethoxybenzenes

In the first series of compounds studied, the 2,2'-dicyanovinyl group was used as the electron acceptor residue, and all possible orientations of the two methoxy groups were considered. The six isomers (5) - (10) were prepared in high yields by condensation of the appropriate dimethoxybenzaldehyde with malononitrile in ethanol in the presence of a catalytic amount of piperidine. 2,5-Dimethoxybenzaldehyde was prepared most conveniently by the Reimer-Tiemann reaction with 4-methoxyphenol, followed by methylation. Other aldehydes were prepared by literature methods.



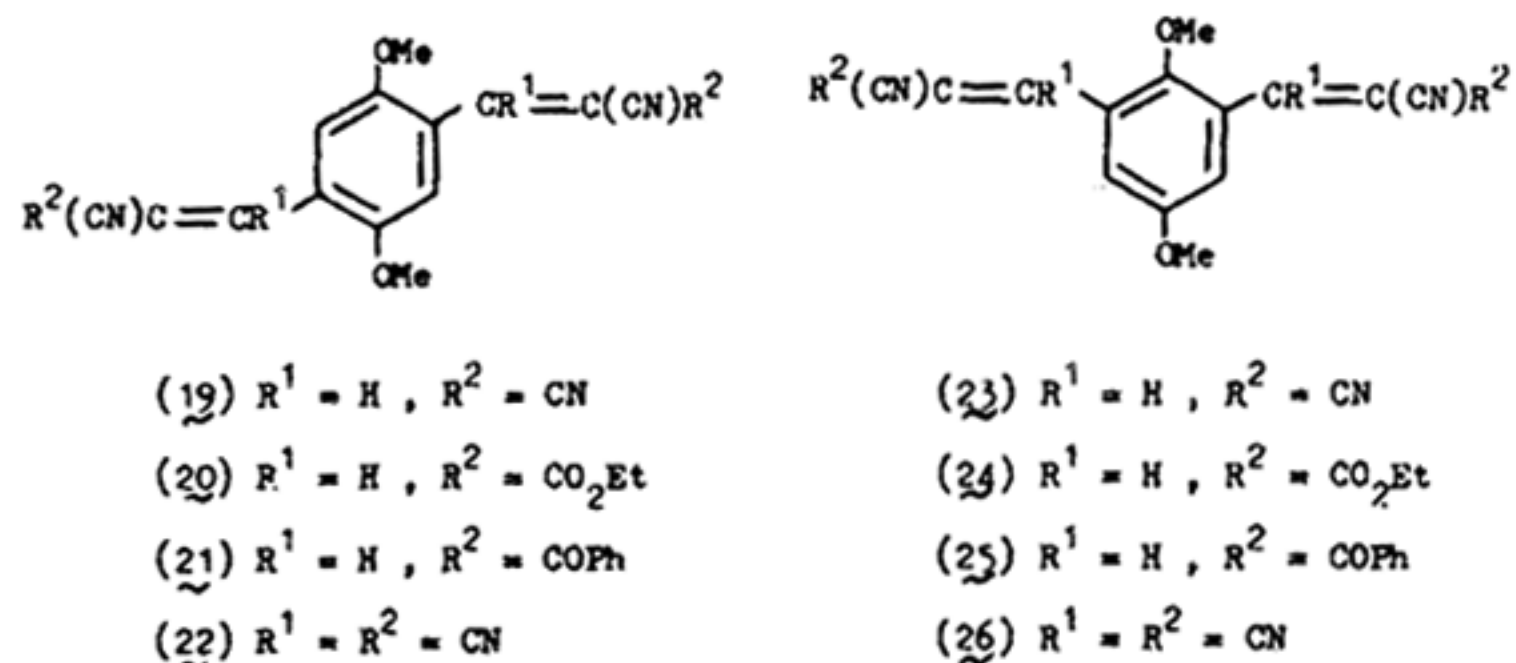
Derivatives (11) - (14) were prepared by condensing 2,5-dimethoxybenzaldehyde with the appropriate active methylene compound in the usual way. The tricyanovinyl derivative (15) was prepared in two stages from (7) by addition of cyanide ion to the double bond, followed by oxidation to (15) with lead (IV) acetate.



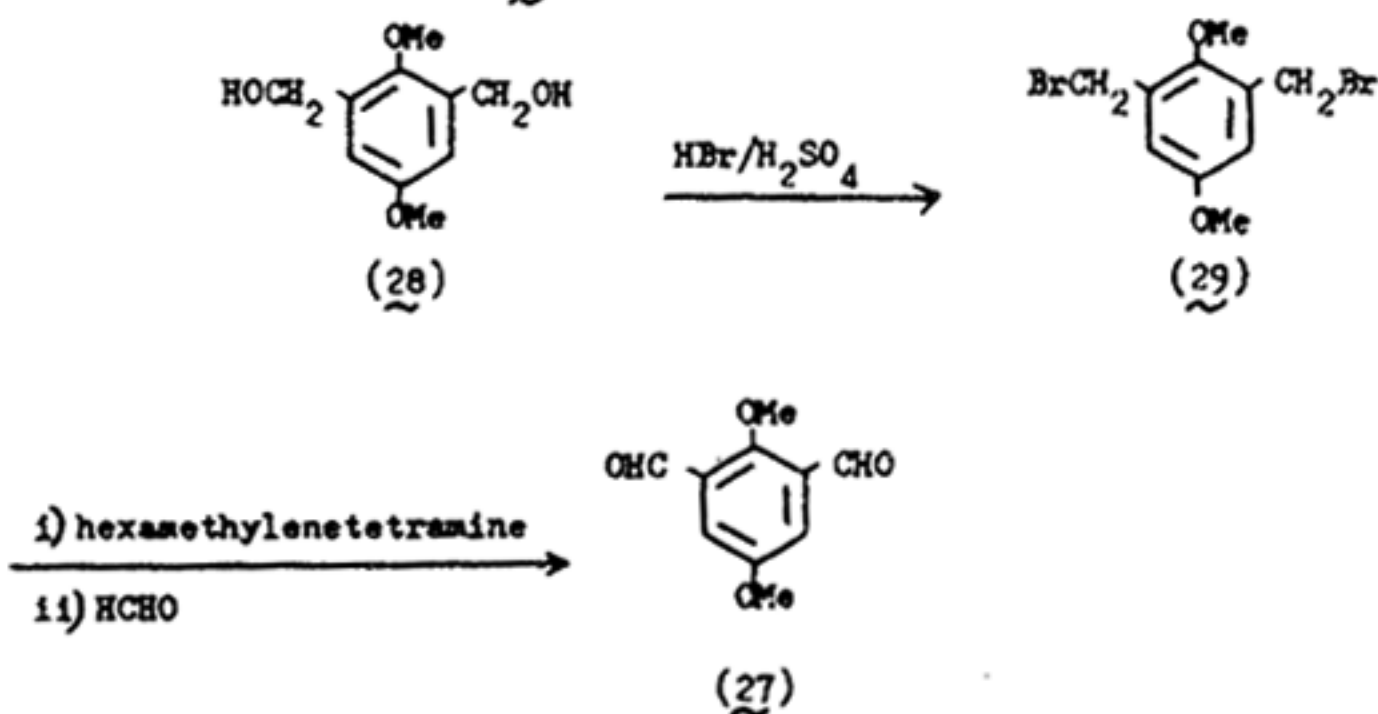
Bromination of 2,5-dimethoxybenzaldehyde gave predominantly the 6-bromo-derivative,³ which condensed smoothly with malononitrile to give (16). The same compound could also be prepared by bromination of (7) in acetic acid. Nitration of 2,5-dimethoxybenzaldehyde at room temperature gave mainly the 6-nitro-derivative together with a small amount of the 3-nitro-isomer.³ The 3-nitro-compound was best prepared by methylation of 2-hydroxy-5-methoxy-3-nitrobenzaldehyde, the latter being obtained by nitration of 2-hydroxy-5-methoxybenzaldehyde using a modification of the procedure of Rubenstein.³ The 6- and 3-nitro-derivatives afforded (17) and (18) respectively on condensation with malononitrile.

To examine the effect of two cyanovinyl acceptor groups on the colour and fluorescence of these chromogens, the derivatives (19) - (26) were prepared.

³ L. Rubenstein, *J. Chem. Soc.*, 1925, 1998.



3,6-Dimethoxyphthalaldehyde was prepared by the method of Wood *et al.*,⁴ and a similar procedure was adopted for 2,5-dimethoxyisophthalaldehyde (27) (Scheme). In the latter case, however, 2,6-bis(hydroxymethyl)-1,4-dimethoxybenzene (28)⁵ was used to prepare the requisite bromomethyl derivative (29). Sommelet reaction of (29) gave the dialdehyde in 31% yield.



Scheme

⁴ J.H. Wood, C.C. Tung, M.A. Perry and R.E. Gibson, *J. Amer. Chem. Soc.*, 1950, 72, 2992.

⁵ W.J. Moran, E.C. Schreiber, E. Engel, D.C. Behn and J.L. Yamine, *J. Amer. Chem. Soc.*, 1952, 74, 127.

Condensation of the dimethoxydialdehydes with two equivalents of the appropriate active methylene compounds gave the bis(cyanovinyl)-derivatives (19) - (21) and (23) - (25) in good yields.

The bis(tricyanovinyl) compounds (22) and (26) were prepared from the bis(dicyanovinyl) compounds (19) and (23) respectively by successive cyanide addition and oxidation.

Electronic Absorption Spectra

The λ_{max} and ϵ_{max} values for the longest wavelength absorption bands of derivatives (5) - (26) are summarised in Table 1 for the solvents acetone and cyclohexane. The cyanovinyl dimethoxybenzenes are typical donor-acceptor chromogens,⁶ the longest wavelength $\pi \rightarrow \pi^*$ transition corresponding to electron density migration from the methoxy groups to the cyanovinyl acceptor residue(s). The increase in dipole moment in the excited state is indicated by the positive solvatochromism observed when acetone and cyclohexane are used as solvents.

The influences of substituents and substitution pattern on the absorption spectra are most conveniently discussed in terms of three variables: (a) the position of the methoxy groups with respect to the acceptor residue, (b) the nature of the acceptor residue, and (c) the position of the acceptor residues when two of these are present.

(a) The effects of methoxy-group substitution pattern

The six possible isomers for a benzene system with two methoxy groups and a single electron acceptor group are represented by the derivatives (5) - (10). As can be seen from the data of Table 1, certain of these derivatives show two overlapping bands in cyclohexane, which may be due to two distinct electronic transitions, or to emerging vibrational fine

structure. In acetone the band systems are broadened and only one maximum is observed. The 2,5-dimethoxy-derivative (7) is the only intensely coloured member of the series. Using the wavelength values observed in acetone solution, the experimental wavelength order is 2,5,7,2,4,7,3,4 > 2,6,7,3,5 > 2,3-diMeO, which is the same as that observed for the 2-dimethoxybenzylideneindan-1,3-dione dyes.² The observation that the 2,5-dimethoxy-derivative is the most bathochromic isomer is in accordance with Kauffmann's 'distribution of auxochromes' rule.⁷ The low absorption intensity of this compound ($\epsilon_{max} = 9400 \text{ l mol}^{-1} \text{ cm}^{-1}$ in C_6H_{12}) appears to be characteristic for this substitution pattern.² The dicyanovinyl acceptor group is not as bathochromic as the indane-1,3-dione residue, and gives rise to lower absorption intensities.

The light absorption characteristics of derivatives (5) - (10) were analysed with the aid of PPP-MO calculations, the results of which are summarised in Table 1. Single long-wavelength transitions were predicted for the 2,4-, 2,5- and 3,4-dimethoxy-derivatives, the agreement between observed and calculated λ_{max} values and relative intensities being quite good. The two closely spaced maxima observed for the 3,4-dimethoxy compound (364, 382 nm; $\epsilon_{max} = 21200$ and 19000) can thus be attributed to vibrational fine structure.

Absolute agreement between the observed and calculated λ_{max} values for the other derivatives (2,3-, 2,6- and 3,5-diMeO) was less

² K.Y. Chu and J. Griffiths, *J. Appl. Chem. Biotech.*, 1978, 28, 144.

⁷ H. Kauffmann, 'Beziehungen zwischen physikalischen Eigenschaften und chemischen Konstitution,' Enke, Stuttgart, 1920; R. Wizinger, *Chimia*, 1965, 19, 339.

Table 1 Electronic absorption spectroscopic properties of derivatives (5)-(26)

Compound	λ_{max} acetone /nm	$\lambda_{max}^{calc.}$ C_6H_{12} /nm	$\epsilon_{max}^{calc.}$ C_6H_{12} / $10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$	$\lambda_{max}^{calc.}$ /nm	$f^{calc.}$
(5)	- ^a	312 (348g)	20.8 (4.1)	340 (377)	0.63 (0.72)
(6)	380	364	23.9	370	0.82
(7)	409	404	9.4	401	0.46
(8)	338	326 (349g)	18.7 (10.2)	359 (405)	0.54 (0.14)
(9)	374	364	21.2	372	0.64
(10)	332	320 (331) (360g)	19.5 (19.3) (3.6)	337 (376)	0.75 (0.02)
(11)	396	387	5.9	-	-
(12)	403	370	5.0	-	-
(13)	396	381	6.1	-	-
(14)	397	394	8.4	-	-
(15)	462	452	2.7	492	0.28
(16)	405	399	13.2	-	-
(17)	388	377	4.6	-	-
(18)	373	372	6.3	-	-
(19)	454	455	17.8	438	1.05
(20)	443	446	17.7	-	-
(21)	446	447	17.6	-	-
(22)	470	465	5.8	507	0.66
(23)	394	396	8.6	415	0.81
(24)	383	387	7.9	-	-
(25)	384	392	9.4	-	-
(26)	410	412	3.5	489	0.50

^a Secondary electronic absorption bands in parentheses; shoulders indicated by g.
^b Oscillator strength calculated by the PPP-MO method assuming a planar structure.
^c Band maximum obscured by solvent absorption.

satisfactory. The poorer agreement in the 2,3- and 2,6-isomers may be due to steric effects, causing the cyanovinyl residue to rotate out of full conjugation with the ring and thus inducing a hypsochromic shift not allowed for in the calculations. For all three compounds, the PPP method predicts two well-separated long wavelength transitions, the more bathochromic one being significantly lower in intensity than the other. Although two distinct maxima could not be distinguished experimentally, the highly unsymmetrical nature of the absorption bands of (5), (8) and (10) is in general agreement with the theoretical predictions.

The donor-acceptor character of the absorption bands of the derivatives (5) - (10) was confirmed by the calculated π -electron density changes between the ground state and the first excited (π, π^*)¹ state. Typical results are shown for the 2,5-dimethoxy-compound (7) in Fig. 1. Particularly interesting is the prediction of a very large electron density build-up at the 1'-position of the dicyanovinyl group. Thus one might expect an electron withdrawing group at this position to exert a strong bathochromic effect, and this is observed experimentally for the 2,5-dimethoxy-tricyanovinyl-analogue (15): $\lambda_{max}(7) = 409 \text{ nm}$; $\lambda_{max}(15) = 462 \text{ nm}$, both measured in acetone.

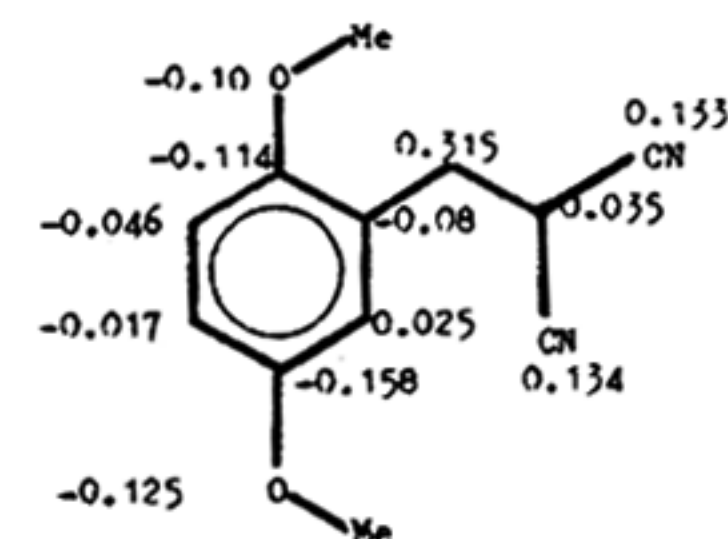


Fig. 1 π -Electron density changes for the first absorption band of 1-(2,2-dicyanovinyl)-2,5-dimethoxybenzene (7), calculated by the PPP method.

It can be seen from Fig. 1 that electron density changes at unsubstituted positions of the ring are small, and thus electron withdrawing groups at these positions would be expected to have only a small effect on λ_{max} . In fact, the nitro group at position 3 or 6 exerts a large hypsochromic effect (cf. (7), (17) and (18), Table 1). This is most certainly due to steric crowding, as indicated by the much lower absorption intensities of (17) and (18). The bromine atom in the compound (16) has a curious effect, in that the absorption band of (7) is displaced only slightly, but the intensity increases by about 40%. This unusual effect may be an example of 'sterically enhanced resonance', previously noted for ground state reactions of methoxy-substituted benzenes.⁸ Thus a bulky ortho substituent (here the bromine atom) can reduce the conformational mobility of a methoxy group and increase overlap between the oxygen lone pair orbital and the π -electron system of the benzene ring. Increased overlap would manifest itself as increased absorption intensity. The preferred conformation in (16) is shown in Fig. 2.

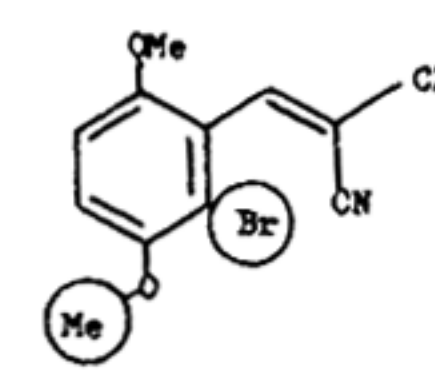


Fig. 2 Preferred conformation of (16), leading to sterically enhanced resonance between the 5-methoxy group and the benzene ring.

⁸ Y. Ballah and V.M. Kanagasabapathy, *Tetrahedron*, 1978, 34, 3611; K. Ganapathy and P. Jayagandhi, *J. Indian Chem. Soc.*, 1979, 56, 1036.

(b) The effects of modified cyanovinyl groups on absorption spectra
 Any factor enhancing the electron withdrawing strength of the acceptor residue in a moderately polar donor-acceptor chromogen will cause a bathochromic shift of the first absorption band. This is well demonstrated by comparison of the λ_{max} values of (7) and the derivatives (11) - (15) (Table 1). Thus replacing one of the cyano groups in the dicyanovinyl residue by carboethoxy, 4-nitrophenyl or an aroyl group causes a small hypsochromic shift, whereas introducing a third cyano group in the 1'-position (dye (15)) causes a large bathochromic shift. The modified dyes (11) - (15) also show a reduction in intensity, which is probably caused by increased steric crowding in these molecules. The tricyanovinyl-derivative (15) was examined by the PPP-MO method, assuming a planar structure. Although a large bathochromic shift was predicted for this compound, this was considerably overestimated (λ_{max} (calc.) = 497 nm; λ_{max} (C₆H₁₂) = 452 nm), presumably because of deviation from planarity.

(c) The effect of two cyanovinyl groups on absorption spectra
 In general, multiplication of the number of acceptor groups in a donor-acceptor chromogen results in a bathochromic shift of the first absorption band, provided such a modification does not introduce additional steric crowding. The magnitude of the shift is critically dependent on the relative positions of the acceptor groups in the chromogen.⁹ To study such effects in the present systems, the 2,5-dimethoxy substitution pattern was retained, and the cyanovinyl residues were situated either *para* or *meta* to each other, as in dyes (19) - (20) and (23) - (26) respectively.

⁹ J.Griffiths, M. Lockwood and B. Roespekar, *J. C. S. Perkin II*, 1977, 1608.

Attempts to prepare related compounds with the cyanovinyl groups *ortho* to each other were unsuccessful because of difficulties encountered in preparing 3,6-dimethoxyphthalaldehyde.

In the series (19) - (22), steric crowding should be small in comparison with the derivatives (23) - (26), thus simplifying the interpretation of substituent effects. As can be seen from Table 1, the second cyanovinyl group, situated *para* to the first, causes a bathochromic shift of about 45 nm, with the notable exception of dye (22). The resultant dyes are brilliant orange in colour. This effect is well predicted by the PPP-MO method (e.g. the shift in λ_{max} for dye (19) relative to (7) is 51 nm in cyclohexane, and the calculated shift is 37 nm). In addition, the bis(cyanovinyl) compounds show approximately double the absorption intensity of the corresponding cyanovinyl compounds, and this is also well predicted for (19) and (7).

The solvatochromic properties of the cyanovinyl and bis(cyanovinyl) compounds also differ, in that the former show a significant bathochromic shift of the absorption band between cyclohexane and acetone as solvents (positive solvatochromism), whereas the latter show a smaller negative solvatochromism in the same solvents. This reflects the much smaller dipole moment change between the ground and excited states of the bis(cyanovinyl) derivatives, which is not unexpected on structural grounds.

The tricyanovinyl derivative (22) differs from the other members of the series in that the bathochromic shift resulting from the second acceptor residue is only 13 nm in cyclohexane. The doubling of the intensity precludes steric crowding as the cause of this effect, but MO calculations showed that the smaller shift than expected was due to the electronic characteristics of the tricyanovinyl residue. Thus the PPP method predicted only a small shift of 15 nm, but with a large intensity increase (Table 1).

Steric crowding is likely to be much more pronounced in the derivatives (23) - (26), where one of the methoxy groups is situated between two cyanovinyl residues, and this was confirmed by comparison of the calculated and experimental spectroscopic properties of parent compound (23). Thus whereas the PPP method predicted a λ_{max} of 415 nm and an intensity some 50% higher than for (7), assuming a planar geometry, the experimental results showed a λ_{max} of 396 nm (in cyclohexane) and a decrease in intensity relative to (7) (Table 1). The low absorption intensity indicates that the chromogen of (23) is non-planar. The greater steric requirement of the tricyanovinyl group can be seen by comparison of the absorption maxima of dyes (26) and (15) (Table 1). Dye (26) with two such groups absorbs 40 nm to shorter wavelengths than (15) with only one tricyanovinyl group, and the absorption intensity is of the same order as that of (15), although MO calculations would indicate almost double the intensity if (26) were planar.

Fluorescence Properties

When dissolved in poly(ethylene terephthalate), all the derivatives (5) - (26) showed fluorescence in ultra-violet light, ranging from intense (e.g. (7)) to very weak (e.g. (18)), and the colours ranging from blue to yellow-green. In many cases the fluorescent effect was perceptible in visible light, and imparted a characteristic brilliance to the colour of the dyed substrate. Related dyes containing amino-auxochromes (e.g. (1)) do not show this effect, and the enhanced fluorescence may be attributed to the methoxy groups peculiar to (5) - (26). In fluid solution at room temperatures, many of the methoxy dyes show no or much-reduced fluorescence. The fluorescence spectra of the more efficient fluorescing dyes were measured in aerobic ethanolic solution at room temperature, using monochromatic

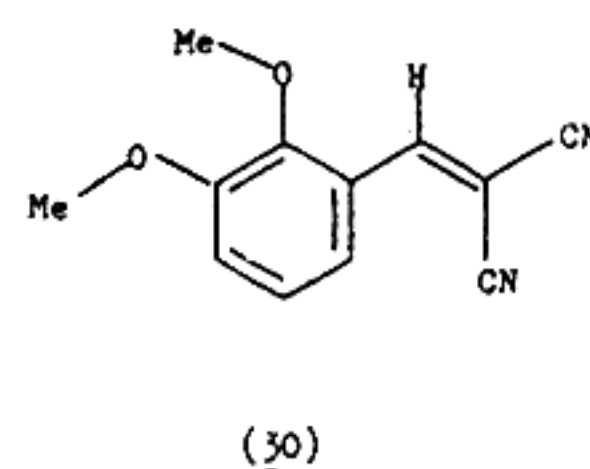
exciting radiation corresponding to the absorption maximum of the dye. Emission maxima and fluorescence quantum yields are summarised in Table 2.

Table 2 Fluorescence properties of cyanovinyl-substituted dimethoxybenzenes

Compound	Cyanovinyl group	MeO groups	λ_{ex}^a /nm	λ_r^b /nm	ϕ_f^c
(5)	-CH=C(CN) ₂	2,5	317	525	0.56
(7)	-CH=C(CN) ₂	2,5	411	520	0.06
(10)	-CH=C(CN) ₂	3,5	324	515	0.03
(11)	-CH=C(CN)CO ₂ Et	2,5	400	515	0.04
(16)	-CH=C(CN) ₂	2,5; 6-Br	405	510	0.03
(19)	1,4-bis -CH=C(CN) ₂	2,5	460	565	0.32
(20)	1,4-bis -CH=C(CN)CO ₂ Et	2,5	460	550	0.53
(21)	1,4-bis -CH=C(CN)CO ₂ Ph	2,5	444	580	0.11
(22)	1,4-bis -C(CN)=C(CN) ₂	2,5	330	500	0.01
(23)	1,3-bis -CH=C(CN) ₂	2,5	385	515	0.08
(24)	1,3-bis -CH=C(CN)CO ₂ Et	2,5	388	510	0.04

^a Excitation wavelength.
^b Fluorescence maximum in absolute ethanol at room temperature.
^c Fluorescence quantum yield in absolute ethanol at room temperature, reference standard quinine bisulphate in 0.05 M H₂SO₄.

Of the series (5) - (10) containing one cyanovinyl group, the 2,5-dimethoxydicyanovinyl compound (5) had the highest fluorescence quantum yield (0.56), the remaining members having quantum yields roughly an order of magnitude lower. The reasons for the greater fluorescence efficiency of the 2,5-dimethoxy compound are not obvious, although it may be connected with the greater steric crowding present in the molecule. This particular compound has a methoxy group flanked by two bulky groups, and free rotation of the former will be effectively restricted. The more favourable conformation shown in structure (30) may be rigidly maintained, thus minimising the rate of internal conversion from the S₁ state and enhancing the fluorescence efficiency.



The differences between the fluorescence efficiencies of (7), (10), (11) and (16) are relatively small and cannot be interpreted in simple steric terms. No correlation was found between the quantum efficiency and the singlet-triplet splitting energies calculated by the PPP method. The bromine atom in (16) may exert a heavy atom effect, thus accounting for the lower fluorescence yield when compared with the non-brominated dye (7). In fluid solution, neither the nitro-substituted derivatives (14), (17), and (18) nor the 2'-aroyl-2'-cyanovinyl derivatives (12) and (13) showed any detectable fluorescence. In the former cases the well known quenching effect of nitro groups on fluorescence is presumably involved,¹⁰ whereas

¹⁰ E.L. Wehry and L.B. Rogers, 'Fluorescence and Phosphorescence Analysis', ed. D.M. Hercules, Interscience, New York, 1966, pp. 81 - 149.

with the latter dyes the presence of n, π* states associated with the carbonyl groups could give rise to rapid deactivation of the excited state by intersystem crossing and internal conversion.

Of the dyes (19) - (26), which contain two cyanovinyl acceptor groups, only the derivatives (25) and (26) showed no significant fluorescence at room temperature in ethanol, and these both had the acceptor groups *meta* to each other. This suggests that steric crowding in the *meta* series adversely affects fluorescence efficiency, and this is confirmed by the low quantum yields found for the other *meta* dyes (23) and (24) (0.08 and 0.04 respectively). In contrast, the *para* series of dyes (19), (20) and (21) had quantum yields of 0.32, 0.53 and 0.11 respectively. The remaining *para* dye (22) is exceptional, in that it has a very low fluorescence efficiency ($\phi_f = 0.01$) even though the cyanovinyl acceptor groups are mutually *para*. The additional steric crowding peculiar to the tricyanovinyl groups present in (22) would account for this apparent anomaly.

The fluorescence properties of the various dyes (5) - (26) in polymeric substrates are more marked, and the compounds (7) and (11) - (26) in particular provide attractive shades ranging from greenish yellow to intense orange, the colours appearing characteristically bright because of the fluorescence effect. The resistance of the dyes to photochemical fading was examined, and in general they showed outstanding photochemical stability, with an obvious correlation between the fluorescence efficiency and fading resistance. Compounds of this type may thus be of value as textile dyes for special applications, or as organic solvent-soluble laser dyes.

Experimental

Electronic absorption spectra were recorded with a Pye-Unicam SP800 spectrophotometer. Fluorescence emission spectra were recorded with a model SP4 luminescence spectrometer (Applied Photophysics Ltd.)

Fluorescence Measurements A solution of the cyanovinyl compound in absolute ethanol was prepared with an absorbance of 0.05 at the wavelength maximum of the first absorption band. Excitation at the λ_{max} value was carried out with monochromatic radiation from a 'chopped' xenon source. The transmitted exciting light was monitored with a rhodamine B quantum counter and reference photomultiplier. The emitted light was viewed at right angles to the fluorescence cell, using a monochromator and photomultiplier. The emission signal (chopper out) was accumulated alternately with the dark signal (chopper in) in separate registers for a preset accumulated signal on the reference photomultiplier. By employing a quantum counter and reference photomultiplier to monitor the transmitted exciting light, the excitation wavelength can be varied provided the absorbance of the sample is always the same. This is because the counting on the emission photomultiplier will be stopped when a preset number of quanta has been absorbed by the sample. The instrument thus compensates automatically for variation in the light intensity, changes in excitation wavelength, and changes in the emission photomultiplier dark current caused by changes in counting times.

A solution of quinine bisulphate in 0.05 M sulphuric acid, with an absorbance of 0.05 at 360 nm, was used as fluorescence reference standard (fluorescence quantum yield, $\phi_f = 0.51$),¹¹ and the fluorescence quantum yield for the sample, ϕ_f , was calculated from the expression:

$$\phi_f = \frac{\phi_q \cdot A_D \cdot n_{H_2O}^2}{A_q \cdot n_{EtOH}^2}$$

where A_D and A_q are the areas of the emission curves for the cyanovinyl dye and quinine bisulphate respectively, and n_{H_2O} and n_{EtOH} are the refractive indices of water and ethanol respectively.

¹¹ V.N. Melnik, *J. Phys. Chem.*, 1961, 65, 229.

Molecular Orbital Calculations. Parameters used for the PPP-MO calculations have been summarised elsewhere,^{9,12} and in all cases a planar geometry with bond angles of 120° were assumed. Two-centre electron repulsion integrals were calculated by the Nishimoto-Mataga method. Transition energies were refined by a configuration interaction treatment involving the first nine singly excited singlet configurations.

2,5-Dimethoxybenzaldehyde. Chloroform (10 g) was added slowly to a stirred solution of 4-methoxyphenol (17 g) and sodium hydroxide (40 g) in water (50 ml) at 65 - 70 °C. Further additions of chloroform (2 x 10 g) were made, and the yellow suspension was heated under reflux for 1 h. Steam distillation gave 2-hydroxy-5-methoxybenzaldehyde as a pale yellow oil (15 g, 72%). The aldehyde was dissolved in aqueous sodium hydroxide solution (10%, 50 ml), and dimethyl sulphate (12.6 g) was added dropwise at 10 °C. The solution was heated at 65 °C for 30 min and the resultant precipitate filtered off. Recrystallisation of the solid from ligroin (b.p. 60-80 °C) gave 2,5-dimethoxybenzaldehyde (10 g, 61%) as colourless crystals, m.p. 52 - 53 °C (lit.¹³ 53 °C).

2,5-Dimethoxy-3-nitrobenzaldehyde. This was prepared by methylation of 2-hydroxy-5-methoxy-3-nitrobenzaldehyde, the latter being obtained by a modification of the procedure of Rubenstein.³ A mixture of nitric acid

³ L. Rubenstein, *J. Chem. Soc.*, 1925, 1998.
⁹ J.Griffiths, M.Lockwood and B.Roespekar, *J. C. S. Perkin II*, 1977, 1608.
¹² X.Y.Chu and J.Griffiths, *J. Chem. Research*, 1978, (S), 180; (M), 2319.
¹³ A.Neuberger, *Biochem. J.*, 1948, 43, 599.

(d. 1.42, 1.5 ml) and acetic acid (1.5 ml) was added to a solution of 2-hydroxy-5-methoxybenzaldehyde (1 g) in acetic acid (10 ml), maintaining the temperature below 10 °C. After 1 h the mixture was poured into ice-water and the yellow precipitate was filtered off. Recrystallisation from ethanol gave 2-hydroxy-5-methoxy-3-nitrobenzaldehyde as yellow needles (0.79 g, 61%) m.p. 127 - 129 °C (lit.³ 132 °C).

Silver oxide (1 g) was added over 20 min to a solution of the nitro-compound (1 g) and iodomethane (2.5 ml) in chloroform (12 ml) with stirring. The mixture was heated under reflux for 1.5 h and then filtered. The residue was washed with chloroform, and the combined filtrate and washings extracted with dilute sodium hydroxide solution. Evaporation of the dried (MgSO₄) chloroform solution gave 2,5-dimethoxy-3-nitrobenzaldehyde as a light yellow solid (0.98 g, 91%), forming pale yellow needles on recrystallisation from methanol (m.p. 108 - 110 °C, lit.³ 113 °C).

2,6-Bis(hydroxymethyl)-1,4-dimethoxybenzene. A mixture of 2,6-bis(hydroxymethyl)-4-methoxyphenol⁵ (8 g), iodomethane (12 ml) and anhydrous potassium carbonate (12 g) in acetone (150 ml) was heated under reflux for 5 h. The mixture was filtered, the residue washed with acetone, and the combined filtrate and washings evaporated under reduced pressure. The residue was digested with dilute aqueous sodium hydroxide solution (10%, 30 ml) and the solid filtered off and dried (6.3 g, 49%), m.p. 112 °C (lit.⁵ 112 °C).

2,6-Bis(bromomethyl)-1,4-dimethoxybenzene. 2,6-Bis(hydroxymethyl)-1,4-dimethoxybenzene (4 g) was added to an ice-cold mixture of sulphuric acid (5 ml) and hydrobromic acid (47%, 10 ml), and the mixture stirred at room

³ L. Rubenstein, *J. Chem. Soc.*, 1925, 1998.
⁵ V.J.Moran, E.C.Schreiber, E.Dugel, D.C.Behn and J.L.Yamini, *J. Amer. Chem. Soc.*, 1952, 74, 127.

temperature for 30 min. Further addition of sulphuric acid (1.5 ml) and hydrobromic acid (5 ml) was made, and stirring was continued for 3 h. The thick suspension was added to water, and the precipitate of the bis(bromomethyl)-compound filtered off, washed with water, and dried (5.5 g, 84%). Recrystallisation of the solid from methanol gave colourless needles, m.p. 94 - 96 °C (lit.⁵ 98.5 °C). The crude product was of adequate purity for the following preparation.

2,5-Dimethoxy-m-phthalaldehyde.— A solution of 2,6-bis(bromomethyl)-1,4-dimethoxybenzene (4 g) and hexamethylenetetramine (4 g) in chloroform (55 ml) was heated under reflux for 2.5 h. The precipitated amine hydrobromide was filtered off and dissolved in a mixture of water (25 ml) and formaldehyde (40% aqueous solution, 2 ml). The solution was heated under reflux for 4 h and the off-white crystals of 2,5-dimethoxy-m-phthalaldehyde that deposited on cooling were filtered off and dried (0.74 g, 31%), m.p. 110 - 111 °C (lit.¹⁴ 113-114 °C).

General procedure for condensation of methoxybenzaldehydes with active methylene compounds.— The aldehyde (4 mmol) and the active methylene compound (malononitrile, ethyl cyanoacetate, α -cyanoacetophenone, 4-methoxy- α -cyanoacetophenone, or 4-nitrobenzotrile) (4 mmol in the case of the benzaldehydes, 8 mmol in the case of the phthalaldehydes) were dissolved in absolute ethanol (10 ml) and one drop of piperidine was added. The solution was boiled for a short period and then kept at room temperature for 15 h. The product was filtered off and recrystallised



from ethanol. The yields, melting points and analytical data for the products are given in Table 3.

2,5-Dimethoxy-1-tricyanovinylbenzene.— An aqueous solution of potassium cyanide (4 M, 1.7 ml) was added dropwise with stirring to a solution of 2,5-dimethoxy-1-(2',2'-dicyanovinyl)benzene (2.5 g) in dimethylformamide (7 ml) under a nitrogen atmosphere at 25 °C. After 4 min the solution was warmed to 35 °C and acetic acid (19 ml) and lead (IV) acetate (1.11 g) added successively, the latter being added over 1 min. After 10 min the red mixture was poured into ice-water, and the red precipitate of 2,5-dimethoxy-1-tricyanovinylbenzene (15) was filtered off, washed and dried (0.49 g, 88%). Recrystallisation from benzene-petroleum ether (b.p. 80 - 100 °C) gave red crystals, m.p. 127 °C. (Found: C, 65.1; H, 3.8; N, 17.8. $C_{13}H_9N_3O_2$ requires C, 65.3; H, 3.8; N, 17.6%).

1,4-Bis(tricyanovinyl)-2,5-dimethoxybenzene (22).— This was prepared as for 2,5-dimethoxytricyanovinylbenzene from the bis(dicyanovinyl)-compound (19), using double the quantities of potassium cyanide and lead (IV) acetate per mole of the dicyanovinyl-compound. 1,4-Bis(tricyanovinyl)-2,5-dimethoxybenzene (22) was obtained as red crystals from benzene (91%), m.p. 226 - 229 °C. (Found: C, 63.7; H, 2.4; N, 24.7. $C_{18}H_8N_6O_2$ requires C, 63.55; H, 2.35; N, 24.7%).

1,3-Bis(tricyanovinyl)-2,5-dimethoxybenzene (26) was obtained as for (22), using the 1,3-bis(dicyanovinyl)-compound (23) as starting material. The product was obtained as orange crystals from ethanol (64%), m.p. 173 - 174 °C. (Found: C, 63.7; H, 2.45; N, 24.5. $C_{18}H_8N_6O_2$ requires C, 63.55; H, 2.35; N, 24.7%).

Table 3 Yields, melting points and analytical data for new cyanovinyl-compounds

Compound	Yield ^a / %	M.p. / °C	Molecular formula	Found (%)			Required (%)		
				C	H	N	C	H	N
(5)	96	102-103	C ₁₂ H ₁₀ N ₂ O ₂	67.35	4.3	12.7	67.3	4.7	13.1
(8)	54	148	C ₁₂ H ₁₀ N ₂ O ₂	67.35	4.7	13.0	67.3	4.7	13.1
(10)	70	87-88	C ₁₂ H ₁₀ N ₂ O ₂	67.4	4.3	13.3	67.3	4.7	13.1
(13)	98	118	C ₁₉ H ₁₇ NO ₄	70.0	5.0	4.6	70.5	5.2	4.3
(14)	98	161-163	C ₁₇ H ₁₄ N ₂ O ₄	65.6	4.9	8.8	65.8	4.5	9.0
(16)	80	170-171	C ₁₂ H ₉ BrN ₂ O ₂	49.0	3.2	9.9	49.1	3.1	9.6
				(Br, 27.6)			(Br, 27.3)		
(17)	96	145-146	C ₁₂ H ₉ N ₃ O ₄	55.5	3.5	16.3	55.6	3.5	16.2
(18)	59	123-125	C ₁₂ H ₉ N ₃ O ₄	55.1	3.5	16.3	55.6	3.5	16.2
(19)	96	252-254	C ₁₆ H ₁₀ N ₄ O ₂	66.2	3.7	19.2	66.2	3.5	19.3
(20)	88	221	C ₂₀ H ₂₀ N ₂ O ₆	62.8	5.2	7.3	62.5	5.2	7.3
(21)	77	225	C ₂₈ H ₂₀ N ₂ O ₄	75.0	4.5	6.4	75.0	4.5	6.3
(23)	71	182-183	C ₁₆ H ₁₀ N ₄ O ₂	66.0	3.7	18.9	66.2	3.5	19.3
(24)	62	156-157	C ₂₀ H ₂₀ N ₂ O ₆	62.6	4.9	7.4	62.5	5.2	7.3
(25)	96	190-191	C ₂₈ H ₂₀ N ₂ O ₄	75.3	4.4	6.5	75.0	4.5	6.3

^a For the condensation reaction between the appropriate aldehyde and active methylene compound. Crude crystalline material.

⁵ W.J.Moran, E.C.Schreiber, E.Engel, D.C.Behn and J.L.Yamins, J. Amer. Chem. Soc., 1952, 74, 127.

¹⁴ C.Manecke and D.Zerpner, Makromol. Chem., 1969, 129, 183.