



## Syntheses with Nitriles. Part 97: Push–Pull Diarylbutadienes and Diarylpentadienes: Known Chromophores—New Facts\*

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### ABSTRACT

*The syntheses and properties of 1,1-dicyano-1,3-butadienes and 3-dicyanomethylene-1,4-pentadienes, readily obtained by Knoevenagel condensations of benzaldehydes with  $\alpha$ -methylbenzylidenemalononitriles and 1,1-dicyano-2-methyl-4-phenyl-1,3-butadienes, respectively, are described. Color-constitution relationships and their possible use for nonlinear optics are discussed. Calculations of excitation energies using the PPP method are in good agreement with experimental values. In contrast, the INDO/S procedure only leads to a satisfactory correlation if solvent effects are included in the calculations.*

### 1 INTRODUCTION

Dicyanovinyl groups are very powerful electron acceptors. Therefore, introduction of a dicyanomethylene group  $[(\text{CN})_2\text{CH}=\text{}]$  has often been used in the synthesis of polymethine dyes.<sup>1–5</sup> Malononitrile and its dimer (2-amino-1,1,3-tricyano-1-propene) are especially suitable building blocks for numerous conventional and functional dyes,<sup>6</sup> e.g. colorformers and NIR dyes.<sup>7–9</sup> Donor–acceptor conjugated compounds also offer promise as materials for nonlinear optics. Nonlinear optical materials require a

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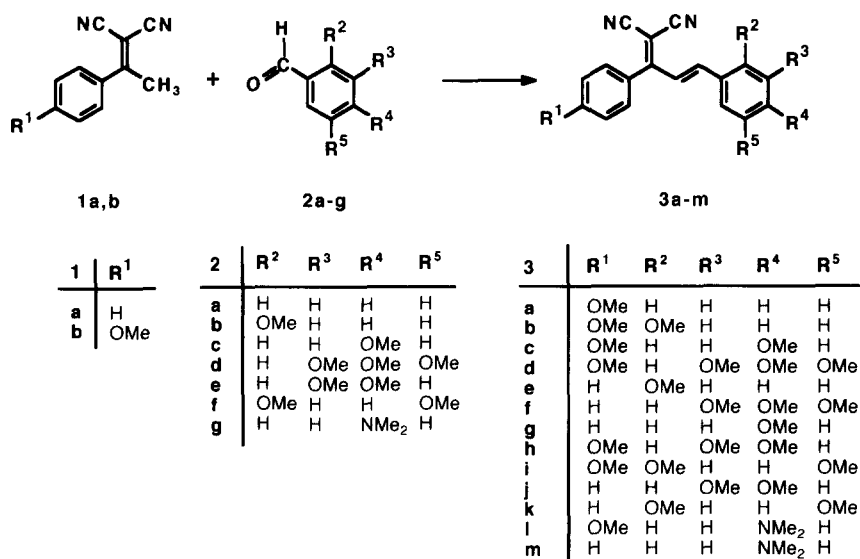
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high first order molecular hyperpolarizability, which can be obtained by increasing the length of the conjugated system. On the other hand, for second harmonic generation, where the emission of a laser is converted from the infrared to the blue region, practically useful materials must be transparent at the second harmonic generation wavelength to avoid self-absorption. It is necessary, therefore, to find the optimal combination of donor and acceptor groups for a conjugated system of a certain length.

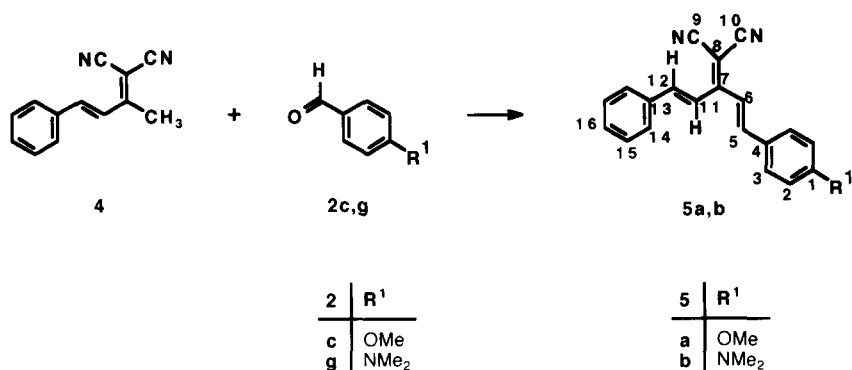
In this paper we report on the synthesis and properties of dicyanomethylenebutadienes (**3a-m**) and -pentadienes (**5a, b**). While two of these compounds (**3g, 3m**) have already been described as disperse dyes,<sup>9</sup> we focussed our interest on the fact that the synthesis of **3a-m** and **5a, b**, starting from aromatic aldehydes, benzalacetones and malononitrile, offers an efficient method to selectively introduce a series of substituents with different electron donating properties in the aromatic rings and thus to vary the absorption wavelengths and polarizability of the resulting colorants.

Our strategy also promises a practical way to the design of products with nonlinear optical properties,<sup>9-11</sup> as shown by the comprehensive computational calculations on these compounds which we have published recently.<sup>12</sup>

Starting materials for **3a-m** and **5a, b** are easily available by Knoevenagel condensations.  $\alpha$ -Methylbenzylidenemalononitriles (**1a, b**) were obtained from (substituted) acetophenones and malononitrile,<sup>13</sup> 1,1-dicyano-2-methyl-4-phenyl-1,3-butadiene (**4**) was prepared from benzalacetone<sup>14</sup>



Scheme 1



Scheme 2

and malononitrile. Subsequent reaction of **1a, b** and **4** with substituted benzaldehydes (**2a-g**) gave dyes **3a-f**, **3h-l** (see Scheme 1) and **5a, b** (see Scheme 2), respectively. All condensations (catalyst: ammonium acetate/glacial acetic acid) were performed in benzene and with continuous removal of water.

## 2 RESULTS AND DISCUSSION

The maximum absorption wavelengths of the dyes were found to be between 340 nm (**3a** in acetone) and 502 nm (**3m** in acetone) for the butadienes and between 372 nm (**5a** in acetone) and 505 nm (**5b** in chloroform) for the pentadienes. Values for  $\log \epsilon$  were between 3.89 (**5b** in chloroform) and 4.76 (**3l** in acetone).

More importantly, there is a distinct dependence of the first absorption band on the number and position of the donor groups. Generally, compounds in which  $R^1 = H$  absorb at longer wavelengths than those where  $R^1 = MeO$  (e.g. **3b** versus **3e**; **3c** versus **3g**; **3d** versus **3f**; **3h** versus **3j**; **3i** versus **3k**; **3l** versus **3m**). The differences in the maximum absorption wavelengths are between 6 and 21 nm (in acetone). If  $R^1$  and/or  $R^4$  are methoxy groups (**3a**, **3c** and **3g**), an interesting effect can be observed. Compound **3a**, in which  $R^1 = OMe$ , absorbs at 340 nm. Introduction of a second methoxy group into the phenyl ring in position 4 of the butadiene (**3c**,  $R^1 = R^4 = OMe$ ) leads to a bathochromic shift to 379 nm, while compound **3g**, which contains only one methoxy group ( $R^4 = OMe$ ) shows a long wavelength absorption of 400 nm. Compared with a 2-methoxy group (**3e**,  $R^2 = OMe$ ), substitution in the 4-position (**3g**,  $R^4 = OMe$ ) yields a bathochromic shift of 13 nm. The 2,5-dimethoxy

substituted compounds ( $R^2 = R^5 = \text{OMe}$ ) **3i** and **3k** absorb at longer wavelengths than the 3,4-dimethoxy derivatives ( $R^3 = R^4 = \text{OMe}$ ) **3h** and **3j**. The trimethoxy derivatives **3d** (386 nm) and **3f** (396 nm) absorb at shorter wavelengths than the corresponding dimethoxy derivatives **3h** (407 nm) and **3j** (413 nm). The formal 'insertion' of a double bond into **3g** (yields **5a**) or into **3m** (yields **5b**) does not shift the absorption to longer wavelengths. The dimethylamino derivatives **3m** and **5b** both absorb at about 500 nm. In the case of **3g** ( $\lambda_{\text{max}}$  400 nm), the 'insertion' of the ethylene group brings about a hypsochromic shift to 372 nm (**5a**).

For the interpretation of such substituent effects, as well as general color–constitution relationships, theoretical methods—especially the Pariser–Parr–Pople method<sup>15,16</sup>—have become increasingly important.<sup>17,18</sup> Specifically, for the cyanovinyl substituted dimethoxybenzenes<sup>19,20</sup> and similar dyes<sup>21</sup> this computational method has been successfully applied. Alternatively, the more elaborate spectroscopic variant of the CNDO (INDO) procedure<sup>22–25</sup> has found increasing application in dye chemistry.<sup>26–28</sup> However, apart from some special cases where  $\sigma$ – $\pi$  interactions due to a nonplanarity of the dyes (which clearly are beyond the scope of the PPP method) are largely responsible for the experimentally observed variation in absorption energies<sup>27,28</sup> the superiority of this latter method over the PPP approach has yet to be proved. Since the effects described

TABLE 1

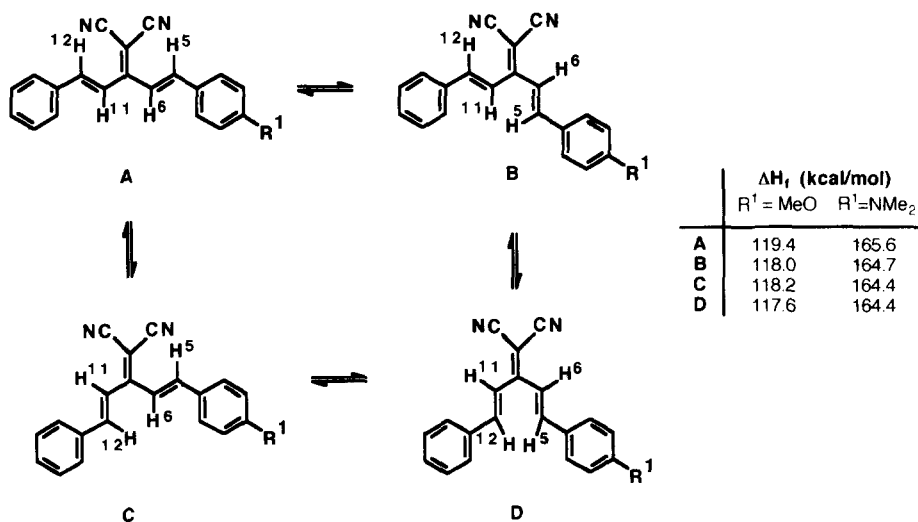
Experimental (in acetone) and Calculated (PPP, ZINDO, ZINDO-SCRF) Excitation Energies ( $\nu$  in  $\text{cm}^{-1}$ ),  $\log \epsilon$  Values and Oscillator Strengths  $f$  for Compounds **3a–m** and **5a, b**

	$\nu_{\text{exp}}$	$\log \epsilon$	$\nu_{\text{PPP}}$	$f_{\text{PPP}}$	$\nu_{\text{ZINDO}}$	$f_{\text{ZINDO}}$	$\nu_{\text{ZINDO-SCRF}}$	$f_{\text{ZINDO-SCRF}}$
<b>3a</b>	29412	4.43	26307	1.05	28594	0.65	27366	0.59
<b>3b</b>	26525	4.47	24657	0.87	28080	0.74	26282	0.72
<b>3c</b>	26385	4.42	25520	1.23	27960	1.03	25468	1.07
<b>3d</b>	25907	4.46	24427	1.11	28291	0.84	26836	0.88
<b>3e</b>	25840	4.20	24107	0.87	28208	0.81	25154	0.71
<b>3f</b>	25252	4.21	23747	1.10	28574	1.02	25337	0.87
<b>3g</b>	25000	4.49	24918	1.21	28064	1.15	23858	1.06
<b>3h</b>	24570	4.53	24735	1.12	27728	0.98	24699	0.90
<b>3i</b>	24272	4.16	22985	0.64	27228	0.54	24234	0.42
<b>3j</b>	24213	4.45	24098	1.10	27357	1.06	23504	0.90
<b>3k</b>	23753	4.16	22354	0.66	27010	0.55	22642	0.38
<b>3l</b>	20534	4.76	22038	1.28	27707	1.06	24756	1.06
<b>3m</b>	19920	4.73	21392	1.28	27294	1.20	21931	1.11
<b>5a</b>	26882 <sup>a</sup>	4.47	24805	1.12	28249	0.97	24648	0.94
<b>5b</b>	20000	4.29	21027	1.08	26845	0.65	23038	0.59

<sup>a</sup> Probably two overlapping bands, shoulder at  $\approx 24400 \text{ cm}^{-1}$ .

above are rather small, the compounds described in this paper also present rather stringent test molecules for the reliability of the various quantum chemical procedures aimed at the prediction of absorption spectra of organic dyes. Consequently, we have used both approaches (PPP and INDO/S-CI). For the PPP calculations we used the standard parameters of Griffiths<sup>17</sup> (for cyano groups the modified parameters<sup>7</sup> were used), while INDO/S-CI calculations were done by the ZINDO<sup>29</sup> program of Ridley and Zerner.<sup>25</sup> In the latter procedure solvent effects have approximately been included with the aid of the self-consistent reaction field method (ZINDO-SCRF).<sup>30,31</sup> The results of these calculations (wavenumbers  $\nu$  (in  $\text{cm}^{-1}$ ) and oscillator strengths  $f$ ) for the first absorption band, as well as experimental values, are collected in Table 1. A complication arises for pentadienes **5a, b**: at least four different conformations have to be considered for these compounds (structures **A-D** in Scheme 3). A distinction between these conformations could be achieved by a combination of semiempirical AM1 calculations<sup>32</sup> and NOE experiments. Irradiation of protons H-5 and H-12 led to NOEs between H-5 (7.24 ppm) and H-11 (7.56 ppm; structure **B**) and between H-12 (7.35 ppm) and H-6 (7.62 ppm; structure **C**), respectively. No NOE between H-5 and H-12 could be detected, thus excluding structure **D**. The small chemical shift differences between H-6 (7.62 ppm) and H-11 (7.56 ppm) precluded a NOE experiment for these two protons. Based on the calculated energies (see Scheme 3), structure **A** appears to be the least likely one.

Most importantly, a reasonable agreement between experimental excitation energies and those calculated by the INDO/S-CI method can only be



Scheme 3

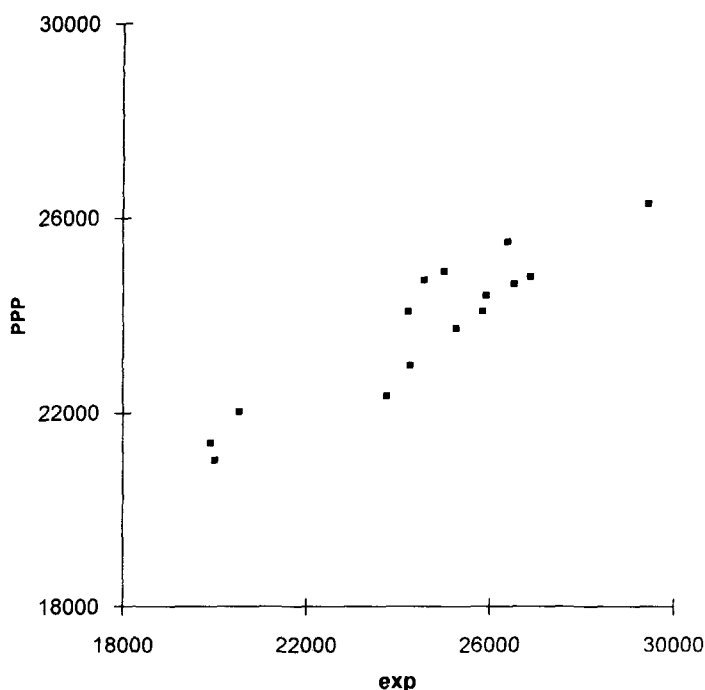


Fig. 1. Plot of calculated (PPP) excitation energies ( $\text{cm}^{-1}$ ) versus experimental values (in acetone).

obtained if the effect of the solvent is included (see Table 1 and Fig. 1; calculations for the isolated molecules give essentially no correlations with experimental values). Solvent effects thus appear to be of considerable importance in the experimentally observed variation of absorption wavelengths. There are, however, still some notable disagreements: the most prominent is the underestimation of the donor strengths of the dimethyl-amino agroup compared with the MeO substituent (**3l**, **5m**, **5b**). Possibly, this deviation might be due to the neglect of the dispersion energy contribution to solvation (the softer  $\text{NMe}_2$  group is expected to be more prone to this effect than the harder MeO). For compound **5a** the experimental Vis spectrum is most likely composed of two overlapping bands (shoulder at  $\approx 24400 \text{ cm}^{-1}$  close to the calculated value).

In striking contrast, the PPP method (see Table 1 and Fig. 2) leads to a rather good agreement with the experimental results. It thus seems clear that solvent effects have been—at least partly—absorbed in the empirical parameters used in this method. Furthermore, unless there are some rather special  $\sigma$ - $\pi$  interactions due to a nonplanarity of the dyes, this procedure is still the method of choice for a reliable and efficient prediction and interpretation of color-constitution relationships.

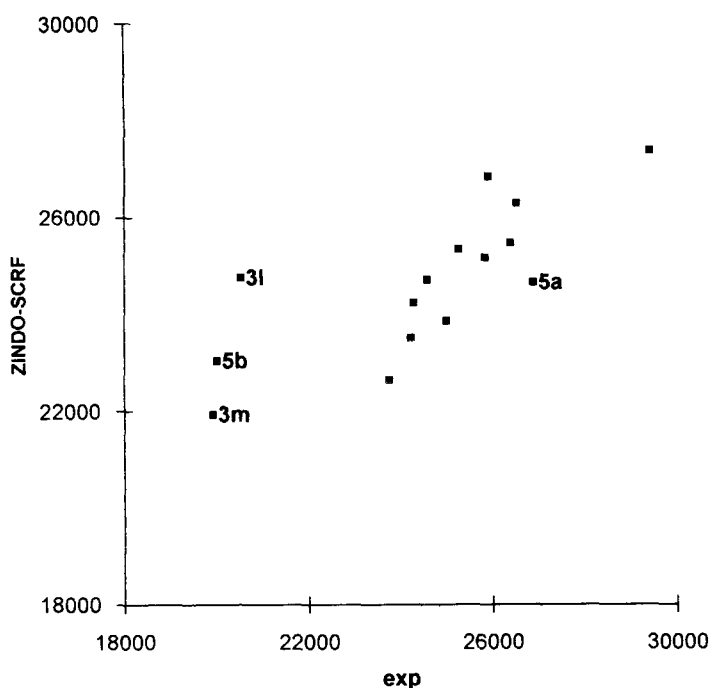


Fig. 2. Plot of calculated (ZINDO-SCRF) excitation energies ( $\text{cm}^{-1}$ ) versus experimental values (in acetone).

### 3 EXPERIMENTAL

#### 3.1 General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra, Perkin-Elmer Spectrophotometer 298 (KBr pellets);  $^1\text{H}$  NMR spectra, Varian Gemini 200;  $^{13}\text{C}$  NMR spectra, Gemini 200 and Bruker 369 AM (all NMR spectra are referenced to tetramethylsilane); UV/Vis spectra, Hitachi U-3501. The starting materials were obtained from commercial suppliers. The aldehydes were distilled immediately before use. Compounds **3g** and **3m** were prepared according to the literature.<sup>9</sup>

#### 3.2 General procedure for syntheses of 1,1-dicyano-1,3-butadienes (**3a-l**)

$\alpha$ -Methylbenzylidenemalononitrile (**1a**<sup>13</sup> or **1b**, 15 mmol) and the appropriate aldehyde (**2a-g**, 15 mmol), ammonium acetate (3 mmol) and 0.6 ml glacial acetic acid were dissolved in dry benzene (50 ml). The mixtures were heated on a Dean and Stark water trap for 10 h. After evaporation of the solvent the solid residues were purified by recrystallization.

### 3.2.1 *1,1-Dicyano-2-(4-methoxyphenyl)-4-phenyl-1,3-butadiene (3a)*

From **1b** and **2a**, yield 35%, m.p. 164°C (methanol). IR: 2930, 2850, 2230, 1605, 1585, 1560, 1515 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.87 (s, 3H, OCH<sub>3</sub>), 6.75–7.65 (m, 11H, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 340 (4.43) nm. C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O (286.3): calculated C 79.70, H 4.93, N 9.78; found C 79.40, H 5.52, N 10.23.

### 3.2.2 *1,1-Dicyano-2-(4-methoxyphenyl)-4-(2-methoxyphenyl)-1,3-butadiene (3b)*

From **1b** and **2b**, yield 66%, m.p. 126°C (methanol). IR: 2220, 1605, 1580, 1505 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.82 (s, 3H, OCH<sub>3</sub>), 3.88 (s, 3H, OCH<sub>3</sub>), 7.00–7.25, 7.40–7.60, 7.65–7.80 (3m, 10H, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 377 (4.47) nm, (chloroform) λ<sub>max</sub> (log ε) = 383 (4.38) nm. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (316.4): calculated C 75.93, H 5.10, N 8.75; found C 76.06, H 5.07, N 8.78.

### 3.2.3 *1,1-Dicyano-2-(4-methoxyphenyl)-4-(4-methoxyphenyl)-1,3-butadiene (3c)*

From **1b** and **2c**, yield 47%, m.p. 105°C (ethanol). IR: 2930, 2850, 2220, 1600, 1575, 1515, 1490 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.83 (s, 3H, OCH<sub>3</sub>), 3.90 (s, 3H, OCH<sub>3</sub>), 6.90–7.80 (m, 10H, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 379 (4.42) nm. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (316.4): calculated C 75.93, H 5.10, N 8.75; found C 76.24, H 5.19, N 8.53.

### 3.2.4 *1,1-Dicyano-2-(2-methoxyphenyl)-4-(3,4,5-trimethoxyphenyl)-1,3-butadiene (3d)*

From **1b** and **2d**, yield 52%, m.p. 199°C (methanol). IR: 2220, 1605, 1580, 1505 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.75 (s, 3H, OCH<sub>3</sub>), 3.85 (s, 6H, 2 OCH<sub>3</sub>), 3.90 (s, 3H, OCH<sub>3</sub>), 6.90–7.30 and 7.45–7.70 (2m, 8H, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 386 (4.46) nm, (chloroform) λ<sub>max</sub> (log ε) = 387 (4.26) nm. C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> (376.4): calculated C 70.20, H 5.36, N 7.44; found C 69.46, H 5.34, N 7.43.

### 3.2.5 *1,1-Dicyano-4-(2-methoxyphenyl)-2-phenyl-1,3-butadiene (3e)*

From **1a** and **2b**, yield 70%, m.p. 130°C (ethanol). IR: 2220, 1600, 1530, 1480 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.82 (s, 3H, OCH<sub>3</sub>), 7.00–7.20 and 7.40–7.85 (2m, 4 and 7H, respectively, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 386 (4.20) nm, (chloroform) λ<sub>max</sub> (log ε) = 394 (4.22), 328 (4.17) nm. C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O (286.3): calculated C 79.70, H 4.93, N 9.78; found C 80.02, H 4.95, N 9.87.



### 3.2.6 *1,1-Dicyano-2-phenyl-4-(3,4,5-trimethoxyphenyl)-1,3-butadiene (3f)*

From **1a** and **2d**, yield 49%, m.p. 163°C (ethanol). IR: 2220, 1600, 1575, 1525, 1500  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO): 3.75 (s, 3H,  $\text{OCH}_3$ ), 3.83 (s, 6H, 2  $\text{OCH}_3$ ), 6.92 (d, 2H, CH), 7.08 (s, 2H, aromatic protons) 7.45–7.75 (m, 5H, one CH-group and 4 aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 396 (4.21) nm, (chloroform)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 402 (4.15) nm.  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3$  (346.4): calculated C 72.82, H 5.24, N 8.09; found C 72.43, H 5.38, N 7.79.

### 3.2.7 *1,1-Dicyano-4-(3,4-dimethoxyphenyl)-2-(4-methoxyphenyl)-1,3-butadiene (3h)*

From **1b** and **2e**, yield 54%, m.p. 156°C (methanol). IR: 2220, 1605, 1595, 1575, 1515, 1485  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO): 3.82 (s, 3H,  $\text{OCH}_3$ ), 3.85 (s, 3H,  $\text{OCH}_3$ ), 3.90 (s, 3H,  $\text{OCH}_3$ ), 6.90–7.60 (m, 9H, CH-groups and aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 407 (4.53) nm, (chloroform)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 407 (4.43) nm.  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3$  (346.4): calculated C 72.82, H 5.24, N 8.09; found C 72.94, H 5.17, N 7.98.

### 3.2.8 *1,1-Dicyano-4-(2,5-dimethoxyphenyl)-2-(4-methoxyphenyl)-1,3-butadiene (3i)*

From **1b** and **2f**, yield 76%, m.p. 150°C (ethanol). IR: 2220, 2210, 1600, 1495  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO): 3.77 (s, 3H,  $\text{OCH}_3$ ), 3.79 (s, 3H,  $\text{OCH}_3$ ), 3.90 (s, 3H,  $\text{OCH}_3$ ), 7.05–7.30 and 7.45–7.85 (2m, 9H, CH-groups and aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 412 (4.16) nm, (chloroform)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 427 (4.10) nm.  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3$  (346.4): calculated C 72.82, H 5.24, N 8.09; found C 73.06, H 5.29, N 8.16.

### 3.2.9 *1,1-Dicyano-4-(3,4-dimethoxyphenyl)-2-phenyl-1,3-butadiene (3j)*

From **1a** and **2e**, yield 47%, m.p. 189°C (ethanol). IR: 2220, 1610, 1595, 1575, 1525, 1510, 1490  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO): 3.80 (s, 3H,  $\text{OCH}_3$ ), 3.83 (s, 3H,  $\text{OCH}_3$ ), 6.90 (d, 1H, CH), 7.05 (d, 1H, CH), 7.20–7.75 (m, 8H, aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 413 (4.45) nm.  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$  (316.4): calculated C 75.93, H 5.10, N 8.85; found C 76.05, H 5.13, N 9.03.

### 3.2.10 *1,1-Dicyano-4-(2,5-dimethoxyphenyl)-2-phenyl-1,3-butadiene (3k)*

From **1a** and **2f**, yield 75%, m.p. 148°C (ethanol). IR: 2220, 2210, 1590, 1585, 1515, 1495, 1485  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{d}_6$ -DMSO): 3.78 (br. s, 6H, 2  $\text{OCH}_3$ ), 7.10 (d, 2H, CH-groups), 7.22 (s, 2H, aromatic protons), 7.45–7.90 (m, 7H, aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 421 (4.16) nm.  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$  (316.4): calculated C 75.93, H 5.10, N 8.85; found C 75.94, H 5.09, N 8.80.

### 3.2.11 1,1-Dicyano-4-(4-*N,N*-dimethylaminophenyl)-2-phenyl-1,3-butadiene (**3I**)

From **1b** and **2g**, yield 69%, m.p. 152°C (methanol). IR: 2210, 1620, 1605, 1580, 1530, 1475 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.05 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.88 (s, 3H, OCH<sub>3</sub>), 6.70–7.10 (m, 10H, CH-groups and aromatic protons) ppm. UV/Vis (acetone) λ<sub>max</sub> (log ε) = 487 (4.76) nm, (chloroform) λ<sub>max</sub> (log ε) = 493 (4.45), 364 (3.86) nm. C<sub>21</sub>H<sub>19</sub>N<sub>3</sub>O (329.4): calculated C 76.57, H 5.81, N 12.76; found C 76.80, H 5.86, N 12.82.

### 3.3 Synthesis of 1,1-dicyano-2-methyl-4-phenyl-1,3-butadiene (**4**)

A mixture of benzalacetone<sup>14</sup> (75 mmol), malononitrile (75 mmol), dry ammonium acetate (8 mmol), and glacial acetic acid (1.8 ml) in 100 ml dry benzene was heated on a Dean and Stark water trap for 12 h. Petroleum ether (20 ml) was then added and the mixture cooled to 0°C. The yellow crystals were collected by suction, washed with petroleum ether and recrystallized from ethanol. Yield 52%, m.p. 127°C. IR: 2230, 1615, 1575, 1545, 1495 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 7.30 (d, 1H, CH), 7.40–7.60 and 7.65–7.85 (2m, 6H, 1 CH-group and aromatic protons) ppm (the signals of the methyl group are hidden in the DMSO signal at 2.5 ppm). C<sub>13</sub>H<sub>10</sub>N<sub>2</sub> (194.2): calculated C 80.39, H 5.19, N 14.42; found C 80.42, H 5.08, N 14.20.

### 3.4 General procedure for syntheses of dicyanomethylene-1,4-pentadienes (**5a**, **b**)

1,1-Dicyano-2-methyl-4-phenyl-1,3-butadiene (**4**, 15 mmol) and the appropriate aldehyde (**2a-g**, 15 mmol), ammonium acetate (3 mmol) and 0.6 ml glacial acetic acid were dissolved in dry toluene (50 ml). The mixtures were heated on a Dean and Stark water trap for 10 h. After evaporation of the solvent the solid residues were purified by recrystallization.

#### 3.4.1 3-Dicyanomethylene-5-(4-methoxyphenyl)-1-phenyl-1,4-pentadiene (**5a**)

From **4** and **2c**, yield 48%, m.p. 148°C. IR: 2930, 2220, 1625, 1600, 1575, 1515, 1500 cm<sup>-1</sup>. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO): 3.87 (s, 3H, OCH<sub>3</sub>), 7.05 (d, 2H, H-2), 7.24 (d, 1H, H-5), 7.35 (d, 1H, H-12), 7.48 (m, 3H, H-15 and H-16), 7.56 (d, 1H, H-11), 7.62 (d, 1H, H-6), 7.76 (m, 4H, H-3 and H-14) ppm. <sup>13</sup>C NMR (d<sub>6</sub>-DMSO): 65.7 (OCH<sub>3</sub>), 76.3 (C-8), 114.1 (C-9), 114.3 (C-10), 114.7 (C-2), 119.3 (C-6), 121.4 (C-11), 127.3 (C-4), 128.4 (C-14), 129.0 (C-15), 130.7 (C-3 and C-16), 134.7 (C-13), 144.0 (C-5), 145.3 (C-12), 161.8

(C-1), 166.9 (C-7) ppm. UV/Vis (acetone)  $\lambda_{\max}$  ( $\log \epsilon$ ) = 372 (4.47) nm.  $C_{21}H_{16}N_2O$  (312.4): calculated C 80.75, H 5.16, N 8.97; found C 80.93, H 5.99, N 8.91.

### 3.4.2 3-Dicyanomethylene-5-(4-*N,N*-dimethylaminophenyl)-1-phenyl-1,4-pentadiene (**5b**)

From **4** and **2g**, yield 65%, m.p. 162°C. IR: 2220, 1630, 1620, 1585, 1530, 1475  $cm^{-1}$ .  $^1H$  NMR ( $d_6$ -DMSO): 3.05 (br. s, 6H,  $N(CH_3)_2$ ), 6.80 (d, 2H, CH), 7.10 (d, 1H, CH), 7.30–8.85 (m, 10H, 1 CH-group and aromatic protons) ppm. UV/Vis (acetone)  $\lambda_{\max}$  ( $\log \epsilon$ ) = 500 (4.29) nm, (chloroform)  $\lambda_{\max}$  ( $\log \epsilon$ ) = 506 (3.89), 342 (4.52) nm.  $C_{22}H_{19}N_3$  (316.4): calculated C 81.20, H 5.89, N 12.91; found C 80.61, H 6.11, N 12.60.

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## REFERENCES

1. Junek, H., Gfrerer, G., Sterk, H., Thierrichter, R. & Zuschmig, G., *Monatsh. Chem.*, **113** (1982) 1045.
2. Junek, H., Dworczak, R., Fabian, W. M. F. & Sterk, H., *Liebigs Ann. Chem.*, (1989) 1065.
3. Dworczak, R., Fabian, W. M. F., Sterk, H., Kratky, C. & Junek, H., *Liebigs Ann. Chem.*, (1992) 7.
4. Junek, H., Klade, M., Biza, P., Geringer, M. & Sterk, H., *Liebigs Ann. Chem.*, (1990) 741.
5. Lonza, *Company Information*, 2nd ed Basel, Switzerland, 1988.
6. Vanmaele, J. L., *Tetrahedron Lett.*, **33** (1992) 961.
7. Bello, K. A., Cheng, L. & Griffiths, J., *J. Chem. Soc. Perkin Trans. II*, (1987) 815.
8. Griffith, J., *Chemie in Unserer Zeit*, **27** (1993) 21.
9. Gokhale, U. V. & Seshadri, S., *Dyes and Pigments*, **7** (1986) 389.
10. Marder, S. R., Sohn, J. E. & Stucky, G. D., *Materials for Nonlinear Optics, Chemical Perspectives*. American Chemical Society, Washington, 1991.
11. Buckley, A., *Adv. Mater.*, **4** (1992) 153.
12. Fabian, W. M. F., Dworczak, R., Junek, H. & Pawar, B. N., *J. Chem. Soc., Perkin Trans.* (1995) 903.
13. Mowry, D. T., *J. Am. Chem. Soc.*, **67** (1945) 1050.
14. Drake, N. L. & Allen, P., *J. Org. Synth. Coll.*, **1** (1941) 77.
15. Pariser, R. & Parr, R. G., *J. Chem. Phys.*, **21** (1953) 466.
16. Pople, J. A., *Trans. Faraday Soc.*, **49** (1953) 1375.

17. Griffiths, J., *Dyes and Pigments*, **3** (1982) 211.
18. Griffiths, J., *Chem. Brit.*, **22** (1986) 997.
19. Chu, K. Y., Griffith, J. & Ward, D., *J. Chem. Research (S)*, (1981) 300.
20. Fabian, W. M. F., *Dyes and Pigments*, **9** (1988) 275.
21. Nakatsuji, S., Yahiro, T., Nakashima, K., Akiyama, S. & Nakazumi, H., *Chem. Express*, **4** (1989) 601.
22. DelBene, J. & Jaffe, H. H., *J. Chem. Phys.*, **48** (1968) 1807.
23. DelBene, J. & Jaffe, H. H., *J. Chem. Phys.*, **48** (1968) 4050.
24. DelBene, J. & Jaffe, H. H., *J. Chem. Phys.*, **49** (1968) 1221.
25. Ridley, J. E. & Zerner, M. C., *Theor. Chim. Acta*, **32** (1973) 111.
26. Adachi, M. & Nakamura, S., *Dyes and Pigments*, **17** (1991) 287.
27. Adachi, M., Murata, Y. & Nakamura, S., *J. Org. Chem.*, **58** (1993) 5238.
28. Adachi, M., Murata, Y. & Nakamura, S., *J. Am. Chem. Soc.*, **115** (1993) 4331.
29. Zerner, M. C., *ZINDO, A Comprehensive Semiempirical Quantum Chemistry Package*. Quantum Theory Project, Gainesville, Florida, USA, 1993.
30. Tapia, O. & Goscinski, O., *Mol. Phys.*, **29** (1975) 1653.
31. Karelson, M. M. & Zerner, M. C., *J. Phys. Chem.*, **96** (1992) 6949.
32. Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P., *J. Am. Chem. Soc.*, **107** (1985) 3902.