

## Reaction of malononitrile with enones

P Murugan<sup>a</sup>, P Shanmugasundaram<sup>a</sup>, V T Ramakrishnan<sup>a\*</sup>,  
N Srividya<sup>b</sup> & P Ramamurthy<sup>b</sup>

<sup>a</sup>Department of Organic Chemistry, <sup>b</sup>Department of Inorganic Chemistry  
School of Chemistry, University of Madras Guindy Campus, Chennai 600 025, India

Received 24 February 1998; accepted 22 June 1998

Reaction of Malononitrile with xanthenes **1a,b** and  $\alpha,\beta$ -unsaturated carbonyl compounds **3a-e** furnishes the acridines **2a,b** and biphenyl derivatives **4a-d,5**. The biphenyl **4a** shows lasing and non-linear optical (NLO) properties.

In continuation of our work on laser dyes<sup>1a-c</sup>, we were interested in synthesising systems containing dicyano methylene groups. 4-Dicyanomethylene-2-methyl-6-(4'-dimethylaminostyryl)-4H-pyran (DCM) is a widely used laser dye<sup>2</sup> because of its broad tunability and high conversion efficiency. This is considered to constitute a family of very effective dyes in the red. Hence, xanthene **1a** was treated with malononitrile and ammonium acetate in acetic acid and benzene which furnished 1,8-(dicyanomethylene)-1,2,3,4,5,6,7,8,9,10-dehydroacridine **2a**. Likewise, the reaction of **1b** gave **2b**. The products were characterised by IR, NMR and MS data and elemental analyses. Both **2a** and **2b** were deep red in methanol but did not show any fluorescence.

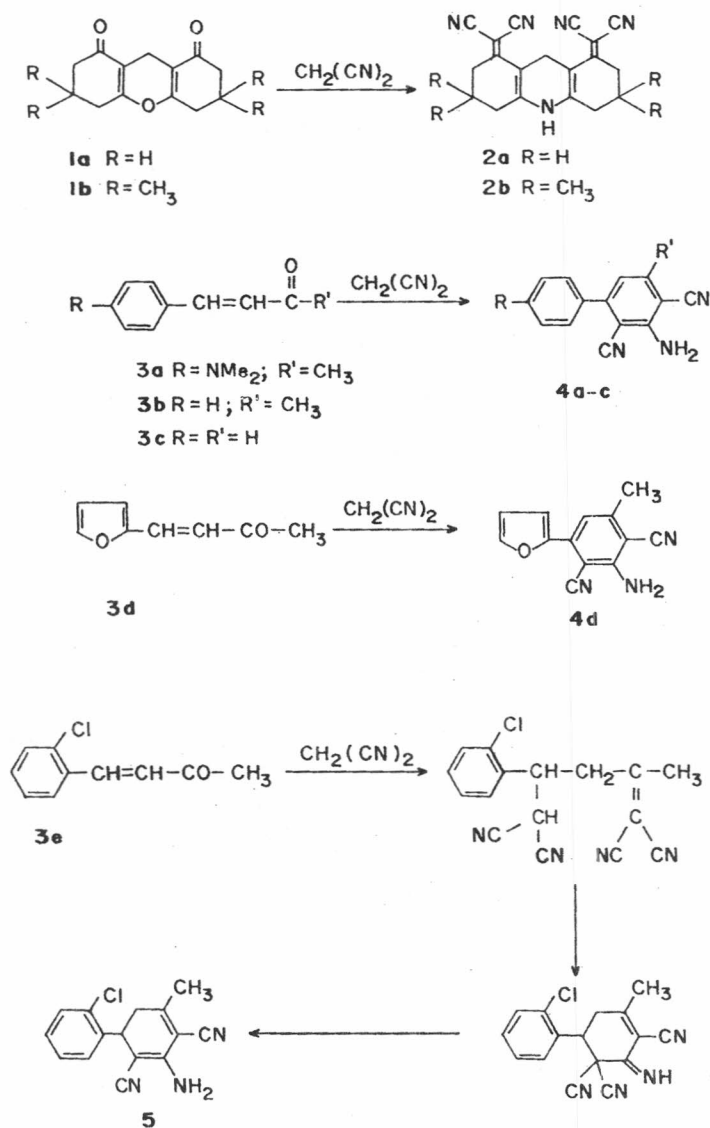
In the above context, we were interested in the reaction of  $\alpha,\beta$ -unsaturated ketones with malononitrile<sup>3a-e</sup>. Hence, 4-dimethylaminobenzalacetone<sup>4</sup> **3a** was treated with malononitrile. The product, a yellow solid, was identified as 3-amino-2,4-dicyano-4'-dimethylamino-5-methylbiphenyl **4a**. The IR spectrum of the dye showed absorption bands at 3520 and 3430 due to NH<sub>2</sub> and at 2224 cm<sup>-1</sup> due to CN. The <sup>1</sup>H NMR showed signals at  $\delta$  2.45 (s, 3H, CH<sub>3</sub>), 3.0 [s, 6H, N(CH<sub>3</sub>)<sub>2</sub>], 5.1 (s, 2H, NH<sub>2</sub>, exchangeable with D<sub>2</sub>O), 6.6 (s, 1H) and 6.7, 7.4 (AB<sub>q</sub>, 4H,  $J = 9$ Hz, Ar-H).

The structure of the biphenyl **4c** was confirmed by X-ray crystallographic studies. The formation of **4a** from **3a** may be rationalized involving Michael addition, condensation, and Thorpe-Ziegler cyclization followed by elimination of HCN and tautomerisation in line with the reported<sup>3c</sup> reaction. Likewise, benzylideneacetone<sup>4</sup> **3b**, cinnamaldehyde **3c** and furfurylideneacetone<sup>4</sup> **3d**, furnished **4b-d** respectively on reaction with malononitrile.

The reaction of 2-chlorobenzalacetone **3e** with malononitrile furnished 3-amino-2,4-dicyano-1-methyl-5-(2-chlorophenyl)cyclohexa-1,5-diene **5**. The formation of **5** can be rationalized as given in Scheme I. The structure of **5** was established on the basis of IR, NMR, MS data and elemental analyses. An AMX pattern was seen between  $\delta$  2.5-3.0 and 4.3 in the <sup>1</sup>H NMR. The mass spectral fragmentations of **5** are depicted in Chart 1.

The biphenyl **4a**, having *N,N*-dimethylamino group as a donor and a cyano group as an acceptor, shows shift in the absorption and emission maxima, with increasing solvent polarity. The absorption maximum appeared at 374 nm and emission maximum at 496 nm in methanol. The absorption and emission data in other solvents are given in Table I. The larger Stokes shift shows the presence of charge transfer nature in the emitting state. The fluorescence quantum yield is unity in non-polar solvents and decreases to 0.7 in polar solvents (Table I).

The biphenyl **4a** shows a lasing yield of 70% at 470 nm in dichloromethane, compared with coumarin-102<sup>1a-d</sup>. The ground state dipole moment (1.5 D) was obtained using the Guggenheim's method<sup>5a,b</sup>. The excited state dipole moment was obtained using Lippert and Mataga continuum dielectric model<sup>6a,b</sup> and the value was 12.5D. the difference (11.0 D) in the dipole moment value between the ground and excited states indicates an increased charge separation in the excited state and hence an ideal situation to have non-linear optical (NLO) properties. Based on the solvent shift behaviour of **4a**, the  $\beta_{CT}$  value was determined as  $20 \times 10^{-30}$  esu using two-level model hyperpolarizability<sup>7</sup>. The  $\beta$  value was obtained by Hyper Rayleigh scattering (HRS)<sup>8a,b</sup> technique. The second harmonic generation efficiency was found using powder reflection technique developed by Kurtz and



Scheme I

Perry<sup>9</sup>. The SHG efficiency was comparable to that of urea.

### Experimental Section

**General.** All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 598 instrument. <sup>1</sup>H NMR were taken on a Varian-Gemini-200 (200 MHz) instrument. <sup>13</sup>C NMR spectra were recorded on a JEOL GS X 400 (100 MHz) instrument. Mass spectra were taken on a JEOL Mass (JMS-Dx 303 HF) spectrometer. Absorption spectra (UV) were recorded on a Hitachi 320 and Hewlett-Packard 8452A diode array spectrophotometers and emission spectra on a

Perkin-Elmer LS 5B luminescence spectrophotometer. Laser studies were performed by Quanta Ray DCR 2 Nd-YAG laser using the third harmonics (355 nm). Second order non-linear optical (NLO) studies were performed by Quanta Ray DCR 2 Nd-YAG laser using the fundamental harmonics (1064 nm).

**Preparation of acridines 2a and 2b.** 2,2'-Methylenebis(cyclohexane-1,3-dione)<sup>10</sup> (0.5g, 2.1 mmoles) was refluxed in acetic anhydride (10 mL) for 8 hr. The solvent was removed under vacuum and the solid which crystallized out was filtered and dried to isolate 1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthene **1a**. mp 163

°C (mp 163 °C)<sup>11</sup>. A mixture of xanthene **1a** (1.0g, 5 mmoles), malononitrile (0.8g, 12 mmoles), acetic acid (2 mL) and ammonium acetate (0.92g, 12 mmoles) in benzene (30 mL) was refluxed using a Dean-Stark apparatus for 2 hr. The solvent was removed to get an oily residue which solidified on cooling and was washed with water and crystallized from chloroform-methanol to get **2a**, yield 0.97g (60%), mp 268-270 °C. Anal. Calcd for C<sub>19</sub>H<sub>15</sub>N<sub>5</sub>: C, 72.87, H, 4.82; N, 22.36. Found: C, 72.59; H, 4.62; N 22.16%; IR (KBr): 3456 (NH), 2200 (CN), 1610, 1520 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 1.77-1.79 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 2.38-2.67 (m, 8H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 3.32 (s, 2H, =C-CH<sub>2</sub>-C=), 10.27 (s, NH); MS: m/z 313 (M<sup>+</sup>, 14), 312 (18), 265 (44), 264

(40), 235 (23), 200 (100).

2,2'-Methylenebis(5,5-dimethylcyclohexane-1,3-dione)<sup>10</sup> on refluxing with acetic anhydride for 3 hr gave the xanthene **1b**, mp 171 °C (mp 171 °C)<sup>11</sup>. Treatment of **1b** (1.37g, 5 mmoles) with malononitrile (12 mmoles) as above in the presence of ammonium acetate furnished **2b**, yield 1.07 (58%), mp 284-286 °C. Anal. Calcd for C<sub>23</sub>H<sub>23</sub>N<sub>5</sub>: C, 74.77; H, 6.27; N, 18.95. Found: C, 74.71; H, 6.11; N, 18.75%; IR (KBr): 3424 (NH), 2224 (CN), 1615 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 0.98 (s, 12H, *gem*-dimethyl), 2.27(s, 4H, =C-CH<sub>2</sub>), 2.51 (s, 4H, CH<sub>2</sub>), 3.32 (s, 2H, =C-CH<sub>2</sub>-C=), 9.66 (s, NH); MS: m/z 369 (M<sup>+</sup>, 8), 339 (4), 321 (100), 291

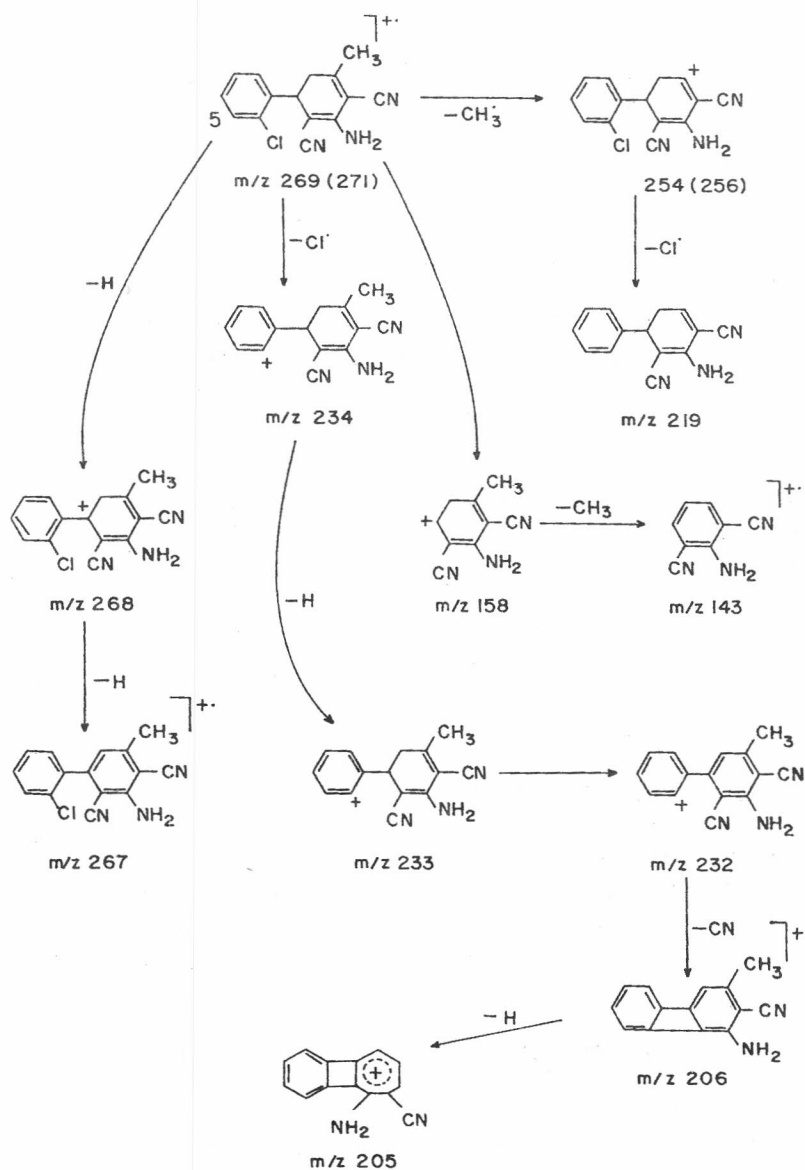


Chart 1

**Table I** — Absorption and emission spectral data and  $\beta$  values of 3-amino-2,4-dicyano-4'-dimethylamino-5-methylbiphenyl **5** in different solvents

Solvents	Absorption		Emission		Stokes Shift (cm <sup>-1</sup> )	$\beta_{OX}$ 10 <sup>10</sup> esu	$\beta_{CTX}$ 10 <sup>30</sup> esu
	$\lambda_{max}$ (nm)	log $\epsilon$	$\lambda_{max+}$ (nm)	$\phi f$			
CCl <sub>4</sub>	372	—	417	1.00	2900	—	—
Benzene	375	4.33	439	1.00	3887	8.3	19.0
Toluene	376	4.37	437	1.00	3712	9.2	21.2
Chloroform	380	4.32	453	0.89	4240	9.3	21.6
Ethylacetate	372	4.41	463	0.86	5283	10.6	23.8
THF	374	4.33	463	0.84	5140	9.5	21.3
DCM	376	4.35	463	0.86	4997	9.8	22.5
1-pentanol	376	4.29	476	0.85	5587	8.5	19.7
2-butanol	376	4.33	484	0.89	5935	9.5	21.6
1-butanol	376	4.36	478	0.82	5675	8.6	24.4
2-propanol	376	4.36	483	0.76	5891	9.6	22.0
1-propanol	376	4.29	483	0.82	5891	8.6	19.7
Acetone	374	4.33	485	0.73	6119	9.1	20.6
Ethanol	374	4.33	487	0.70	6204	9.6	21.6
Benzonitrile	374	4.42	481	0.83	5948	9.8	23.5
Methanol	374	4.33	496	0.74	6577	9.7	22.0
DMF	376	4.34	495	0.83	6393	8.7	20.4
Acetonitrile	372	4.33	494	0.74	6638	9.7	21.7
DMSO	382	4.31	503	0.93	6297	9.7	21.8

\* THF- Tetrahydrofuran, DCM-Dichloromethane, DMF-Dimethylformamide, DMSO-Dimethyl sulphoxide

(24), 274 (12), 256 (27), 238 (27), 215 (14).

**3-Amino-2,4-dicyano-4'-dimethylamino-5-methylbiphenyl 4a: General Method.** A mixture of 4-dimethylaminobenzalacetone **3a** (1.0g 5.2 mmoles), malononitrile (0.71g, 10.6 mmoles) and pyrrolidine (few drops) in ethanol (25 mL) was heated under reflux for 7 hr. The reaction mixture was concentrated under reduced pressure and purified by column chromatography over alumina (neutral). Elution with a mixture of petroleum ether-benzene (1:4) gave the product **4a** as a yellow solid, which was recrystallized from petroleum ether-benzene mixture, yield 0.6g (45%), mp 226-228 °C. Anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>: C, 73.89; H, 5.84; N, 20.27. Found: C, 74.30; H, 5.91; N, 20.25%; <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.3, 41.2, 93.2, 95.6, 110.8, 115.8, 117.0, 120.1, 126.3, 129.3, 147.0, 150.6, 151.3, 152.6; MS: m/z 276(100), 275(50), 260(5), 248(3), 232(5), 205(5).

**3-Amino-2,4-dicyano-5-dimethylbiphenyl 4b:** Yield 46%, mp 163-165 °C. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>: C, 77.23; H, 4.75; N, 18.02. Found: C, 77.61; H, 4.98; N, 18.38%; IR (CHCl<sub>3</sub>): 3420, 3310 (NH<sub>2</sub>), 2240 (CN)

cm<sup>-1</sup>; UV (MeOH):  $\lambda_{max}$  366 nm; Flu (MeOH):  $\lambda_{max}$  415nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.45 (s, 3H, CH<sub>3</sub>), 5.8 (s, NH<sub>2</sub>, exchangeable with D<sub>2</sub>O), 7.4 (s, 5H, Ar-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.5, 96.5, 115.8, 116.2, 120.3, 128.7, 128.9, 129.3, 138.3, 147.7, 151.8, 154.51; MS: m/z 232 (M - 1, 100), 218(18), 217(85), 205(85), 191(15), 178(25), 177(25).

**3-Amino-2,4-dicyanobiphenyl 4c:** Yield 49%, mp 149-151 °C. Anal. Calcd for C<sub>14</sub>H<sub>9</sub>N<sub>3</sub>: C, 76.88; H, 4.14; N, 19.17. Found: C, 77.01; H, 4.15; N, 18.82%; IR (KBr): 3410, 3344 (NH<sub>2</sub>), 2208 (CN) cm<sup>-1</sup>; UV (MeOH):  $\lambda_{max}$  355 nm; Flu (MeOH):  $\lambda_{max}$  421 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.7-6.9 (bs, 3H, C<sub>6</sub>-H and NH<sub>2</sub>, exchangeable with D<sub>2</sub>O), 7.5 (s, 5H, Ar-H), 7.8 (d, 1H, C<sub>5</sub>-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  94.9, 95.3, 115.9, 116.4, 117.5, 128.4, 128.7, 129.4, 137.6, 138.0, 153.1; MS: m/z 219(100), 218(55), 192(75), 191(55), 164(50).

**2,6-Dicyano-3-(2-furyl)-5-methylaniline 4d:** Yield 49%, mp 196-198 °C. Anal. Calcd for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>: C, 69.95; H, 4.06; N, 18.82. Found: C, 70.29; H, 4.48; N, 18.42%; IR (KBr): 3408, 3360 (NH<sub>2</sub>), 2224 (CN) cm<sup>-1</sup>;

UV (MeOH):  $\lambda_{\max}$  371 nm; Flu (MeOH):  $\lambda_{\max}$  422 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.5 (s, 3H,  $\text{CH}_3$ ), 6.73 (s,  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ), 6.83 (s,  $\text{C}_4\text{-H}$ ), 7.14 ( $\text{C}_6\text{-H}$ ), 7.42 ( $\text{C}_3\text{-H}$ ) and 8.04 ( $\text{C}_5\text{-H}$ ) (*AMX* pattern);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.9, 87.7, 112.5, 114.6, 115.5, 116.3, 136.0, 145.3, 148.2, 148.8, 153.7; MS:  $m/z$  223(100), 194(30), 180(18), 168(5), 167(5), 166(5), 141(8), 140(20).

**3-Amino-5-(2-chlorophenyl)-2-4-dicyano-1-methylcyclohexa-1,3-diene 5:** Yield 66%, mp 180-182 °C. Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_3\text{Cl}$ : C, 66.79; H, 4.48; N, 15.57. Found: C, 66.91; H, 4.91; N, 15.68%; IR (KBr): 3458, 3312 ( $\text{NH}_2$ ), 2210 (CN)  $\text{cm}^{-1}$ ; UV (MeOH):  $\lambda_{\max}$  350 nm; Flu (MeOH):  $\lambda_{\max}$  414 nm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.2 (s, 3H,  $\text{CH}_3$ ), 2.5-3.0 (2H) and 4.3 (1H *AMX* pattern), 5.6 (bs, 2H  $\text{NH}_2$ , exchangeable with  $\text{D}_2\text{O}$ ), 7.15-7.55 (m, 4H, Ar-H); MS:  $m/z$  269(271) (50), 268(10), 267(15), 254(256)(8), 234(18), 233(5), 232(4), 219(5), 206(5), 205(4), 158(100), 143(20).

#### Acknowledgement

The authors thank UGC (Special Assistance Programme) and DST, New Delhi for financial support, and Dr V Jayathirtha Rao, IICT, Hyderabad for NMR data. The authors are also thankful to Dr P K Das for HRS measurement.

#### References

- 1a Prabahar K J, Ramakrishnan V T, Sastikumar D, Selladurai S & Masilamani V, *Indian J Pure Appl Phys*, 29, 1991, 382.
- 1b Shanmugasundaram P, Prabahar K J & Ramakrishnan V T, *J Heterocycl Chem*, 30, 1993, 1003.
- 1c Shanmugasundaram P, Murugan P & Ramakrishnan V T, *Heteroatom Chem.*, 7, 1996, 17.
- 1d Murugan P, Shanmugasundaram P, Ramakrishnan V T, Venkatachalapathy B, Srividhya N, Ramamurthy P, Gunasekaran K & Velmurugan D, *J Chem Soc Perkin Trans-2*, 1998, 999.
- 1e Srividhya N, Ramamurthy P, Shanmugasundaram P & Ramakrishnan V T, *J Org Chem*, 61, 1996, 5083.
- 2 Meyar M & Mialocq J C, *Opt Commun*, 64, 1987, 264.
- 3a Fatiadi A J, *Synthesis*, 1978, 165; 241.
- 3b Freeman F, *Chem Rev*, 49, 1969, 591.
- 3c Ducker J W & Gunter M J, *Aust J Chem*, 28, 1975, 581.
- 3d Green B, Khaidem I S, Crane R I & Newaz S S, *Tetrahedron*, 32, 1976, 2997.
- 3e Khaidem I S, Singh S L, Singh L R & Rahman Khan M Z, *Indian J Chem*, 35B, 1996, 911.
- 4a Drake N L & Allen P, *Org Syn*, 3, 1923, 17.
- 4b Leuck G J & Cejka L, *Org Syn*, 7, 1927, 42.
- 4c Kohler E P & Chadwell, *Org Syn*, 1, 1922, 2.
- 5a Guggenheim E A, *Trans Faraday Soc*, 45, 1949, 714.
- 5b Guggenheim E A, *Trans Faraday Soc*, 44, 1948, 1007.
- 6a Lippert E, *Z Elektrochem*, 61, 1957, 962.
- 6b Mataga N, Kaifu Y & Kozumi M, *Bull Chem Soc Jpn*, 29, 1956, 465.
- 7 Oudar J L & Chemla D S, *J Chem Phys*, 66, 1977, 2664.
- 8a Mohanalingam K, Ray P C & Das P K, *Synth Metals*, 82, 1996, 47.
- 8b Clays K & Persoons A, *Phys Rev Lett*, 66, 1991, 2980.
- 9 Kurtz S K & Perry T T, *J Appl Phys*, 67, 1968, 3798.
- 10a King F E & Felton D G I, *J Chem Soc*, 1948, 1371.
- 10b Horning E C & Horning M G, *J Org Chem*, 11, 1946, 95.
- 10c Vogel A I, *A text book of practical organic chemistry*, III Edn (ELBS, London) 1948, p. 332.
- 11 Vorlander D & Kallow F, *Ann*, 1899, 309; 356.