Supplementary Material (ESI) for New Journal of Chemistry


# Brightly Shining Nano Particles: Lipophilic Perylene Bisimides in Aqueous Phase

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**Synthesis of 5,5'-di-*tert*-butylindigo (3):**[1]

**4-(1,1'-Dimethylethyl)nitrobenzene:**[2] A mixture of conc. nitric acid (138 mL, 65.3%, density = 1.40 $g \cdot mL^{-1}$, 2.00 mol) and conc. sulphuric acid (218 mL, 98%, density = 1.84 $g \cdot mL^{-1}$, 4.00 mol) was added to 1,1'-dimethylethylbenzene (*tert*-butylbenzene, 310 mL, 268 g, 2.00 mol) with stirring and ice cooling within 1 1/4 h (reaction temp. 25 ... 30°C), stirred at 28°C for 2 h and 1 h at 40°C, pored on crushed ice (1 kg) and extracted three times with toluene (200 mL each). The combined organic phases were washed twice with 5% aqueous $NaHCO_3$ (200 mL each), washed with distilled water (500 mL), evaporated and steam distilled (4 L condensate, separation of the *p*-isomer). The organic phase of the residue was collected and its aqueous phase was three times extracted with toluene (200 mL each). The combined organic phases were dried with magnesium sulphate and evaporated in vacuo. The residue was used without further purification.Yield 251 g (70%), $^1$H NMR ($CDCl_3$/TMS): $\delta$ = 1.3 (s, 9 H, *tert*-butyl), 7.4 (d, $J$ = 8 Hz, 2 H, 2-H and 6-H), 7.95 (d, $J$ = 8 Hz, 2 H, 3-H and 5-H).

**4-(1,1'-Dimethylethyl)aminobenzene:**[2b,3] Conc. hydrochloric acid (5.2 mL) in ethanol (25 mL, 50%) was added dropwise with heating and mechanical stirring within 1 h to 4-(1,1'-dimethylethyl)nitrobenzene (89.6 g, 500 mmol) and iron powder (85 g, 1.5 mol) in ethanol (100 mL 50%, reflux), vigorously stirred under reflux for further 2 h, still warm neutralised with a solution of KOH (85%, 3.5 g, 53 mmol) and ethanol (20 mL), filtered and washed twice with ethanol (96%, 50 mL each). The combined organic phases were distilled in vacuo. Yield 61.1 g (82%), b.p. 111-113°C/12-13 Torr (ref. 134°C/35 Torr and 234-235°C/760 Torr); $^1$H NMR: $\delta$ = 1.2 (s, 9 H, *tert*-butyl), 3.3 (s, 2 H, $NH_2$), 6.45 (d, 2 H, $J$ = 8 Hz, 2-H and 6-H), 7.0 (d, 2 H, $J$ = 8 Hz, 3-H and 5-H).

**6-(1,1'-Dimethylethyl)-4-hydroxy-2(1 *H*)quinoline:**[4] Malonic acid (45.8 g, 440 mmol) was dissolved with stirring and warming in a mixture of *p-tert*-butylaniline 29.9 g (200 mmol) and 1,4-dioxane (60 mL), treated within 10 min with phosphoroxychloride (60 mL, foaming and warming to 80°C), refluxed for 30 min (HCl evolution), allowed to cool, versed into distilled water (1 L), heated at 80°C for 30 min,

collected by vacuum filtration and treated three times with 2 N NaOH. The collected alkaline aqueous phases were acidified with 2 N HCl to *pH* 1…2 and the solid collected by vacuum filtration, extracted with refluxing toluene (50 mL) and then with refluxing 1,4-dioxane (300 mL) and dried in air. Yield 7.0 g (16%); IR (KBr): $\tilde{\nu}$ = 3420 w, 3177 w, 2964 m, 2905 w, 2870 w, 1654 s, 1616 s, 1605 s, 1559 w, 1506 w, 1476 w, 1464 w, 1437 w, 1365 m, 1349 w, 1316 m, 1274 w, 1241 m, 1127 w, 828 $cm^{-1}$ m.

**3,3-Dichlor-6-(1,1'-dimethylethyl)-2,4-dioxo-1,2,3,4-tetrahydroquinoline:**[4] Sulfurylchloride (7.0 mL (11.7 g, 86.5 mmol) was added dropwise with stirring to finely powdered 6-(1,1'-dimethylethyl)-4-hydroxy-2(1 *H*)quinoline (5.50 g, 25.3 mmol) in 1,4-dioxane (18 mL), briefly refluxed, allowed to cool, treated with ice (10 g), collected by vacuum filtration (yellow crystals), four times washed with toluene, crystallized from toluene and dried in medium vacuum for 2 h. Yield 1.85 g (26%), m.p. 211-212°C; IR (KBr): $\tilde{\nu}$ = 3135 w, 3083 w, 2963 s, 2906 w, 1732 s, 1722 s, 1692 s, 1614 s, 1507 m, 1501 m, 1415 w, 1368 m, 1352 w, 888 w, 844 m, 822 w, 744 w, 736 m, 668 w, 622 $cm^{-1}$ w; $^1$H NMR: $\delta$= 1.3 (s, 9 H, *tert*-butyl), 7.05 (d, *J* = 8 Hz, 1 H, aromat. 8-H), 7.6 (dd, *J* = 8 Hz, *J* =2 Hz, 1 H, aromat. 7-H), 7.95 (d, *J* = 2 Hz, 1 H, aromat. 5-H), 9.6 (s, 1 H, -NH).

**5,5'-Di-*tert*-butylindigo (2):**[4] 3,3-Dichlor-6-(1,1'-dimethylethyl)-2,4-dioxo-1,2,3,4-tetra-hydroquinoline (7.0 g, 32 mmol) in anhydrous methanol (20 mL) was added to a solution of sodium metal (2.1 g) in anhydrous methanol (21 mL, vigorous reaction, colour change to orange), refluxed for 5 min and treated with 1 N NaOH (70 mL, yellow precipitate). Methanol was removed by distillation until a b.p. of 100°C. The residue was refluxed for further 50 min, treated with conc. HCl (40 mL) and ethanol (14 mL, bluish black precipitate) allowed to cool and to stand for 16 h, collected by vacuum filtration, washed two times with warm 10% HCl, crystallised from 1,4-dioxane (40 mL) and dried in medium vacuum. A second fraction could be obtaind from the mother liquor. Yield 450 mg (7.5 %), m.p. >250°C; $R_f$ (silica gel/$CHCl_3$) = 0.60; IR (KBr): $\tilde{\nu}$ = 3362 s, 2961 s, 1634 s, 1589 m, 1485 s, 1462 m, 1443 m, 1404 m, 1365 w, 1312 m, 1285 m, 1256 m, 1191 s, 1147 m, 1125 s, 1101 s, 1064 m, 835 m, 656 m, 602 $cm^{-1}$ m; $^1$H NMR ($CDCl_3$/TMS): $\delta$= 1.3 (s, 18 H, 2 x *tert*-butyl), 6.9-7.7 (m, 6 H, aromat. H), 8.75 (s, 2 H, NH). For solvatochromism of **2** see Table 1.

**Synthesis of 6,6'-di-*tert*-butylindigo (3)[5]:**

**4-(1,1'-Dimethylethyl)-2-nitrobenzene:**[4,6] 4-(1,1'-Dimethylethyl)methylbenzene (*p*-*tert*-butyltoluene, 263 mL, 224 g, 1.51 mol) was added dropwise with cooling at 5…10°C within 4 h to a mixture of conc. $HNO_3$ (170 mL) and conc. $H_2SO_4$ (210 mL), stirred at 5 …10°C for 75 min and versed on ice. The reddish black organic phase was collected and the yellow aqueous phase was extracted six times with low boiling petroleum ether. The combined organic phases were washed three times with distilled water,

five times with 5% aqueous $NaHCO_3$, dried with sodium sulphate, evaporated an distilled in vacuo. Yield 93.4 g (32.2%) yellow oil, b.p 149-151°C/18-19 Torr (ref. 140°C/15 Torr); $^1$H NMR ($CDCl_3$/TMS): $\delta$= 1.3 (s, 9 H, *tert*-butyl); 2.5 (s, 3 H, methyl); 7.1 (d, $J_{5,6}$ = 8 Hz (1 H, aromat. 6-H); 7.4,(dd, $J_{3,5}$ = 2 Hz, $J_{5,6}$ = 8 Hz, 1 H, aromat. 5-H); 7.8 , d, $J_{3,5}$ = 2 Hz, 1 H, aromat. 3-H).

**4-(1,1-Dimethylethyl)-2-nitrobenzaldehyd:**[4,6] Ice cold conc. $H_2SO_4$ (40 mL) and an ice cold solution of $CrO_3$ (50.0 g, 500 mmol) in acetanhydride (200 mL) were simultaneously added dropwise within 75 min to a mechanically stirred solution of 4-*tert*-butyl-2-nitrotoluene (40.0 g, 207 mmol) in acetanhydride (220 mL) so that the temperature does not exceeds 10°C, stirred for 180 min at 5…10°C, versed on ice, diluted with distilled water (3 L) and extracted with diethyl ether (three times, 200 mL each). The combined ether phases were washed with saturated $Na_2CO_3$, dried with $MgSO_4$, filtrated, evaporated (diacetate), refluxed with a mixture of conc. HCl (150 mL), distilled water (175 mL) and ethanol (100 mL) for 1 h and extracted with toluene (500 mL in three portions). The combined organic phases were dried with $Na_2SO_4$, filtrated, evaporated in vacuo (33 g, 78% ) and distilled in medium vacuum Yield 21.7 g (51%) b.p. 110-120°C/3-4 Torr; $^1$H NMR ($CDCl_3$) of the diacetate: $\delta$= 1.4 (s, 9 H, *tert*-butyl), 2.1 (s, 6 H, O-CO-$CH_3$), 7.65 (s) and 7.9-8.0 (d) (3 H, aromatic H); $^1$H NMR ($CDCl_3$) of the aldehyde: $\delta$= 1.4 (s, 9 H, *tert*-butyl), 7.7 (s, 2 H, aromat. 5-H und 6-H), 8.0 (s, 1 H, aromat. 3-H), 10.15 (s, 1 H, aldehyde-H). The aldehyde reacts spontaneously with $Na_2S_2O_5$ (4 g) in water (6 ml).

**6,6'-Di-*tert*-butylindigo (3):**[4,7] A mixture of 0.4 N NaOH (125 mL) and acetone (25 mL) was added dropwise to the yellow suspension of 4-(1,1-dimethylethyl)-2-nitrobenzaldehyde (10.1 g, 0.0483 mol) in acetone (60 mL) and distilled water (30 mL); *pH* change to 10…11, allowed to stand for 2 d, collected by vacuum filtration (bluish black solid), thoroughly washed with distilled water, extractively[8] crystallised from methanol (120 mL) and dried in a vaccum dissicator over phorphorpentoxide. The product is soluble in acetic acid, toluene, chloroform and diethylether, medium soluble in ethanol, sparingly soluble in methanol and insoluble in water. Yield 2.18 g (12%); $R_f$ (silica gel/$CHCl_3$) = 0.72; IR (KBr): $\tilde{\nu}$ = 3333 m, 2963 m, 1635 s, 1616 s, 1582 m, 1496 w, 1441 s, 1390 w, 1324 m, 1284 m, 1232 m, 1204 m, 1149 s, 1121 m, 1085 s, 1070 m, 928 m, 706 m, 604 m, 550 $cm^{-1}$ w; $^1$H NMR ($CDCl_3$/TMS): $\delta$= 1.3 (s, 18 H, 2 x *tert*-butyl), 6.9 bis 7.8 (m, 6 H, aromat. H), 8.85 (s, 2 H, -NH). For solvatochromism of **3** see Table 1.

**Table 1**. Solvatochromism of indigo derivatives: Absorption maximum ($\lambda$) in nm and difference ($\Delta\lambda$) between 5,5'- (**2**) and 6,6'-di-*tert*-butylindigo (**3**) in various solvents.

| Solvents | **2** $\lambda$ in nm | **3** $\lambda$ in nm | $\Delta\lambda$ in nm |
|---|---|---|---|
| Cyclohexane | 583.65 | 599.3 | 15.65 |
| $C_2Cl_4$ | 591.75 | 606.8 | 15.05 |
| Mesitylene | 592.3 | 607.9 | 15.6 |
| *m*-Xylene | 593.9 | 609.3 | 15.4 |
| *o*-Xylene | 595.1 | 610.45 | 15.35 |
| Toluene | 595.55 | 610.0 | 15.35 |
| Benzene | 596.95 | 612.0 | 15.05 |
| 1-Methylnaphthalene | 603.8 | 619.1 | 15.3 |
| $CCl_4$ | 590.6 | 607.0 | 16.4 |
| 1,2-Dichloroethane | 594.95 | 611.5 | 16.55 |
| Dichloromethane | 595.5 | 612.15 | 16.65 |
| *p*-Xylene | 596.0 | 613.8 | 17.8 |

**Characterisation of technical Bomol-4N**

For the spectroscopic characterisation of Bomol-4N see Figs. 1 …6.

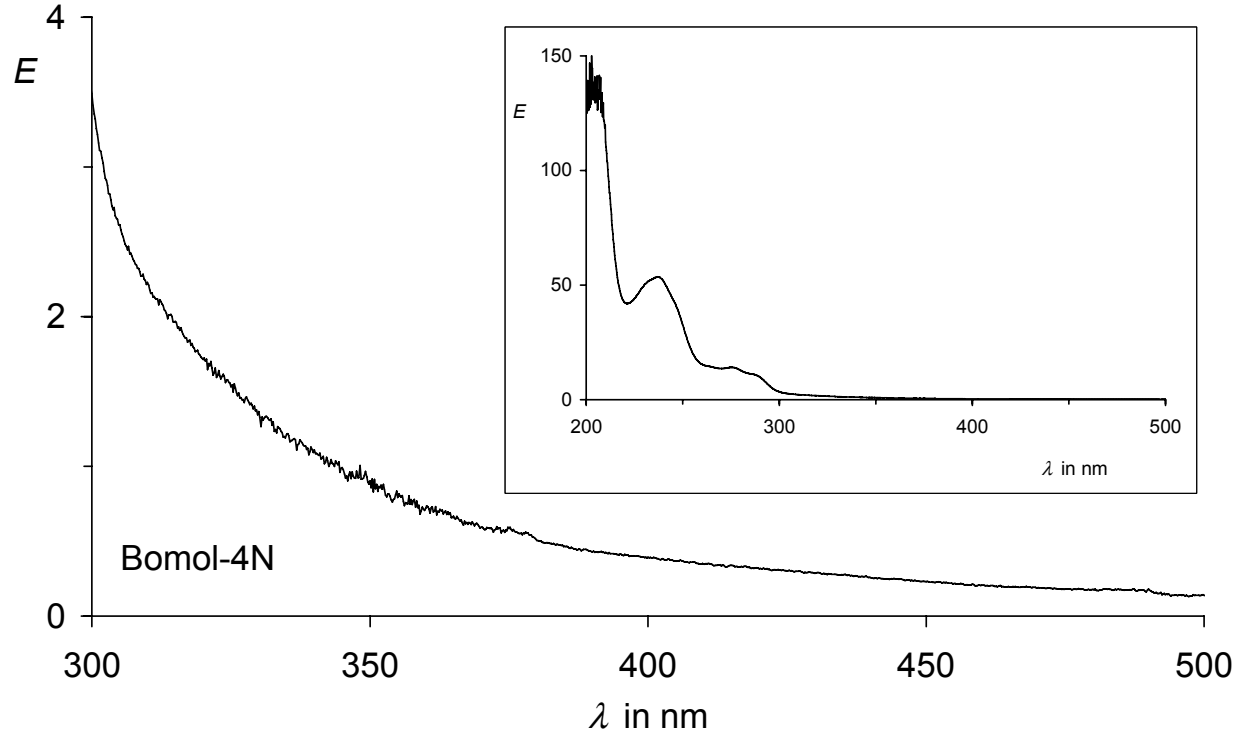



**Fig. 1**. UV/Vis absorption spectrum of Bomol-4N versus water (1 cm path lengths). Insert: Extension of the spectrum calculated from measurements with smaller path lengths.

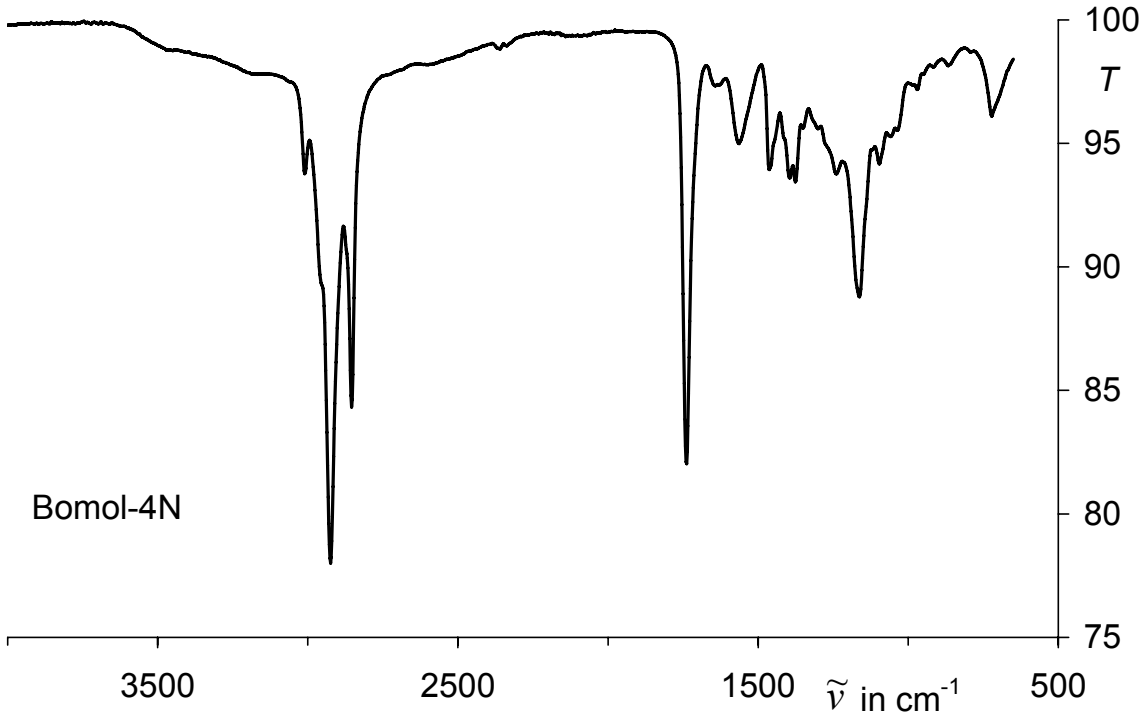



**Fig. 2**. Infrared spectrum of Bomol-4N (neat).

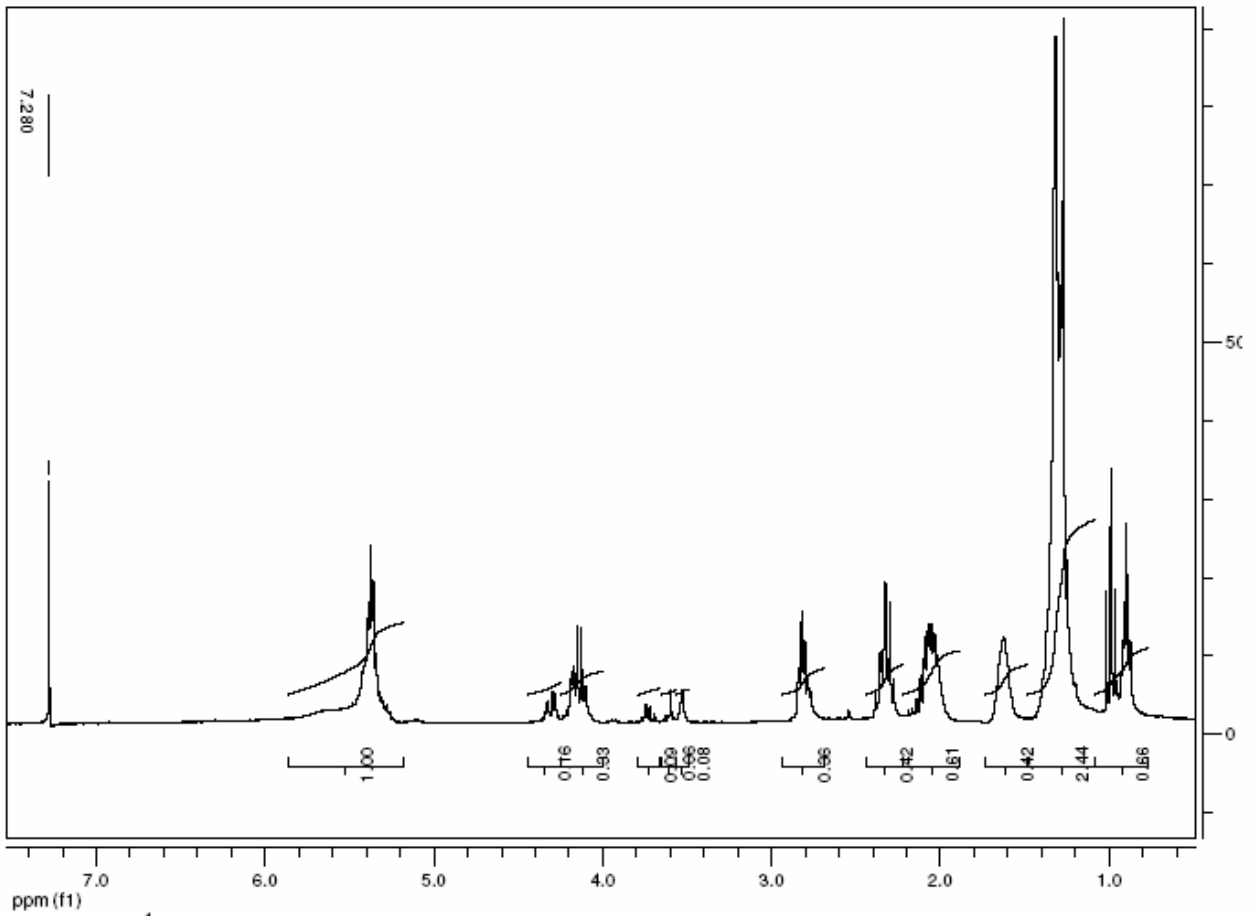



**Fig. 3**. $^{1}$H NMR spectrum of Bomol-4N (300 MHz, $CDCl_3$), reference $CHCl_3$ at $\delta$= 7.28).

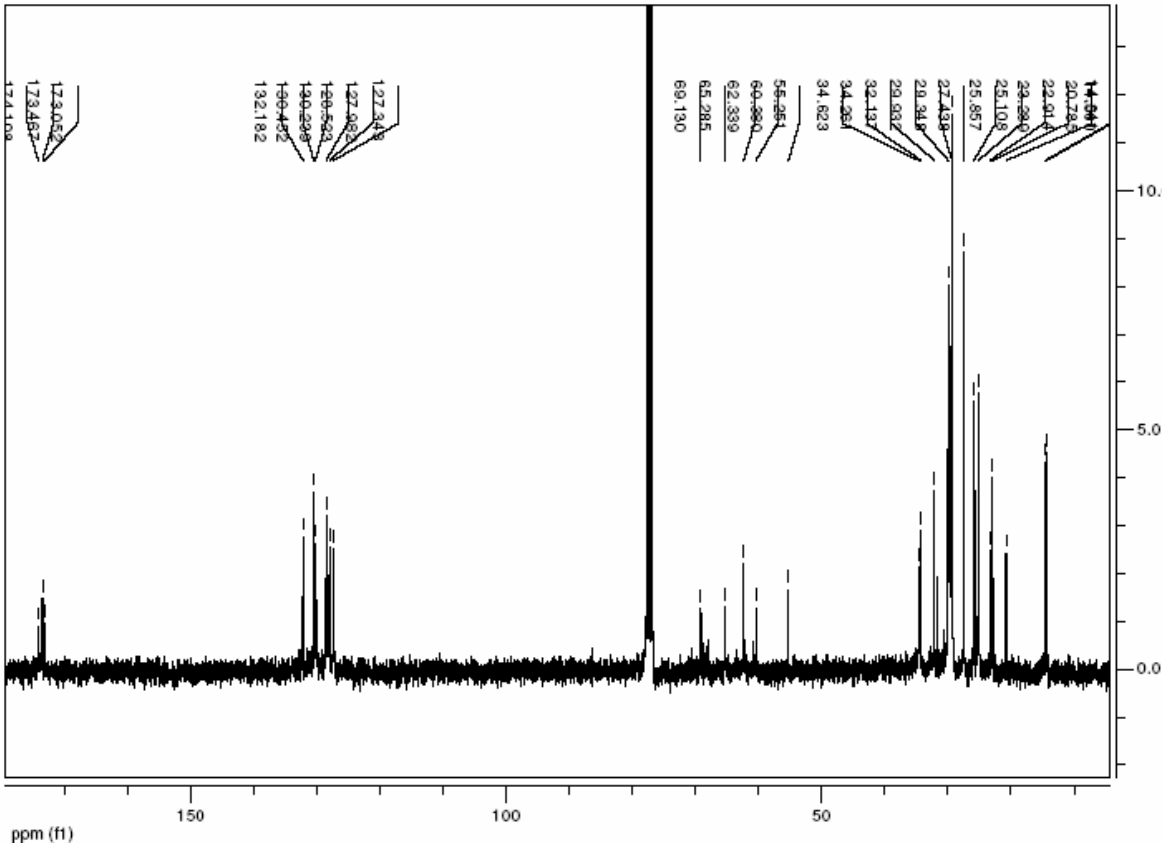



**Fig. 4**. $^{13}C$ NMR spectrum of Bomol-4N (75 MHz, $CDCl_3$)).

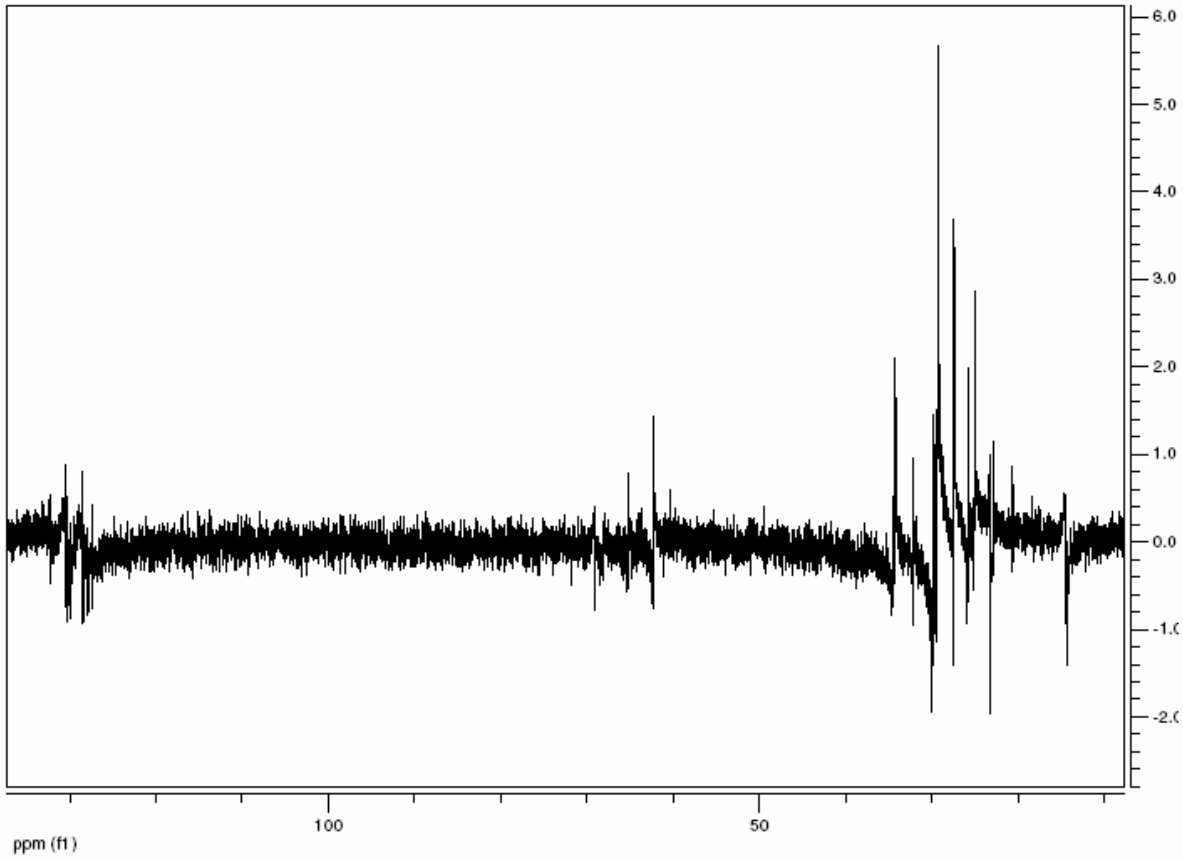
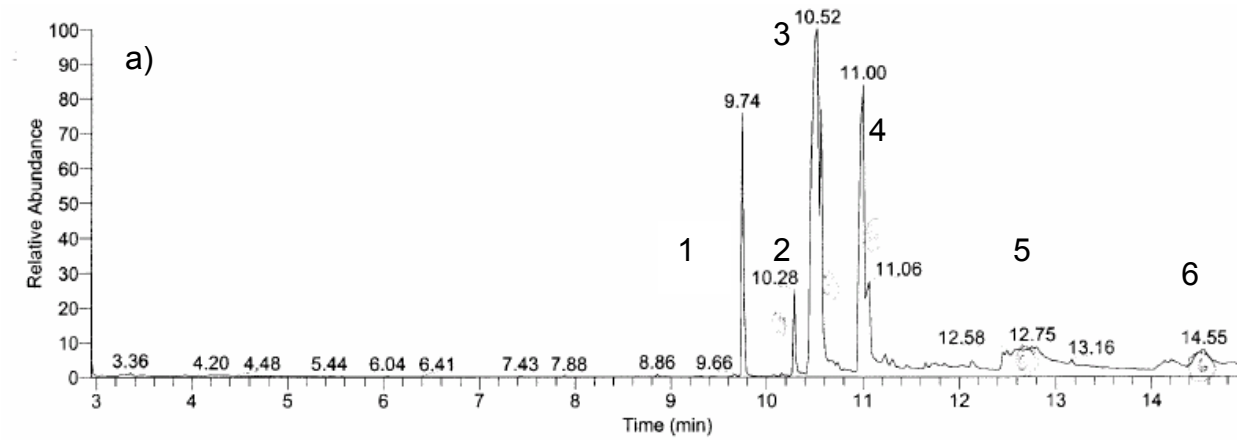
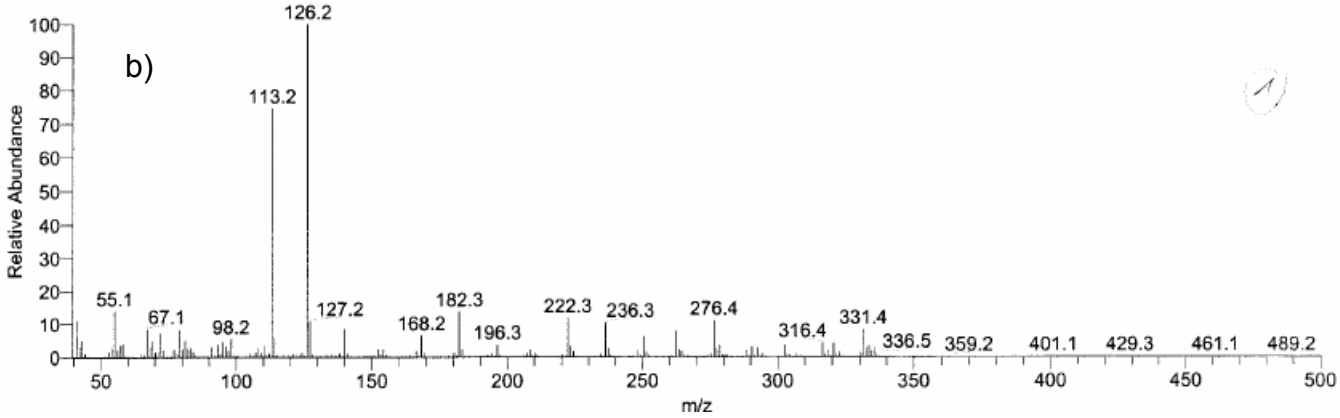



**Fig. 5**. $^{13}C$ NMR DEPT spectrum of Bomol-4N (75 MHz, $CDCl_3$).


a)
Relative Abundance
Time (min)
1
2
3
4
5
6
9.74
10.28
10.52
11.00
11.06
12.58
12.75
13.16
14.55
3.36
4.20
4.48
5.44
6.04
6.41
7.43
7.88
8.86
9.66


b)
Relative Abundance
m/z
126.2
113.2
55.1
67.1
98.2
127.2
168.2
182.3
196.3
222.3
236.3
276.4
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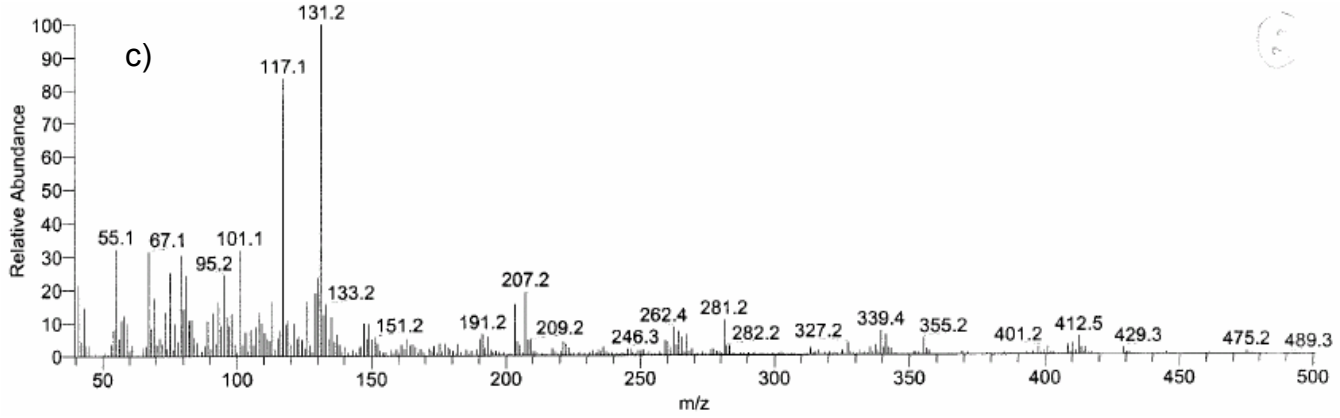
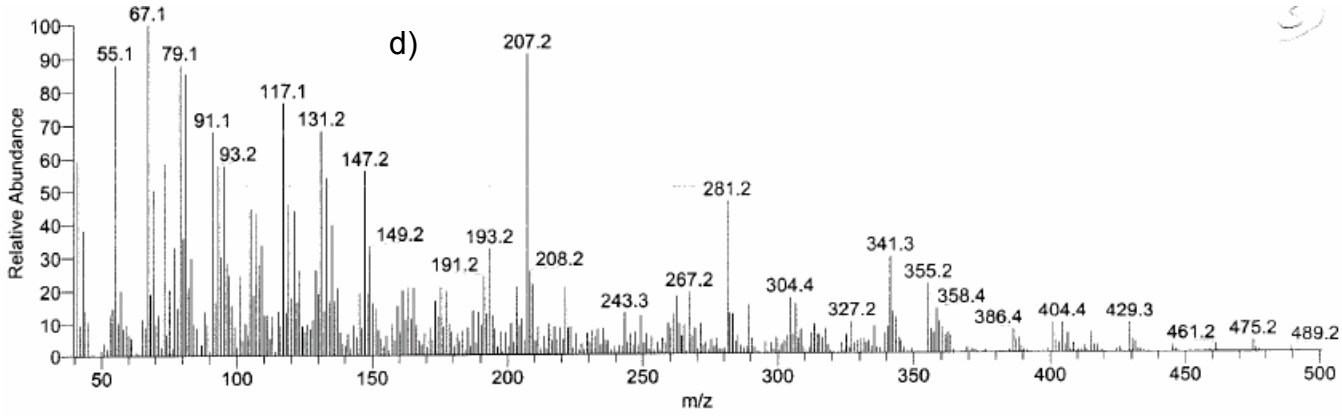
336.5
359.2
401.1
429.3
461.1
489.2


c)
Relative Abundance
m/z
131.2
117.1
55.1
67.1
101.1
95.2
133.2
151.2
191.2
207.2
209.2
246.3
262.4
281.2
282.2
327.2
339.4
355.2
401.2
412.5
429.3
475.2
489.3


d)
Relative Abundance
m/z
67.1
55.1
79.1
91.1
93.2
117.1
131.2
147.2
149.2
191.2
193.2
207.2
208.2
243.3
267.2
281.2
304.4
327.2
341.3
355.2
358.4
386.4
404.4
429.3
461.2
475.2
489.2

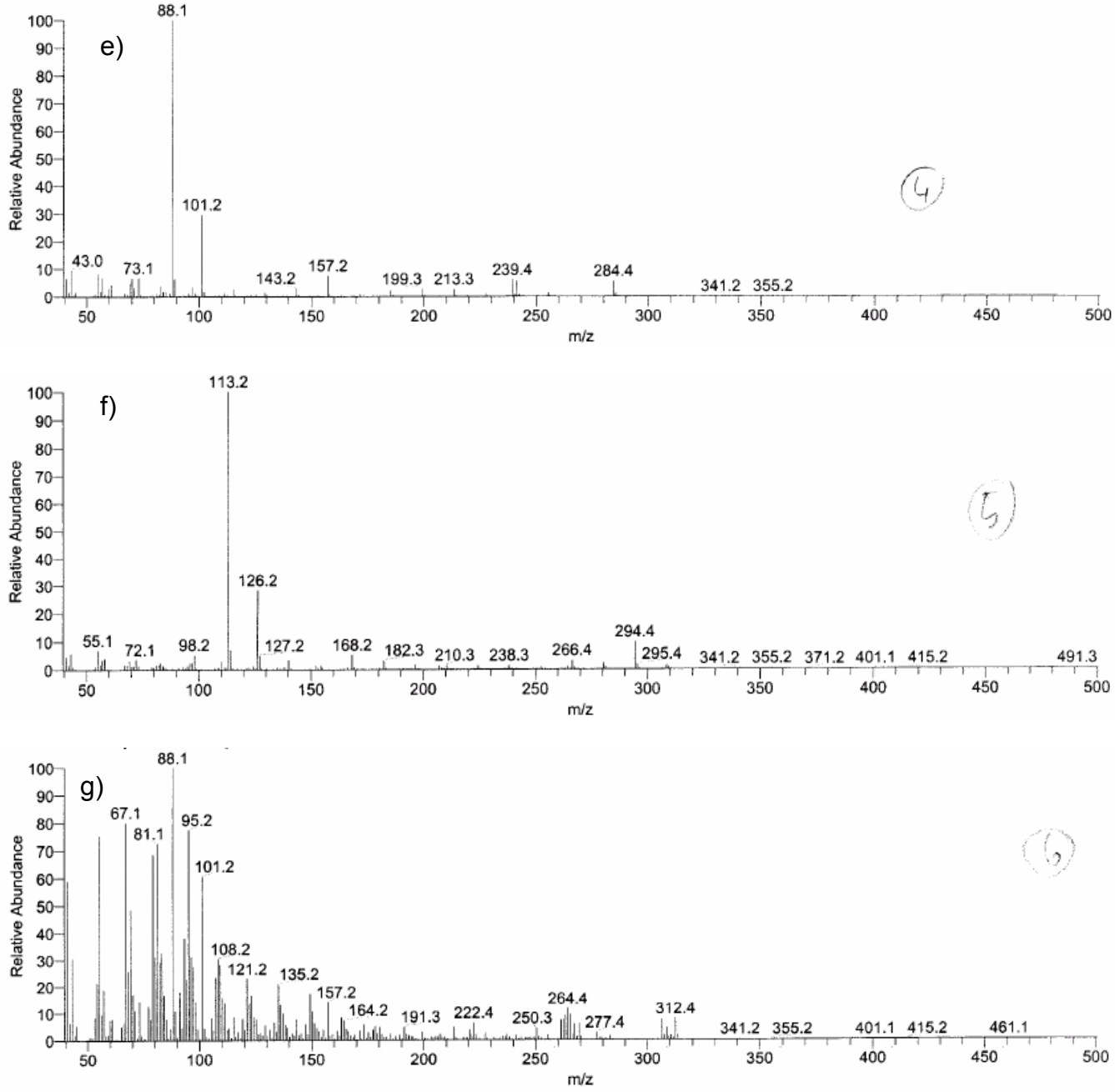



**Fig. 6.** Mass spectrum of Bomol-4N. a) CS Supreme 5, 50 …300°C, 25°C·min$^{-1}$. b) Full EI MS of peak 1. c) Full EI MS of peak 2. d) Full EI MS of peak 3. e) Full EI MS of peak 4. f) Full EI MS of peak 5. g) Full EI MS of peak 6.

**Density (pyknom.):** $\rho^{20}$ = 0.984 g·cm$^{-3}$. **Index of refraction:** $n_D^{20}$ = 1.488.

**Elemental analysis of Bomol-4N.** Found: C 71.71, H 10.57, N 1.13.

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