Photochemical reactions of 1-naphthylamines and haloforms: formation of bis(4-amino-1-naphthyl)methylium salts with remarkably long-wave electronic absorption

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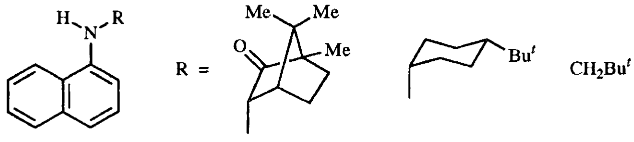
The photochemical colour change from colourless to green of *N*-substituted 1-naphthylamines 1a–c in CH_2Cl_2 containing a haloform was found to be irreversible, although optically active 3-(1-naphthylamino)camphor 1a had been reported to exhibit reversible photochromism in $CHCl_3$. Irradiation of *N*-(*cis*-4-*tert*-butylcyclohexyl)-1-naphthylamine 1b with CHI_3 in hexane gave bis-1,1′-[4,4′-(*N*-*cis*-4-*tert*-butylcyclohexyl)aminonaphthyl]methylium triiodide as green needles and *N*-(*cis*-4-*tert*-butylcyclohexyl)-1-naphthylamine hydroiodide as colourless crystals. A plausible pathway for the photochemical reaction of the *N*-substituted 1-naphthylamines with a haloform, which is initiated by electron-transfer from the nitrogen in the amines to the haloform followed by radical reactions which liberate hydrogen halide, is proposed.

The photochromic colour change of optically active 3-(1-naphthylamino) camphor **1a** has been described by Singh and his co-workers.[1,2] The colour of the chloroform solution of **1a** changes from colourless to green on exposure to sunlight accompanying a change in the optical rotation. It was suggested that the green colour might be related to the quinhydrone-like combination of the keto and enol forms of the camphor moiety. An alternative suggestion was that the coloured species might be photoionized carbinol or halide derived from a bi- or tri-naphthylmethane intermediate, which had been produced by the condensation of the substrate and solvent with liberation of hydrogen halide.[3] However, the structure of the coloured species has not been determined unambiguously. Since we have been interested in the mechanisms for various photochromic colour changes,[4] we reinvestigated the photochemical behaviour of **1a** in chloroform to reveal the mechanism of the photocolour change. Not only **1a** but also various aryl- or alkyl-substituted 1-naphthylamines and even 1-naphthylamine itself were found to show colour changes upon irradiation with $CHCl_3$, $CHBr_3$ or CHI_3. In this paper we describe isolation and identification of photoproducts from *N*-(*cis*-4-*tert*-butylcyclohexyl)-1-naphthylamine **1b** and *N*-neopentyl-1-naphthylamine **1c** upon reaction with CHI_3 and propose a pathway for the formation of the photoproducts.

Results and discussion

Irradiation of 3-*endo*-(1-naphthylamino)camphor† **1a**[5] with $CHCl_3$ in CH_2Cl_2 gave a green solution together with a new UV absorption band at 680 nm showing two isosbestic points.[6] After the absorbance of the new band had been maximized, the irradiation was stopped and the solution was left in the dark. Although the green colour gradually disappeared, the absorption spectrum failed to revert to that observed before irradiation; this indicated that the colour change of **1a** is not reversible photochromism. Irradiation with $CHCl_3$ in CH_2Cl_2 of compounds containing a bornyl or norbornyl group on the nitrogen instead of a carbonyl-containing camphoryl group also gave rise to green solutions and changes in the absorption spectra. This observation rules out the involvement of the carbonyl group in **1a** with the photocolouration.



1a–c **a** **b** **c**

In order to isolate a pure specimen of the green photoproduct for the purposes of structure determination, we photoirradiated a variety of naphthylamines and haloforms in several solvents. Irradiation of equimolar amounts of **1b** and CHI_3 in hexane under nitrogen gave deposition of a deep-green product on the inside wall of the reaction vessel. This was collected by filtration, repeatedly washed with hexane and dried *in vacuo*. The green solid **Gb** was insoluble in non-polar solvents (hexane or benzene) but dissolved in polar ones (EtOH, MeOH, $CHCl_3$ or CH_2Cl_2). The ^1H NMR spectrum of **Gb** measured in $CDCl_3$ was similar to that of **1b** except for the following differences. (1) Almost all the signals were shifted to lower field. (2) Two types of NH protons appeared at δ 6.62 (δ 4.52 for **1b**) and δ 10.21. (3) A new characteristic singlet signal appeared at δ 9.35. (4) Naphthyl ring proton signals appeared as two sets which overlapped. These observations suggested that **Gb** was a mixture containing at least two products and, indeed by differential dissolution of the compound in ethanol, two components, a deep-green solid and colourless crystals, were obtained; the former was the less soluble component. Recrystallization of the green solid from $CHCl_3$ gave deep-green needles of **2b**. In its ^1H NMR spectrum an AX system and a four-spin system due to six protons on the 1,4-disubstituted naphthalene were observed. These signals were assigned on the basis of the ^1H-^1H COSY experiment and NOE effects observed between NH and 5-H and between CH= and 8-H. The ^{13}C NMR spectrum showed 10 carbon atoms in the naphthyl ring as well as a methine carbon attached to the 1-position in aromatic region. These spectral characteristics together with elemental analytical results support identification of the green product **2b** as bis-1,1′-[4,4′-(*cis*-4-*tert*-butylcyclohexylamino)-naphthyl]methylium triiodide. The UV–VIS spectrum of **2b** in

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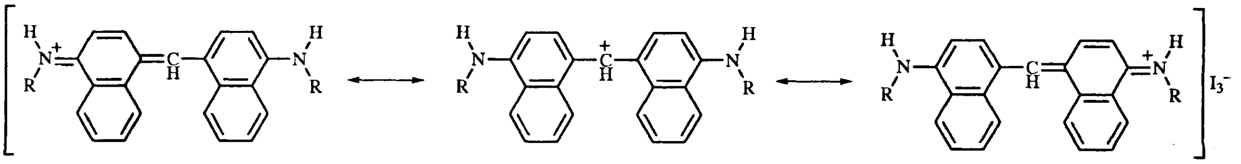
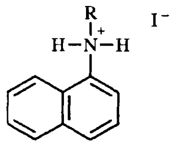
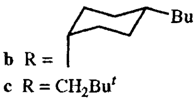
† The stereochemistry of **1a** was determined to be *endo* form by means of X-ray structure determination.[5]



2b, c



3b, c



b R =
c R = CH_2Bu^t

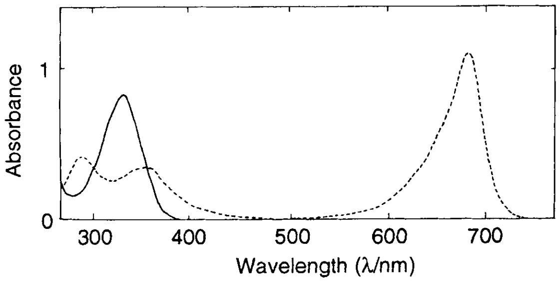
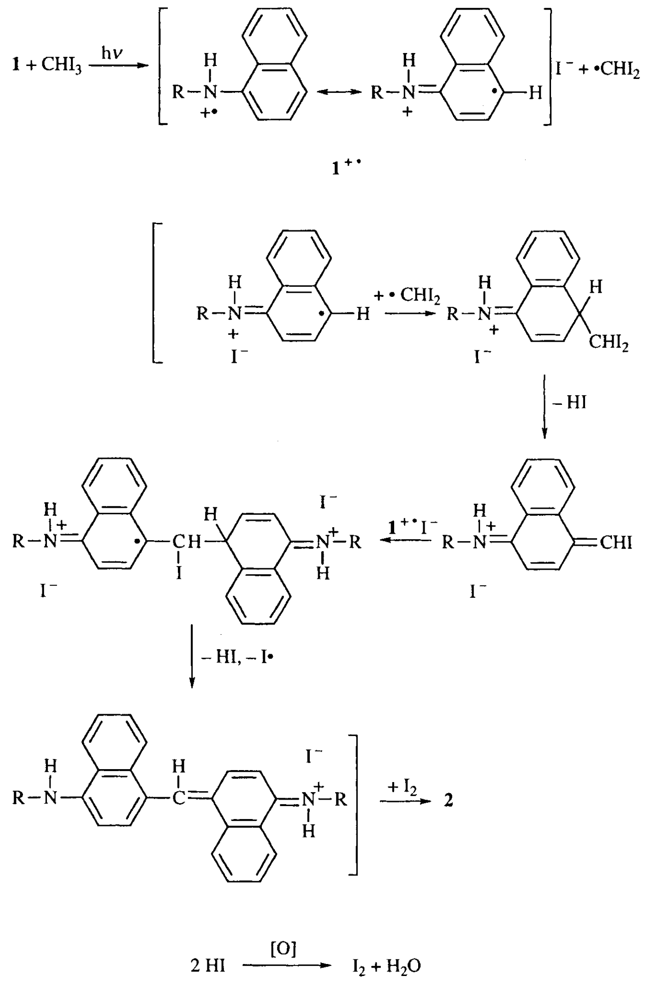


Fig. 1 The absorption spectra of **1b** (——; 2.25 × 10^{-4} mol dm^{-3}) and **2b** (– – –; 1.27 × 10^{-5} mol dm^{-3}) in $CHCl_3$

$CHCl_3$ (Fig. 1) shows intense long-wave absorption at 680 nm (ε_{max} 1.3 × 10^5 dm^3 mol^{-1} cm^{-1}) arising from the extended resonance hybrid structure. Hallas *et al.* reported that the bis(4-dimethylamino-1-naphthyl)methylium cation showed absorption at 692 nm in acetic acid solution but the molar absorptivity was rather low;[7] they also prepared tris(4-dimethylamino-1-naphthyl)methylium.[7] In the present work, no trinaphthyl-substituted cation was formed. The methine group in **2b** is considered to arise from CHI_3. To confirm this a photochemical reaction similar to that of **1b** and CHI_3 was carried out with **1b** and CDI_3, the latter prepared from [$^2H_6$]acetone and KI. The ^1H NMR spectrum of the deep-green product corresponded to that of **2b** except that there was no signal at δ 9.35 for a methine proton.

The other product **3b**, with greater solubility in ethanol than **2b**, repeatedly recrystallised from ethanol–hexane to colourless crystals. From a comparison of its spectral data with those of the hydroiodic acid salt of **1b** prepared independently, **3b** was identified as *N*-(*cis*-4-*tert*-butylcyclohexyl)-1-naphthylamine hydroiodide. The photochemical reaction of **1b** and $CHBr_3$ or $CHCl_3$ in hexane under nitrogen was carried out as in the case of CHI_3. Green precipitates were given in both cases the UV and ^1H NMR spectra of which showed the formation of salts corresponding to **2b**, although in amounts too small to allow their isolation. The *trans* isomer of **1b**, which was a minor product on the reductive condensation of 1-naphthylamine and 4-*tert*-butylcyclohexanone (see Experimental section), was irradiated in hexane in the presence of a haloform. Similar colouration and spectral changes to those observed with the *cis* form were noted.

Irradiation of equimolar proportions of *N*-neopentyl-1-naphthylamine **1c** and CHI_3 in hexane under nitrogen also gave a green precipitate **Gc**. The absorption spectrum of **Gc** in CH_2Cl_2 was similar to that of **Gb**, and its ^1H NMR spectrum obtained in $CDCl_3$ showed that it too was a mixture of two components. By differential dissolution of the mixture in $CHCl_3$, less-soluble, green plate-like crystals of **2c** and colourless crystals of **3c** were obtained. From ^1H and ^{13}C NMR spectral results and the analytical data for **2c** the compound was identified as bis-1,1′-(4,4′-neopentylaminonaphthyl)methylium triiodide, while **3c** was identified as *N*-neopentyl-1-naphthylamine hydroiodide, by a comparison of its IR and ^1H NMR spectral results with those of an authentic sample prepared from **1c** and hydroiodic acid.



Scheme 1

The photochemical reaction of **1b** and CHI_3 in degassed hexane was monitored by means of ESR spectroscopy. Upon irradiation of the solution a weak ESR signal (*g* 2.0043) appeared which was consistent with colouration and formation of a radical species. When irradiation was stopped the ESR signal was significantly decreased, and it completely disappeared on exposure of the solution to the air. A photoreaction between **1** and CHI_3 in which the mixture was exposed to the air gave both compounds **2** and **3** as in the experiment carried out under nitrogen; the isolated yields of **2** and **3** from **1b** and **1c** are shown in Table 1. From the Table the ratio **2**/**3** is larger in the presence of oxygen than that under nitrogen; this suggests that some oxidation step(s) is probably involved in the formation of **2**.

From these observations we suggest a reaction pathway as

Table 1 Isolated yields (%) of **2** and **3**

Compd.	Atmosphere	**2**	**3**	**2**/**3**
1b	N_2	25.3	41.8	0.6
1b	Air	19.8	15.5	1.3
1c	N_2	16.7	23.2	0.8
1c	Air	19	2.3	8.3

shown in Scheme 1. In the initial stage of the photoreaction an electron transfer occurs from the excited-state in the naphthylamino substituent nitrogen to CHI_3 to give $\mathbf{1}^{+\bullet}$ and a diiodomethyl radical.[8,9] The path then involves radical coupling of $\mathbf{1}^{+\bullet}$ and a diiodomethyl radical followed by elimination of two molecules of hydrogen iodide. The eliminated hydrogen iodide would then be employed to form **3** (**1**·HI) or transformed to I_2 by oxidation with molecular oxygen, which contributes to the formation of I_3^- in **2**. This mechanism accounts for the ratio of **2**/**3** in the product being larger for reactions carried out in the presence of oxygen than those carried out under nitrogen.

Experimental

Absorption spectra were recorded on a Shimadzu UV240 spectrophotometer. ^1H (270 MHz) and ^{13}C (67.5 MHz) NMR spectra were obtained on a JEOL JNM-GX270 spectrometer in $CDCl_3$ solution unless otherwise noted. *J* Values are given in Hz. IR spectra were taken on a JASCO A-302 spectrometer as KBr disks. Mass spectra (EI, 70 eV) were recorded on a JEOL JMS-DX300 spectrometer. ESR spectra were obtained on a JEOL JES-FE2XG spectrometer. Melting points were obtained with a Yanaco micro-apparatus and uncorrected. Solvent used for measurement of absorption spectra was of spectroscopic grade. Other solvents were dried as usual.

Materials

***N*-(*cis*-4-*tert*-Butylcyclohexyl)-1-naphthylamine 1b.** 1-Naphthylamine (1.67 g, 11.7 mmol) and 4-*tert*-butylcyclohexanone (2.03 g, 13.2 mmol) were treated with a catalytic amount of PtO_2 in dry cyclohexane (5 cm^3) under a H_2 atmosphere (2 kg cm^{-2}). After the catalyst had been filtered off, the filtrate was evaporated under reduced pressure to give an oily residue which was chromatographed on silica gel with hexane–diethyl ether (20 : 1) as eluent to give **1b** (2.09 g, 63%) as the first fraction followed by the *trans* isomer (118 mg, 5.4%). The stereochemistry was determined on the basis of the ^1H and ^{13}C chemical shifts. In the *trans* isomer in which the naphthylamino group is equatorially linked, all the carbon signals in the cyclohexane moiety appear at lower field than the corresponding signals of the *cis* isomer with the 1′-H signal being shifted to higher field.

Compound **1b** formed colourless needles; mp 55–56 °C (hexane); ν_{max}/cm^{-1} 3460 (ν_{NH}); δ_H 0.89 (9 H, s, 3 × Me), 1.10 (1 H, tt, *J* 11.7, 3.2, 4′-H), 1.2–1.4 (2 H, m, 3′,5′-H_{ax}), 1.5–1.7 (4 H, m, 2′-, 6′-H_{ax} and 3′,5′-H_{eq}), 2.1 (2 H, m, 2′-, 6′-H_{eq}), 3.86 (1 H, br s, 1′-H), 4.52 (1 H, br s, NH), 6.61 (1 H, d, *J* 7.8, 2-H), 7.19 (1 H, d, *J* 7.8, 4-H), 7.33 (1 H, t, *J* 7.8, 3-H), 7.4 (2 H, m, 6-H and 7-H) and 7.8 (2 H, m, 5-H and 8-H); δ_C 21.88 (C-3′,5′), 27.51 (3 × Me), 30.31 (C-2′,6′), 32.57 (*C*Me$_3$), 46.83 (C-4′), 47.99 (C-1′), 104.84 (C-2), 116.57 (C-4), 119.64 (C-8), 123.61 (C-4a), 124.57 (C-7), 125.59 (C-6), 126.74 (C-3), 128.80 (C-5), 134.63 (C-8a) and 142.35 (C-1); *m*/*z* 281 (M^+; 65%), 182 (100), 168 (12) and 143 (57) (Found: C, 85.2; H, 9.8; N, 5.0. Calc. for $C_{20}H_{27}N$: C, 85.4; H, 9.7; N, 5.0%).

The *trans*-isomer had mp 131 °C; ν_{max}/cm^{-1} 3440 (ν_{NH}); δ_H 0.91 (9 H, s, 3 × Me), 1.29–1.36 (5 H, m, 2′-, 6′-H_{ax}, 3′-, 5′-H_{ax} and 4′-H), 1.77–1.97 (2 H, m, 3′-, 5′-H_{eq}), 2.25–2.4 (2 H, m, 2′-, 6′-H_{eq}), 3.38 (1 H, br s, 1′-H), 4.22 (1 H, br, NH), 6.65 (1 H, d, *J* 8, 2-H), 7.20 (1 H, d, *J* 8, 4-H), 7.34 (1 H, t, *J* 8, 3-H), 7.41–7.44 (2 H, m, 6-H and 7-H) and 7.77–7.80 (2 H, m, 5-H and 8-H); δ_C 26.43 (C-3′,5′), 27.69 (3 × Me), 32.47 (*C*Me$_3$), 33.93 (C-2′,6′), 47.89 (C-4′), 52.62 (C-1′), 104.77 (C-2), 116.99 (C-4), 119.89 (C-8), 123.47 (C-4a), 124.45 (C-7), 125.59 (C-6′), 126.67 (C-3), 128.73 (C-5), 134.63 (C-8a) and 142.61 (C-1).

***N*-Neopentyl-1-naphthylamine 1c.** This compound was prepared from pivalaldehyde (1.59 g, 18.4 mmol) and 1-naphthylamine (4.28 g, 29.9 mmol) by a similar procedure to that adopted for **1b**; yield 81%; mp 45–46 °C (hexane); ν_{max}/cm^{-1} 3460 (ν_{NH}); δ_H 1.01 (9 H, s, 3 × Me), 2.95 (2 H, s, NCH_2), 4.26 (1 H, br s, NH), 6.53 (1 H, d, *J* 7.6, 2-H), 7.12 (1 H, d, *J* 7.6, 4-H), 7.25 (1 H, t, *J* 7.6, 3-H), 7.28–7.37 (2 H, m, 6-H and 7-H) and 7.67–7.74 (2 H, m, 5-H and 8-H); δ_C 27.89 (3 × Me), 31.69 (*C*Me$_3$), 55.82 (*C*H$_2$NH), 104.14 (C-2), 116.91 (C-4), 119.65 (C-8), 123.46 (C-4a), 124.52 (C-7), 125.58 (C-6), 126.67 (C-3), 128.69 (C-5), 134.38 (C-8a) and 144.02 (C-1); *m*/*z* 213 (M^+; 20%), 156 (100) and 129 (29) (Found: C, 84.5; H, 9.1; N, 6.6. Calc. for $C_{15}H_{19}N$: C, 84.4; H, 9.0; N, 6.6%).

[^{2}H] Iodoform. To a mixture of [$^2H_6$]acetone (0.5 cm^3) and 40% NaOD–D_2O (2.72 g) was added a solution of KI–I_2 in D_2O to give CDI_3 (433 mg) which was filtered off.

Photochemical reactions of compound 1 and CHI_3

A typical procedure is as follows. A hexane solution (300 cm^3) of **1b** (282 mg, 1.0 mmol) and CHI_3 (391 mg, 0.99 mmol) under a nitrogen atmosphere in a round-bottomed flask was irradiated with a Pyrex-filtered 400W high-pressure mercury lamp from a distance of *ca.* 5 cm for 1.5 h. The resulting dark green precipitate (295 mg) was filtered off.

Bis-1,1′-[4,4′-(*cis*-4-*tert*-butylcyclohexylamino)naphthyl]-methylium triiodide 2b

A little ethanol was added to **Gb** and the insoluble part was separated and recrystallised from $CHCl_3$ to give deep green needles; λ_{max}($CHCl_3$)/nm 679 (ε/dm^3 mol^{-1} cm ^{1} 1.3 × 10^5); ν_{max}/cm^{-1} 3400 (ν_{NH}); δ_H(24 °C; *c* 9 × 10^{-3} mol dm^{-3})‡ 0.93 (18 H, s, 6 × Me), 1.16–1.36 (6 H, m, 3′-, 5′-H_{ax} and 4′-H), 1.78–1.93 (8 H, m, 2′-, 6′-H_{ax} and 3′-, 5′-H_{eq}), 2.23 (4 H, m, 2′-, 6′-H_{eq}), 4.29 (2 H, br s, 1′-H), 6.62 (2 H, d, *J* 6.1, NH), 7.15 (2 H, d, *J* 8.7, 3-H), 7.63 (2 H, dd, *J* 8.2, 6.7, 6-H), 7.73 (2 H, dd, *J* 7.9, 6.7, 7-H), 7.88 (2 H, d, *J* 8.2, 5-H), 8.13 (2 H, d, *J* 8.7, 2-H), 8.25 (2 H, d, *J* 7.9, 8-H) and 9.35 (1 H, s, CH=); δ_C 22.16 (C-3′,5′), 27.49 (6 × Me), 30.33 (C-2′,6′), 32.60 (*C*Me$_3$), 47.42 (C-1′), 48.86 (C-4′), 110.47 (C-3), 121.45 (C-5), 122.23 (C-1), 123.34 (C-8a), 124.58 (C-6), 127.44 (C-7), 130.86 (C-3), 135.08 (C-4a), 144.59 (C-8), 149.10 (CH=) and 153.72 (C-4) (Found: C, 51.0; H, 5.6; N, 2.8; I, 40.2. Calc. for $C_{41}H_{53}I_3N_2$: C, 51.6; H, 5.6; N, 2.9; I, 39.9%).

Bis-1,1′-(4,4′-neopentylaminonaphthyl)methylium triiodide 2c

A little $CHCl_3$ was added to **Gc** and the insoluble part was separated and recrystallised from acetone to give deep-green plates; λ_{max}(acetone)/nm 675 (ε/dm^3 mol^{-1} cm^{-1} 9.2 × 10^4); ν_{max}/cm^{-1} 3410 (ν_{NH}); δ_H([$^2H_6$]acetone) 1.09 (18 H, s, 6 × Me), 3.64 (4 H, d, *J* 6.7, NCH_2), 7.35 (2 H, d, *J* 9.2, 3-H), 7.69 (2 H, ddd, *J* 7.8, 7.1, 1.2, 6-H), 7.83 (2 H, ddd, *J* 7.8, 7.1, 1.2, 7-H), 8.12 (2 H, d, *J* 9.2, 2-H), 8.40–8.47 (4 H, m, 5-H and NH), 8.62 (2 H, d, *J* 7.8, 8-H) and 9.75 (1 H, s, CH=); δ_C([$^2H_6$]acetone) 28.43 (6 × Me), 35.20 (*C*Me$_3$), 56.13 (NCH_2), 110.54 (d), 124.12 (d), 124.64 (s), 126.69 (d), 128.64 (d), 132.24 (d), 136.95 (s), 144.70 (d), 150.77 (s) and 157.91 (s) (Found: C, 45.8; H, 4.6; I, 45.9; N, 3.4. Calc. for $C_{31}H_{37}I_3N_2$: C, 45.5; H, 4.6; I, 46.5; N, 3.4%).

N-(*cis*-4-*tert*-Butylcyclohexyl)-1-naphthylamine hydroiodide 3b

The ethanol-soluble fraction of **Gb** was obtained upon evaporation of the extract and the residue was repeatedly

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‡ The chemical shifts of the aromatic protons were concentration- and temperature-dependent.

recrystallised from ethanol–hexane; δ_H 0.86 (9 H, s, 3 × Me), 1.00 (1 H, m, 4-H), 1.3–1.9 (6 H, m, 2-, 6-H_{ax}, 3-, 5-H_{ax} and 3-, 5-H_{eq}), 2.37 (2 H, m, 2-, 6-H_{eq}), 3.95 (1 H, br s, 1-H), 7.23 (1 H, dd, *J* 8.3, 7.6, 3-H), 7.53 (1 H, dd, *J* 8.5, 6.9, 6-H), 7.63 (1 H, dd, *J* 8.1, 6.9, 7-H), 7.72 (1 H, d, *J* 8.3, 4-H), 7.83 (1 H, d, *J* 8.1, 8-H), 8.01 (1 H, d, *J* 7.6, 2-H) and 8.45 (1 H, d, *J* 8.5, 5-H); δ_C 21.65 (C-3,5), 27.71 (C-2,6), 27.94 (3 × Me), 32.75 (*C*Me$_3$), 47.78 (C-4), 60.23 (C-1), 122.61 (d), 124.17 (s), 124.42 (d), 125.43 (s), 127.01 (d), 127.60 (d), 128.88 (d), 129.75 (d) and 134.3 (s) (Found: C, 58.7; H, 6.9; I, 30.9; N, 3.3. Calc. for $C_{20}H_{28}IN$: C, 58.6; H, 6.9; I, 31.0; N, 3.4%).

N-Neopentyl-1-naphthylamine hydroiodide 3c

The $CHCl_3$-soluble fraction of **Gc** was obtained upon evaporation of the extract and the residue was recrystallised from $CHCl_3$; δ_H([$^2H_6$]acetone) 1.25 (9 H, s, 3 × Me), 3.30 (2 H, s, NCH_2), 7.29 (1 H, dd, *J* 8.3, 7.6, 3-H), 7.54–7.68 (2 H, m, 6-H and 7-H), 7.75 (1 H, d, *J* 8.3, 4-H), 7.87 (1 H, d, *J* 8.1, 8-H), 8.10 (1 H, d, *J* 7.6, 2-H) and 8.8 (1 H, d, *J* 8.3, 5-H); δ_C([$^2H_6$]-acetone) 28.25 (3 × Me), 32.03 (NCH_2), 64.98 (*C*Me$_3$), 120.7 (s), 121.08 (d), 124.72 (d), 125.23 (d), 127.07 (d), 127.59 (d), 128.32 (s), 129.07 (d), 133.40 (s) and 134.50 (d).

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