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Synthesis and molecular structures of (2-dialkylaminophenyl)alcohols and of 2-phenylaminoalkyl-dimethylaminobenzene derivatives

Harbi Tomah Al-Masri,[a] Joachim Sieler,[a,†] Peter Lönnecke,[a,†] Steffen Blaurock,[a,†] Konstantin Domasevitch[b,†] and Evamarie Hey-Hawkins[a,*]

[a]*Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany*
[b]*Inorganic Chemistry Department, Kiev University, Volodimirska Str. 64, Kiev, Ukraine*

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Abstract—*N*,*N*-Dimethyl-*o*-toluidine, *N*,*N*-dimethylaniline, and *N*,*N*-diethylaniline were treated with *n*-butyllithium-tmeda in diethyl ether–hexane solution to give *o*-lithioarylamines, which react with various electrophiles (benzophenone, dicyclohexyl ketone, benzaldehyde, and Ph(H)C=NPh) to form the corresponding (2-dialkylaminophenyl)alcohols 1-HOCPh$_2$-2-NMe$_2$C$_6$H$_4$ (**1**), 1-HOCCy$_2$-2-NMe$_2$C$_6$H$_4$ (**2**), 1-HOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$ (**4**), 1-HOC(H)PhCH$_2$-2-NMe$_2$C$_6$H$_4$ (**6**), and 1-HOCPh$_2$-2-NEt$_2$C$_6$H$_4$ (**7**), and the 2-phenylaminoalkyl-dimethylaminobenzene derivatives 1-NMe$_2$-2-NH(Ph)C(H)PhC$_6$H$_4$ (**3**) and 1-NMe$_2$-2-NH(Ph)C(H)PhCH$_2$C$_6$H$_4$ (**5**). Compounds **1**–**7** were characterized spectroscopically (NMR, IR, MS) and by crystal structure determination.

1. Introduction

Organolithium compounds are very versatile reagents in organic and organometallic chemistry.[1] The use of nitrogen as a neighboring heteroatom to effect selective metalation with *n*-butyllithium has been investigated,[2–4] and the reaction of the *ortho*-metalation product with ketones[4–11] has already been described. *ortho*-Lithiation is, however, not restricted to compounds containing nitrogen donor atoms; other directing groups are also frequently encountered.[12] Here we report the reaction of *N*,*N*-dimethyl-*o*-toluidine, *N*,*N*-dimethylaniline, and *N*,*N*-diethylaniline with *n*-butyllithium-tmeda in diethyl ether–hexane solution to give *o*-lithioarylamines, which react in situ with benzophenone, dicyclohexyl ketone, bezaldehyde, and Ph(H)C=NPh to form the corresponding (2-dialkylaminophenyl)alcohols 1-HOCPh$_2$-2-NMe$_2$C$_6$H$_4$ (**1**), 1-HOCCy$_2$-2-NMe$_2$C$_6$H$_4$ (**2**), 1-HOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$ (**4**), 1-HOC(H)PhCH$_2$-2-NMe$_2$C$_6$H$_4$ (**6**), and 1-HOCPh$_2$-2-NEt$_2$C$_6$H$_4$ (**7**), and the 2-phenylaminoalkyl-dimethylaminobenzene derivatives 1-NMe$_2$-2-NH(Ph)C(H)PhC$_6$H$_4$ (**3**) and 1-NMe$_2$-2-NH(Ph)C(H)PhCH$_2$C$_6$H$_4$ (**5**). Compounds **1**–**7** were characterized spectroscopically (NMR, IR, MS), and crystal structures were determined for **1**–**7**. Compounds **1**[11] and **4**[10] were previously reported but not structurally characterized. A modified procedure for the synthesis of **1** is reported.

The Li derivatives of compounds **1**–**7**[13] are useful starting materials for main group and transition metal compounds,[14] in which they act as hemilabile *O*,*N*- or *N*,*N*-chelating ligands forming six- and seven-membered chelate rings.

2. Results and discussion

2.1. Synthesis

N,*N*-Dimethylaniline and *N*,*N*-diethylaniline were treated with *n*-butyllithium in diethyl ether–hexane solution for one week, but the yields of the *ortho*-lithiated products were low. It was anticipated that *N*,*N*-dimethyl-*o*-toluidine should undergo metalation with *n*-butyllithium at the 2-methyl position, since the 2-methyl protons are more acidic than the ring protons, and a five-membered cyclic intermediate could be formed.[10] We found that when *N*,*N*-dimethyl-*o*-toluidine, *N*,*N*-dimethylaniline, and *N*,*N*-diethylaniline were treated with *n*-butyllithium-tmeda in diethyl ether–hexane, not only did metalation occur much more rapidly (2–3 h) and selectively than with *n*-butyllithium alone, but the overall yields were also increased. The lithium reagents 1-Li-2-NR$_2$C$_6$H$_4$ (R=Me, Et) and 1-LiCH$_2$-2-NMe$_2$C$_6$H$_4$ were treated with various electrophilic compounds, followed by hydrolytic acidic workup to form the corresponding

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* Corresponding author. Tel.: +49-341-9736151; fax: +49-341-9739319; e-mail address: hey@rz.uni-leipzig.de
† Crystal structure determination.

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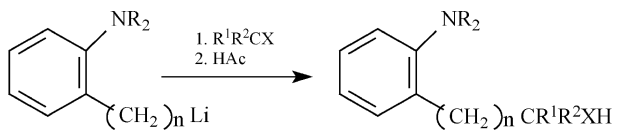


n	R	R^1	R^2	X	
0	Me	Ph	Ph	O	**1**
0	Me	Cy	Cy	O	**2**
0	Me	H	Ph	N(Ph)	**3**
1	Me	Ph	Ph	O	**4**
1	Me	H	Ph	N(Ph)	**5**
1	Me	H	Ph	O	**6**
0	Et	Ph	Ph	O	7

Scheme 1. Preparation of **1**–**7**.

(2-dialkylaminophenyl)alcohols and 2-phenylaminoalkyl-dimethylaminobenzene derivatives, as illustrated in Scheme 1.

The NMe_2-substituted compounds **1**–**6** were obtained in 60–70% yield, while the NEt_2 derivative **7** was obtained in only 20% yield.

2.2. Spectroscopic properties

2.2.1. IR spectra. The infrared spectra of **1**, **2**, **4**, **6**, and **7** showed broad hydroxyl bands in the 3450–3290 cm^{-1} region. The spectrum of the 2-phenylaminoalkyl-dimethyl-aminobenzene derivatives **3** and **5** exhibited sharp peaks around 3290 cm^{-1} and 1600–1540 cm^{-1} for secondary amino groups.[15] These bands have their origin in strong O–H···N and N–H···N intramolecular hydrogen bonds. The presence of both acidic and basic groups in these molecules makes this type of hydrogen bonding the most favorable interaction. In many amino acids such intra-molecular interaction between the acidic and the basic groups in the form $^{+}N–H\cdots O^{-}$ was found in the solid state.[16]

The IR spectrum of each compound showed one sharp peak in the range of 770–690 cm^{-1}, indicative of an *ortho*-disubstituted aromatic ring and ascribable to the four adjacent aromatic hydrogen atoms.[17] In addition to the peaks mentioned above, the IR spectrum of each compound, except for **7**, showed a strong peak in the range of 855–837 cm^{-1}, which can be attributed to the unaltered dimethylaminomethyl group.[16] Absorptions in the range of 1042–1010, 690–670 and 760–750 cm^{-1} are observed for the phenyl groups.

2.2.2. Mass spectrometry. The mass spectra of **1**–**7** showed parent-ion peaks at *m/z* 302.9 (**1**), 314.9 (**2**), 302.4 (**3**), 316.8 (**4**), 316.0 (**5**), 241.3 (**6**) and 331.3 (**7**), which agree with the calculated distribution pattern.

2.2.3. ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra, the most noticeable signal is that due to the $N(CH_3)_2$ protons, which give rise to a singlet for each compound in the range 2.38–2.78 ppm. The resonances corresponding to the benzylic protons are observed at 3.74 (**4**) as a singlet, and at 2.93, 4.32 (**5**) and 3.10, 4.94 ppm (**6**) as doublets. The singlet at 4.39 (**3**) and the triplets at 3.20 (**5**) and 3.21 ppm

Table 1. Selected bond lengths (Å) and angles (deg) for **1**, **2**, **3** and **7**

	C(3)–N(1)	C(3)–C(8)	C(8)–C(9)	C(9)–O(1) or C(9)–N(2)	N(1)–C(3)–C(8)	C(3)–C(8)–C(9)	C(8)–C(9)–O(1) or C(8)–C(9)–N(2)	C(3)–N(1)–C	C(1)–N(1)–C(2)	C(9)–O(1)–H or C(9)–N(2)–H
1	1.457(2)	1.401(2)	1.544(2)	1.440(2)	119.7(2)	121.7(2)	109.9(2)	111.9(2), 111.9(2)	111.2(2)	104(1)
2	1.453(2)	1.399(2)	1.550(2)	1.426(2)	121.0(1)	124.9(1)	112.2(1)	113.4(2), 111.4(1)	111.6(2)	107(1)
3	1.432(2)	1.408(2)	1.522(2)	1.452(2)	119.0(1)	121.6(1)	108.4(1)	115.7(2), 112.0(1)	111.4(2)	116.7(8)
7	1.453(2)	1.405(2)	1.548(2)	1.429(2)	119.6(2)	121.7(2)	110.2(1)	113.4(2), 111.2(2)	112.0(2)[a]	104(1)

[a] Corresponds to C(23)–N(1)–C(2).

Table 2. Selected bond lengths (Å) and angles (deg) for **4**–**6**

	4a	4b	5	6
C(3)–N(1)	1.449(2)	1.447(3)	1.427(2)	1.435(2)
C(3)–C(8)	1.403(2)	1.406(2)	1.408(2)	1.398(2)
C(8)–C(9)	1.517(2)	1.512(2)	1.508(3)	1.518(2)
C(9)–C(10)	1.547(2)	1.546(2)	1.540(3)	1.533(2)
C(10)–O or C(10)–N(2)	1.435(2)	1.435(2)	1.447(2)	1.472(2)
N(1)–C(3)–C(8)	118.4(2)	118.4(2)	118.6(2)	118.8(2)
C(3)–C(8)–C(9)	123.1(2)	122.5(2)	122.7(2)	122.7(2)
C(8)–C(9)–C(10)	113.9(2)	113.7(2)	112.9(2)	114.2(2)
C(9)–C(10)–O or C(9)–C(10)–N(2)	109.7(2)	109.9(2)	108.3(2)	110.8(2)
C(3)–N(1)–C	114.8(2), 112.0(2)	115.0(2), 112.6(2)	114.6(2), 112.1(2)	113.5(2), 111.9(2)
C(1)–N(1)–C(2)	109.5(2)	110.0(2)	111.3(3)	110.0(2)
C(10)–O(1)–H or C(10)–N(2)–H	108.7	106.6	114.4(2)	110.4(2)

(**6**) are characteristic for an X–CH proton (X=O, N), while a signal at 6.17 ppm (**3**) or 6.10 ppm (**5**) is indicative of an NH proton. Also, a signal for the OH proton is observed at 9.80 (**1**), 10.69 (**2**), 8.55 (**4**), 7.02 (**6**), and 10.50 ppm (**7**). A quartet at 2.61, 2.77 and a triplet at 0.92 ppm (**7**) are characteristic for NCH_2CH_3 protons. The resonances corresponding to the cyclohexyl protons are observed at 1.10–1.80 ppm (**2**) as broad peaks. The aromatic rings of each compound give rise to the characteristic proton signals in the expected range of 6.70–7.42 ppm.

The ^{13}C NMR spectra of **1**–**6** reveal signals of the $N(CH_3)_2$ carbon atoms at 45.4–47.3 ppm. Singlets at 76.5–84.6 ppm are assigned to the C–O carbon atom in **1**, **2**, **4**, **6**, and **7**. Signals for the methylene carbon atoms are observed at 45.0 (**4**), 42.0 (**5**), and 44.6 ppm (**6**), while the resonances at 56.2 (**3**), 62.1 (**5**), and 65.9 ppm (**6**) are characteristic of X–CH carbon atoms (X=O, N). The resonances at 12.5 and 49.1 ppm (**7**) are characteristic for NCH_2CH_3 carbon atoms. The resonances of the aromatic carbon atoms (111.8–154.0 ppm) and the cyclohexyl groups (27.4–47.1 ppm) are in the expected ranges.

2.3. Molecular structures of 1–7

Colorless crystals of **1**–**7** were obtained as described in the experimental section. Selected interatomic distances and angles are collected in Tables 1 and 2. The molecular structures are depicted in Figures 1–7.

The common feature of the molecular structures of **1**, **2**, **4**, **5**, **6**, and **7** is the intramolecular O(1)–H···N(1) or N(2)–H···N(1) hydrogen bond (Table 3), which results in six-membered $C_3OH\cdots N$ rings in **1**, **2**, and **7** (the atoms N(1)–C(3)–C(8)–C(9) are coplanar), and seven-membered $C_4XH\cdots N$ (X=O(1), N(2)) rings in **4**–**6** (the atoms N(1)–C(3)–C(8)–C(9)–C(10) are coplanar). No intramolecular N(2)–H···N(1) or intermolecular hydrogen bond is observed in **3**.

The intramolecular O(1)–H···N(1) hydrogen bonds of **1**, **2**, **4**, **6**, and **7** are stronger than the intramolecular N–H···O hydrogen bonds reported for $(p\text{-}CH_3C_6H_4)_2BOCH_2CH_2NH_2$ and $(C_6H_5)_2BOCH_2CH_2NH_2$ (N···O=2.982(2) or 2.896(2) Å),[18] as well as those reported for related

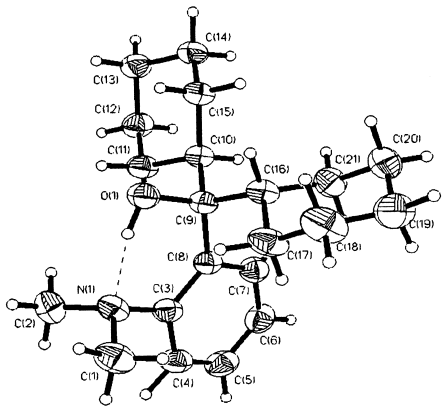


Figure 2. Molecular structure of **2**.

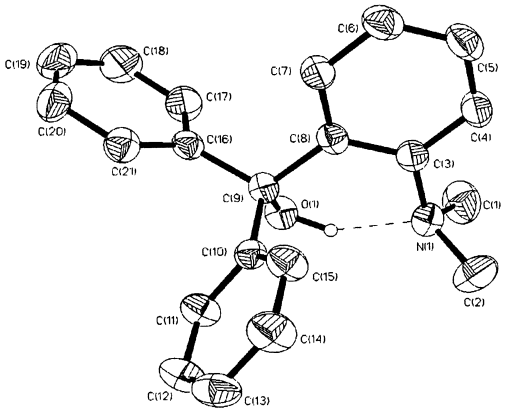


Figure 1. Molecular structure of **1**.

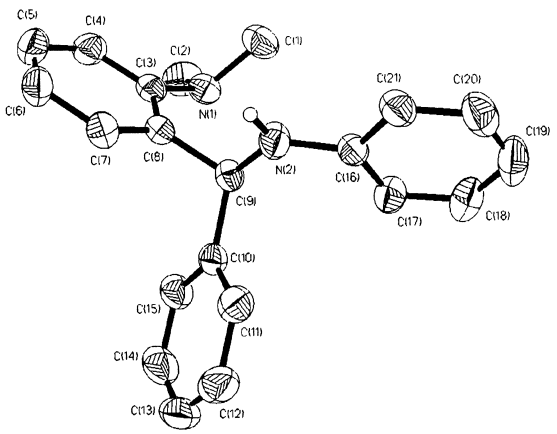
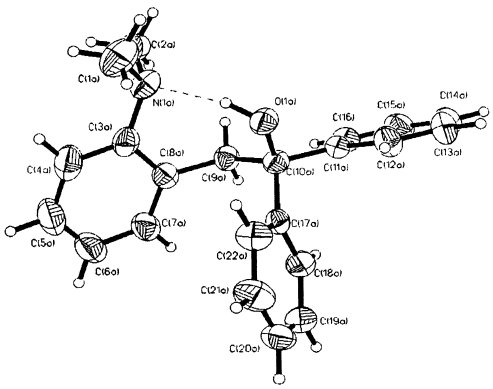


Figure 3. Molecular structure of **3**.



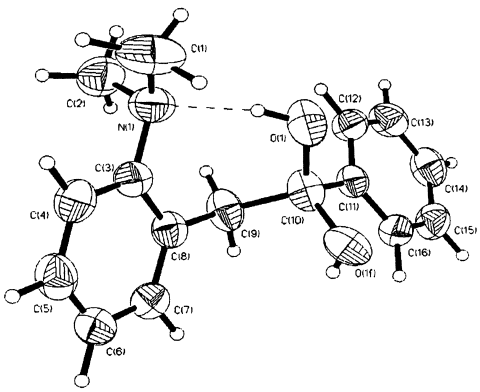


Figure 6. Molecular sturcture of **6** (disordered COH group is shown).

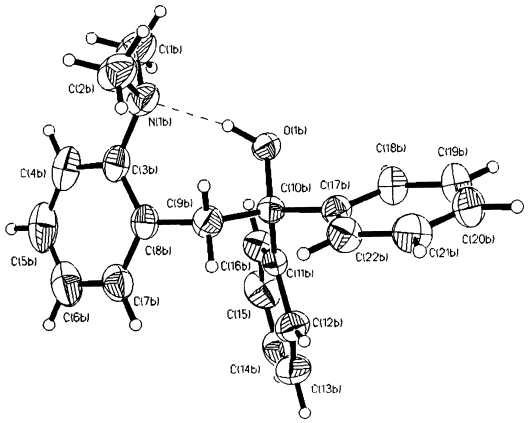


Figure 4. Molecular structure of **4a** and **4b**.

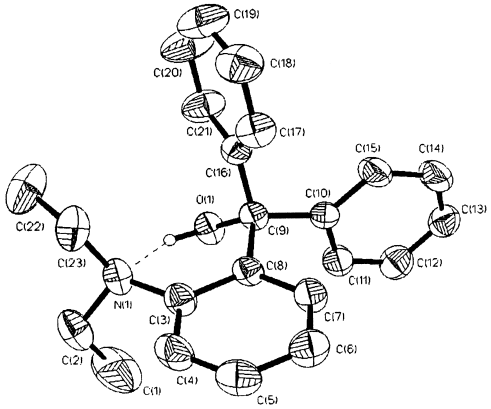


Figure 7. Molecular structure of **7**.

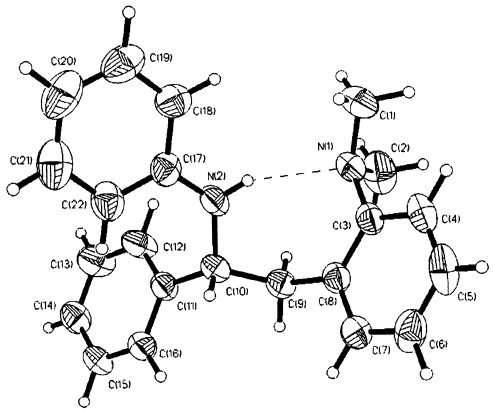


Figure 5. Molecular structure of **5**.

five- and six-membered rings (N–H···O: N···O=2.702(2)–2.752(3) Å, O–H···O: O···O=2.674(2)–2.703(3) Å, and N–H···N: N···N=3.024(4)–3.054(2) Å).[19]

The intramolecular N(2)–H···N(1) hydrogen bond of **5** is weaker than intramolecular N–H···N, N–H···O, and O–H···O hydrogen bonds reported previously.[19] Unlike compounds **1**, **2**, and **7**, in which the O–H moiety forms an intramolecular hydrogen bond with a nitrogen atom, the N(2)–H proton in **3** is not involved in any hydrogen bonding (N···N=4.134 Å). This is presumably the result of steric blocking of the N(2)–H proton by the bulky phenyl groups. The N···N distance for the N(2)–H···N(1) interaction in **5** is longer than those observed for N–H···N hydrogen bonds in monocationic compounds, which range up to 2.626 Å for linear systems[20] and comparable to the mean value of the 2.949 Å for noncationic N–H···N hydrogen bonds in crystalline organic compounds.[21] The O(1)–H···N(1)

Table 3. Hydrogen bond data for **1**, **2**, **4a**, **4b**, **5**, **6**, and **7**

	O(1)–H or N(2)–H	N(1)···H	O(1)···N(1) or N(2)···N(1)	O(1)–H···N(1) or N(2)–H···N(1)
1	0.95(2)	1.82(2)	2.659(2)	146(2)
2	0.92(2)	1.73(2)	2.591(1)	155(2)
4a	0.94[a]	1.83[a]	2.757(2)	167[a]
4b	0.94[a]	1.82[a]	2.747(2)	166[a]
5	0.84(2)	2.23(2)	3.019(2)	155(2)
6	0.89(3)	1.80(3)	2.686(6)	168(3)
7	0.91(2)	1.83(2)	2.663(2)	151(2)

[a] No standard deviation given as OH proton is in a calculated position.

hydrogen bonds in **1**, **2**, and **7** are stronger than the X–H···N(1) (X=O(1), N(2)) hydrogen bonds in **4**, **5**, and **6**, consistent with the fact that increasing the ring size from six- to seven-membered weakens the O(1)–H···N(1) hydrogen bond. Also, the O(1)–H···N(1) hydrogen bond is stronger than the N(2)–H···N(1) hydrogen bond.

The structural data of the six-membered $C_3OH\cdots N$ rings in **1**, **2**, **3** and **7** (Table 1) show the expected bond lengths and angles.[19–21] Only in **1**, **2**, and **7** the C(8)–C(9)–O(1) bond angles (109.9–112.3°) are slightly larger, and the C(9)–O(1)–H bond angles (104–107°) slightly smaller, than expected, owing to the formation of intramolecular O(1)–H···N(1) hydrogen bonds.

The structural data of compounds **4**–**6** with seven-membered $C_4XH\cdots N$ (X=O(1), N(2)) rings (Table 2) are as expected.[19,20,21] Only the C(8)–C(9)–C(10) bond angle is slightly larger (112.9–114.2°) than expected. The C(3)–C(8) distances in **1**–**7** agree with the mean literature value of 1.394 Å.[22]

The nitrogen atom N(1), which is bound to the aromatic ring, has a distorted environment with large C(1)–N(1)–C(2) (109.5–11.3°) and C(3)–N(1)–C (113.5–115.0°; 111.9–112.6°) bond angles.

Compounds **3**, **5** and **6** are obtained as racemic mixtures. The molecular structure of **6** shows disorder of the (C)–O–H and (C(10))–H groups (71.3% C–O(1)–H and 28.7% C–O(1f)–H).

3. Experimental

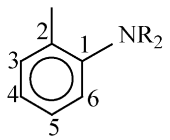
3.1. General

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker). Infrared spectra were recorded with a Perkin–Elmer System 2000 FT-IR spectrometer between 4000 and 400 cm^{-1} using KBr disks. Elemental analyses were determined with a VARIO EL (Heraeus). Melting points (Gallenkamp) are uncorrected. Mass spectra were recorded with a MAT-8230 (EI-MS, 70 eV). Crystallographic data were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction with SADABS.[23] The structures were solved by direct methods (SHELXTL PLUS).[24] H atoms were located by difference maps and refined isotropically. Details concerning the crystal structure determination are given in Table 4.

3.1.1. (2-Dimethylaminophenyl)diphenylmethanol (1). A dry 250 ml two-necked flask was filled with 10 g (0.082 mol) of *N*,*N*-dimethylaniline, 120 ml of anhydrous diethyl ether and 12.37 ml of tmeda and the solution was stirred under nitrogen atmosphere. 60 ml of a 1.5 M solution of *n*-butyllithium in hexane was added at −78 °C. The solution was allowed to warm to room temperature, stirred for 2 h and refluxed for 2 h. Then a solution of 14.9 g (0.082 mol) of benzophenone in 40 ml of anhydrous diethyl ether was added dropwise to the reaction mixture and with stirring over 30 min. The resulting deep green solution was stirred for an additional 0.5 h and then poured into a vigorously stirred solution of 13 g (0.22 mol) glacial acetic acid in 40 ml of diethyl ether. The solution was stirred overnight at room temperature. Then the solution was successively extracted with 50 ml of distilled water and with five 50 ml portions of aqueous 5% hydrochloric acid. The aqueous extracts were combined and made alkaline with aqueous 10% sodium hydroxide.

The alkaline aqueous mixture was heated to boiling and maintained at this temperature until the escaping vapor was no longer basic to moistened pH paper. The mixture was then cooled, and the white solid product which separated was collected on a Buchner funnel and washed with three 20 ml portions of water. The crude product was recrystallized from hexane/ethyl acetate solution at 20 °C to give the product as colorless crystals in 70% yield. Mp 177–178 °C. ^1H NMR ($CDCl_3$, δ/ppm): 2.38 (s, 6H, $N(CH_3)_2$), 6.70–7.38 (m, 14H, C_6H_4 and C_6H_5), 9.80 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 46.3 (s, $N(CH_3)_2$), 83.6 (s, C–O), 124.2 (s, C6 in C_6H_4), 125.8 (s, C4 in C_6H_4), 126.4 (s, C3 in C_6H_4), 127.5 (s, C5 in C_6H_4), 128.3 (s, *p*-C in C_6H_5), 128.9 (s, *o*-C in C_6H_5), 131.1 (s, *m*-C in C_6H_5), 143.7 (s, C2 in C_6H_4), 148.3 (s, C1 in C_6H_4), 152.8 (s, *ipso*-C in C_6H_5). IR (KBr): 3423–2800 br., 1989 w, 1600 w, 1597 w, 1546 vs, 1392 vs, 1313 s, 1267 vs, 1205 s, 1166 s, 1154 vs, 1078 vs, 1051 vs, 1010 vs, 986 s, 969 s, 962 vs, 907 vs, 876 vs, 848 s, 771 s, 703 s, 587 s, 524 m, 516 m, 496 s, 442 m, 414 m cm^{-1}. MS: *m*/*z* 302.9 (68%, M^+), 225.9 (65%, M^+-Ph), 209.8 (94%, $M^+-Ph-OH$), 193.8 (20%, $M^+-Ph-OH-CH_3$), 164.9 (30%, $M^+-Ph-OH-N(CH_3)_2$), 90.9 (100%, $C_7H_7^+$), 76.9 (86%, $C_6H_5^+$), 50.9 (20%, $C_4H_3^+$). Found: C 84.0; H 7.65; N 4.37%. Calcd for $C_{21}H_{21}NO$: C 83.13; H 6.98; N 4.62%.

Phenyl ring numbering scheme:



3.1.2. (2-Dimethylaminophenyl)dicyclohexylmethanol (2). The reaction was carried out by the same procedure as described for **1**, except that 16.0 g (0.082 mol) of dicyclohexyl ketone was used instead of benzophenone, and that the colorless crystals were obtained from a saturated hexane/benzene solution (5:1) at 0 °C in 70% yield. Mp 160–165 °C. ^1H NMR ($CDCl_3$, δ/ppm): 1.10–1.80 (br., 22H, C_6H_{11}), 2.65 (s, 6H, $N(CH_3)_2$), 7.10–7.32 (m, 4H, C_6H_4), 10.69 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 27.4 (s, C4 in C_6H_{11}), 27.5 (s, C3/C5 in C_6H_{11}), 28.6 (s, C2/C6 in C_6H_{11}), 47.1 (s, C1 in C_6H_{11}), 47.3 (s, $N(CH_3)_2$), 84.6 (s, C–O), 123.7 (s, C6 in C_6H_4), 126.0 (s, C4 in C_6H_4), 127.6 (s, C3 in C_6H_4), 128.6 (s, C5 in C_6H_4), 139.3 (s, C2 in C_6H_4), 154.0 (s, C1 in C_6H_4). IR (KBr): 2930 vs, 2850 vs, 2788 s, 1919 w, 1703 w, 1601 s, 1574 w, 1451 s, 1335 w, 1263 w, 1187 s, 1145 s, 1101 s, 1043 s, 993 s, 932 s, 851 w, 892 s, 827 s, 759 s, 716 s, 565 s, 517 m, 483 w cm^{-1}. MS: *m*/*z* 314.9 (6%, M^+), 298.0 (10%, M^+-OH), 232.8

Table 4. Crystal data and structure refinement for **1**–**7**

	1	2	3	4	5	6	7
Formula	$C_{21}H_{21}NO$	$C_{21}H_{33}NO$	$C_{21}H_{22}N_2$	$C_{22}H_{23}NO$	$C_{22}H_{24}N_2$	$C_{16}H_{19}NO$	$C_{23}H_{25}NO$
M_r	303.39	315.48	302.41	317.41	316.43	240.31	331.44
Temp (K)	213(2)	218(2)	223(2)	223(2)	213(2)	223(2)	213(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$Pca2_1$	Cc	$Pbca$	$Pbca$
a (Å)	8.856(2)	9.929(1)	26.774(3)	17.765(1)	14.220(2)	14.916(1)	8.532(1)
b (Å)	12.538(3)	10.330(1)	9.3063(9)	5.9999(3)	13.679(2)	8.1647(8)	16.361(2)
c (Å)	15.556(3)	10.926(1)	18.661(2)	33.712(2)	11.553(2)	22.681(2)	27.735(4)
α (°)	90	101.609(2)	90	90	90	90	90
β (°)	100.77(3)	101.094(2)	132.950(1)	90	125.227(2)	90	90
γ (°)	90	114.919(2)	90	90	90	90	90
V (Å^3)	1696.8(6)	945.9(2)	3403.3(6)	3593.3(3)	1835.7(5)	2762.2(5)	3871.5(9)
Z	4	2	8	8	4	8	8
ρ_{calcd} (mg m^{-3})	1.188	1.108	1.180	1.173	1.145	1.156	1.137
$F(000)$	648	348	1296	1360	680	1032	1424
Abs coeff (mm^{-1})	0.072	0.066	0.069	0.071	0.067	0.072	0.069
No. of rflns coll.	10063	6226	11103	19386	5639	16472	23266
No. of indep rflns	2647	4293	4202	7338	3004	3439	4614
R_{int}	0.0489	0.0158	0.0291	0.0232	0.0217	0.0385	0.0292
No. of params	209	341	296	433	313	249	326
$R1$ ($I>2\sigma(I)$)	0.0431	0.0434	0.0384	0.0375	0.0349	0.0512	0.0467
$wR2$ (all data)	0.0925	0.1420	0.0893	0.0994	0.0821	0.1480	0.1279
$(\Delta/\rho)_{min}$ (e Å^{-3})	0.225	0.210	0.160	0.162	0.108	0.242	0.210
$(\Delta/\rho)_{max}$ (e Å^{-3})	−0.185	−0.184	−0.164	−0.152	−0.136	−0.140	−0.181
CCDC depos. no.	190705	190712	190708	190707	190711	190709	190710

(100%, M^+-Cy), 214.7 (15%, $M^+-Cy-OH$), 148.0 (8%, M^+-2Cy), 132.4 (30%, $M^+-2Cy-OH$), 83.4 (10%, Cy^+), 54.9 (15%, $C_4H_7^+$). Found: C 80.10; H 12.40; N 4.17%. Calcd for $C_{21}H_{33}NO$: C 79.95; H 10.54; N 4.44%.

3.1.3. 2-(Phenylamino-phenyl)methyl-dimethylamino-benzene (3). The reaction was carried out by the same procedure as described for **1**, except that 14.9 g (0.082 mol) of *N*-benzylidenaniline was used instead of benzophenone, and that the colorless crystals were obtained from toluene/hexane solution (1:3) at 20 °C in 65% yield. Mp 133–135 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): 2.61 (s, 6H, $N(CH_3)_2$), 4.39 (s, 1H, CH), 6.17 (s, 1H, NH), 6.54–7.36 (m, 14, C_6H_4 and C_6H_5). ^{13}C NMR ($CDCl_3$, δ/ppm): 45.5 (s, $N(CH_3)_2$), 56.2 (s, CH), 113.1 (s, C6 in C_6H_4), 117.2 (s, C4 in C_6H_4), 121.4 (s, C3 in C_6H_4), 124.3 (s, C5 in C_6H_4), 126.7 (s, *p*-C in C_6H_5), 129.1 (s, *o*-C in C_6H_5), 138.9 (s, *m*-C in C_6H_5), 144.1 (s, C2 in C_6H_4), 147.6 (s, C1 in C_6H_4), 152.4 (s, *ipso*-C in C_6H_5). IR (KBr): 3315 vs, 3100 m, 3080 m, 3000 s, 2920 m, 2900 m, 2840 s, 2820 m, 2785 vs, 1950 w, 1601 vs, 1583 vs, 1506 vs, 1448 vs, 1429 vs, 1351 s, 1314 vs, 1300 vs, 1266 s, 1183 vs, 1154 vs, 1047 s, 1027 m, 945 vs, 888 s, 840 vs, 744 vs, 730 vs, 695 vs, 585 m, 509 m cm^{-1}. MS: *m*/*z* 302.4 (50%, M^+), 286.9 (10%, M^+-NH), 209.9 (100%, $M^+-Ph-NH$), 193.9 (25%, $M^+-Ph-NH-CH_3$), 179.9 (8%, $M^+-Ph-NH-2CH_3$), 90.9 (64%, $C_7H_7^+$), 76.9 (25%, $C_6H_5^+$), 50.9 (8%, $C_4H_3^+$). Found: C 83.60; H 7.29; N 9.48%. Calcd for $C_{21}H_{22}N_2$: C 83.40; H 7.33; N 9.26%.

3.1.4. 2-(2-Dimethylaminophenyl)-1,1′-diphenylethanol (4). Compound **4** was prepared as described in the literature.[10] The crude product was recrystallized from hexane/ethyl acetate (4:1) solution at 20 °C to give the product as colorless crystals in 70% yield. Mp 151–153 °C (lit. 153–155 °C, from benzene/hexane).[10] ^{1}H NMR ($CDCl_3$, δ/ppm): 2.74 (s, 6H, $N(CH_3)_2$), 3.74 (s, 2H, CH_2), 6.49–7.40 (m, 14H, C_6H_4 and C_6H_5), 8.55 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 45.0 (s, CH_2), 45.4 (s, $N(CH_3)_2$), 78.6 (s, C–O), 120.0 (s, C6 in C_6H_4), 125.0 (s, C4 in C_6H_4), 126.2 (s, C3 in C_6H_4), 126.3 (s, C5 in C_6H_4), 128.4 (s, *p*-C in C_6H_5), 128.5 (s, *o*-C in C_6H_5), 133.2 (s, *m*-C in C_6H_5), 133.5 (s, C2 in C_6H_4), 147.9 (s, C1 in C_6H_4), 151.8 (s, *ipso*-C in C_6H_5). IR (KBr): 3428 br., 3083 s, 3054 s, 3021 s, 2994 m, 2946 m, 2931 m, 2861 s, 2831 vs, 2801 s, 2784 s, 1948 w, 1597 w, 1580 vs, 1492 vs, 1474 s, 1460 s, 1446 vs, 1230 m, 1180 s, 1105 s, 1058 s, 1038 m, 955 s, 937 s, 862 s, 845 w, 786 s, 767 vs, 757 vs, 701 vs, 647 m, 608 s, 534 m cm^{-1}. MS: *m*/*z* 316.8 (8%, M^+), 299.8 (5%, M^+-OH), 239.8 (9%, M^+-Ph), 134.9 (100%, $M^+-2Ph-2CH_3$), 90.9 (15%, $C_7H_7^+$), 76.9 (25%, $C_6H_5^+$), 50.9 (6%, $C_4H_3^+$). Found: C 83.10; H 7.10; N 4.71%. Calcd for $C_{22}H_{23}NO$: C 83.24; H 7.30; N 4.41%.

3.1.5. 2-(2-Phenylamino-2-phenyl)ethyl-dimethylamino-benzene (5). The reaction was carried out by the same procedure as described for **3**, except that 11.1 g (0.082 mol) of *N*,*N*-dimethyl-*o*-toluidine was used instead of *N*,*N*-dimethylaniline, and that the colorless crystals were obtained from toluene at 20 °C in 60% yield. Mp 145–150 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): 2.78 (s, 6H, $N(CH_3)_2$), 3.20 (t, $^3J_{H-H}$=12 Hz, 1H, CH), 2.93 (d, $^3J_{H-H}$=12 Hz, 1H, CH_2), 4.32 (d, $^3J_{H-H}$=12 Hz, 1H, CH_2), 6.10 (s, 1H, NH), 6.20–7.42 (m, 14H, C_6H_4 and C_6H_5). ^{13}C NMR ($CDCl_3$, δ/ppm): 42.0 (s, CH_2), 46.1 (s, $N(CH_3)_2$), 62.1 (s, CH), 113.5 (s, C6 in C_6H_4), 116.8 (s, C4 in C_6H_4), 120.6 (s, C3 in C_6H_4), 125.2 (s, C5 in C_6H_4), 127.5 (s, *p*-C in C_6H_5), 129.6 (s, *o*-C in C_6H_5), 135.2 (s, *m*-C in C_6H_5), 145.2 (s, C2 in C_6H_4), 148.6 (s, C1 in C_6H_4), 153.5 (s, *ipso*-C in C_6H_5). IR (KBr): 3290 vs, 3105 m, 3082 m, 2996 s, 2980 m, 2944 m, 2880 s, 2825 m, 2785 vs, 1960 w, 1600 vs, 1523 vs, 1490 vs, 1450 vs, 1435 vs, 1351 s, 1324 vs, 1293 vs, 1277 s, 1179 vs, 1154 vs, 1041 s, 1028 m, 940 vs, 845 vs, 774 s, 758 vs, 748 vs, 693 vs, 546 m, 527 m cm^{-1}. MS: *m*/*z* 316.0 (11%, M^+), 223.9 (5%, $M^+-Ph-NH$), 207.9 (5%, $M^+-Ph-NH-CH_3$),

192.9 (8%, $M^+-Ph-NH-2CH_3$), 180.9 (100%, $M^+-Ph-NH-NMe_2$), 90.9 (20%, $C_7H_7^+$), 76.9 (38%, $C_6H_5^+$), 50.9 (18%, $C_4H_3^+$). Found: C, 82.60; H, 8.13; N, 8.62%. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85%.

3.1.6. 2-(2-Dimethylaminophenyl)-1-phenylethanol (6). The reaction was carried out by the same procedure as described for **4**, except that 8.7 g (0.082 mol) of benzaldehyde instead of benzophenone was used and that the colorless crystals were obtained from toluene at 25 °C in 70% yield. Mp 152–157 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): 2.78 (s, 6H, $N(CH_3)_2$), 3.21 (t, $^3J_{H-H}$=12 Hz, 1H, CH), 3.10 (d, $^3J_{H-H}$=12 Hz, 1H, CH_2), 4.94 (d, $^3J_{H-H}$=12 Hz, 1H, CH_2), 7.02 (s, 1H, OH), 7.24–7.39 (m, 9H, C_6H_4 and C_6H_5). ^{13}C NMR ($CDCl_3$, δ/ppm): 44.6 (s, CH_2), 45.6 (s, $N(CH_3)_2$), 65.9 (s, CH), 76.5 (s, C–O), 120.8 (s, C6 in C_6H_4), 126.0 (s, C4 in C_6H_4), 126.3 (s, C3 in C_6H_4), 127.6 (s, C5 in C_6H_4), 128.6 (s, *p*-C in C_6H_5), 129.2 (s, *o*-C in C_6H_5), 132.7 (s, *m*-C in C_6H_5), 135.6 (s, C2 in C_6H_4), 146.1 (s, C1 in C_6H_4), 152.6 (s, *ipso*-C in C_6H_5). IR (KBr): 3366 br., 3060 w, 2940 m, 2859 m, 2829 m, 2786 s, 1951 w, 1597 s, 1580 vs, 1492 vs, 1451 vs, 1293 vs, 1267 vs, 1156 vs, 1100 vs, 1057 vs, 1005 vs, 939 s, 863 vs, 845 w, 759 vs, 699 vs, 635 s cm^{-1}. MS: *m*/*z* 241.3 (18%, M^+), 164.9 (5%, M^+-Ph), 134.0 (100%, $M^+-Ph-2CH_3$), 118.0 (22%, $M^+-Ph-NMe_2$), 90.9 (20%, $C_7H_7^+$), 76.9 (15%, $C_6H_5^+$), 50.9 (8%, $C_4H_3^+$). Found: C 79.30; H 8.09; N 6.48%. Calcd for $C_{16}H_{19}NO$: C 79.62; H 7.87; N 5.81%.

3.1.7. (2-Diethylaminophenyl)diphenylmethanol (7). The reaction was carried out by the same procedure as described for **1**, except that 12.5 g (0.082 mol) of *N*,*N*-diethylaniline was used instead of *N*,*N*-dimethylaniline and that the colorless crystals were obtained from diethyl ether at −10 °C in 20% yield. Mp 165–170 °C. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.92 (t, $^3J_{H-H}$=8 Hz, 6H, $N(CH_2CH_3)_2$), 2.61 (q, $^3J_{H-H}$=8 Hz, 2H, $N(CH_2CH_3)_2$), 2.77 (q, $^3J_{H-H}$=8 Hz, 2H, $N(CH_2CH_3)_2$), 6.75–7.29 (m, 14H, C_6H_4 and C_6H_5), 10.50 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ/ppm): 12.5 (s, $N(CH_2CH_3)_2$), 49.1 (s, $N(CH_2CH_3)_2$), 83.3 (s, C–O), 111.8 (s, C6 in C_6H_4), 115.4 (s, C4 in C_6H_4), 124.4 (s, C3 in C_6H_4), 124.9 (s, C5 in C_6H_4), 126.8 (s, *p*-C in C_6H_5), 128.3 (s, *o*-C in C_6H_5), 132.1 (s, *m*-C in C_6H_5), 144.7 (s, C2 in C_6H_4), 146.0 (s, C1 in C_6H_4), 148.1 (s, *ipso*-C in C_6H_5). IR (KBr): 3060–2845 br., 1951 w, 1596 s, 1567 w, 1427 vs, 1385 vs, 1361 s, 1295 s, 1218 s, 1161 vs, 1115 vs, 1102 s, 1027 vs, 938 s, 833 vs, 759 vs, 699 vs, 636 vs, 596 s, 564 m, 523 m, 490 m, 452 m cm^{-1}. MS: *m*/*z* 331.3 (34%, M^+), 316.2 (15%, M^+-CH_3), 298.2 (5%, M^+-CH_3-OH), 254.2 (45%, M^+-Ph), 238.1 (47%, $M^+-Ph-CH_3$), 210.2 (15%, $M^+-Ph-CH_3-Et$), 165.0 (13%, $M^+-Ph-OH-N(CH_2CH_3)_2$), 76.9 (64%, $C_6H_5^+$), 50.9 (20%, $C_4H_3^+$). Found: C, 82.40; H, 7.54; N, 3.99%. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23%.

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