



Sterically encumbered 2,6-dibenzhydryl-4-methylphenyl derived ligand systems: synthesis and structures

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MS received 9 June 2017; revised 18 July 2017; accepted 19 July 2017; published online 29 August 2017

Abstract. Bulky 2,6-dibenzhydryl-4-methylaniline, **I** undergoes diazotization upon treatment with $\text{H}_2\text{SO}_4/\text{NaNO}_2$, which upon further reaction with KI affords 1-iodo-2,6-dibenzhydryl-4-methylbenzene, **1**. Reaction of **I** with one equivalent of acetylacetone in ethanol under reflux condition affords mono-Schiff base, 4-(2,6-dibenzhydryl-4-methylphenylamino)pent-3-ene-2-one, **2**. Similarly, **I** reacts with half equivalent of 2-hydroxy-5-methylisophthalaldehyde or one-third equivalent of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde in ethanol under reflux condition to afford bis-Schiff base, 2,6-bis(((2,6-dibenzhydryl-4-methylphenyl)imino)methyl)-4-methylphenol, **3** and tris-Schiff base, 2,4,6-tris(((2,6-dibenzhydryl-4-methylphenyl)amino)methylene)cyclohexane-1,3,5-trione, **4**, respectively. Further, **I** upon reaction with triflic acid affords (2,6-dibenzhydryl-4-methylphenyl)ammonium triflate, **5** whereas upon reaction with HBr and HCl affords co-crystals **I**·HBr, **6** and **I**·HCl, **7**. All the new products were isolated in moderate to good yield and characterized by spectroscopic (IR, ESI-mass, NMR, UV-Vis) and microanalytical (CHN) techniques, in addition to a single crystal X-ray diffraction study for **1**, **2** and **4-7**.

Keywords. Sterically encumbered ligands; bulky aryl groups; Schiff bases; acid-base adducts; co-crystals.

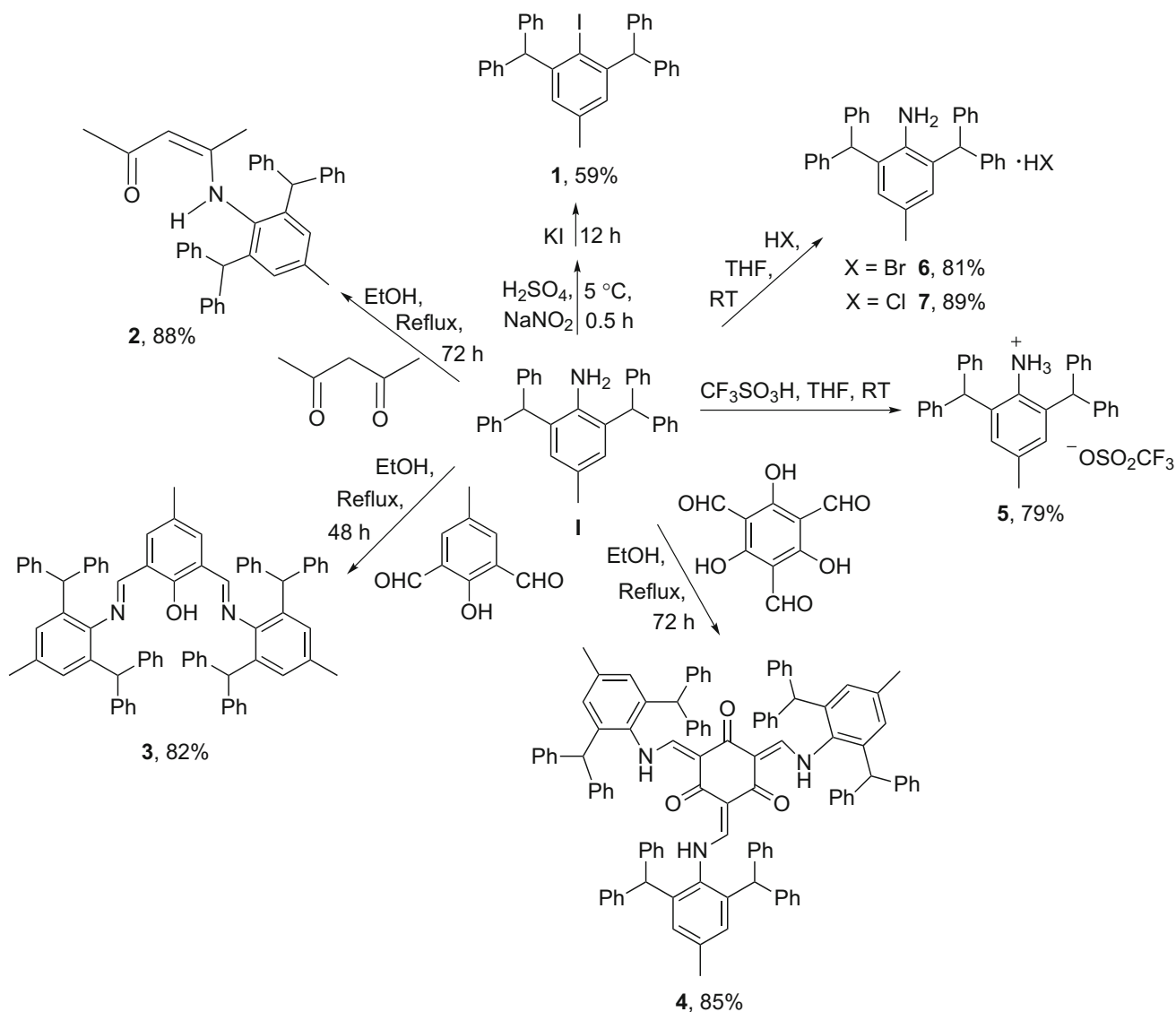
1. Introduction

Incorporation of sterically bulky ligands into metal complexes is a well explored but ever growing field due to the fact that the steric bulk of the ligand facilitates the fine-tuning of physical and chemical properties of the complexes.¹⁻⁶ This feature is highly pivotal specially in tailoring activity and selectivity of catalytically active complexes⁷⁻¹⁰ as well as for the synthesis and stabilization of low-valent metal complexes.¹¹⁻¹⁵ Among these, bulky Schiff base derivatives are of special importance due to their ease of synthesis and strong affinity of the imino-nitrogen for most of the metal systems. Complexes employing bulky Schiff base derivatives have been used as efficient and selective catalysts for several organic transformations, stabilisation of low valent complexes as well as for biological applications.¹⁶⁻²⁴ Of particular mention here are the nickel and palladium complexes of Schiff base derivatives containing 2,6-Dibenzhydryl-4-methylphenyl moiety which have been

employed as excellent catalysts for ethylene polymerisation.²⁵⁻²⁷ Further, such Schiff base derivatives containing bulky 2,6-Dibenzhydryl-4-methylphenyl moiety have been employed in the stabilization of highly low valent transition as well as main group metal complexes such as those containing Zn, Bi, Sb, As, Mg and Mn.²⁸⁻³¹ In addition to the aforementioned aspects, the salts and co-crystals of various organic ligands are important class of compounds due to the presence of interesting hydrogen bond interactions which lead to supramolecular frameworks resulting in interesting photophysical, chemical and biological properties.³²⁻³⁵

In the past, we have reported on bulky ligands derived metal complexes and employed them in catalytic transformations.^{36,37} Continuing our efforts to isolate newer and even bulkier ligand systems, starting from 2,6-dibenzhydryl-4-methylaniline **I**, herein we report on the synthesis, spectroscopic and structural aspects of 2,6-dibenzhydryl-4-methylphenyl appended ligand systems, which include an iodo-derivative and three bulky Schiff bases, apart from salt or acid-base adducts of **I**.

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Scheme 1. Synthesis of 1 – 7.

2. Experimental

2.1 Materials and methods

2,6-Dibenzhydryl-4-methylaniline was synthesised following a reported procedure.³⁸ Acetylacetone (acac), mineral acids, KI and NaNO_2 were purchased from Spectrochem Pvt. Ltd. (India) and used without any further purification. 2-Hydroxy-5-methylisophthalaldehyde and 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde were synthesised using reported procedures.^{39,40} Solvents were dried and distilled using standard procedures prior to their use.⁴¹

Elemental analyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyser. IR spectral studies of KBr diluted compounds were performed on a Perkin Elmer Spectrum One Infrared Spectrometer. UV-Vis spectra were measured on Varian Cary Bio 100 spectrophotometer. ^1H , ^{13}C and DEPT 135 NMR spectra were recorded on Bruker Avance III 400 or 500 MHz NMR spectrometers. Mass spec-

tral data were collected using Waters Q-TOF micro mass spectrometer.

2.2 Synthesis and characterization of compounds

2.2a 1-Iodo-2,6-dibenzhydryl-4-methylbenzene 1: To a rapidly stirred mixture of 2,6-dibenzhydryl-4-methylaniline (**I**) (2.00 g, 4.55 mmol) in CHCl_3 - CH_3OH (80 mL, 1:1 (v/v)) was slowly added H_2SO_4 (18 M, 1.5 mL, 27.0 mmol). The solution was cooled in an ice-bath to $\leq 5^\circ\text{C}$, and a solution of NaNO_2 (0.64 g, 9.22 mmol) in H_2O (10 mL) was added dropwise over 15 min to maintain the reaction temperature at $\leq 5^\circ\text{C}$. After 10 min, a solution of KI (1.53 g, 9.22 mmol) in water (10 mL) was slowly added. The mixture was stirred at 0°C for 30 min and at RT for 12 h. The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 - H_2O . The organic layer was dried over Na_2SO_4 , decolorized with charcoal and thereafter solvent removed under vacuum

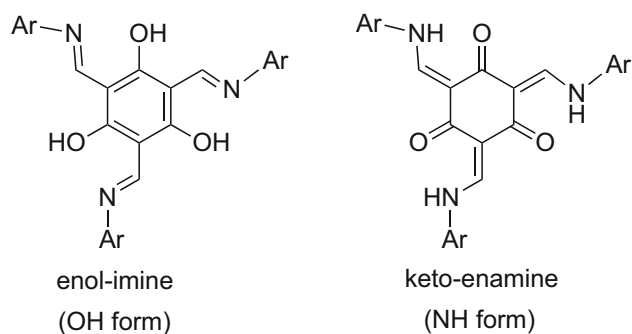


Figure 1. Two tautomers possible for **4**.

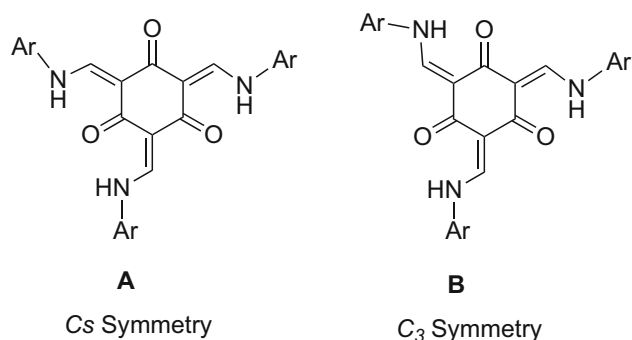


Figure 2. Two geometrical isomers possible for the keto-enamine form of **4**.

to afford a yellow solid. Column chromatography over silica gel using petroleum ether as an eluent and crystallisation from the concentrated solution (40 mL) of the same solvent afforded **1** as colourless prismatic crystals over 3–5 days at ambient temperature. Yield: 59% (1.48 g, 2.68 mmol). M.p.: 265–266°C. Anal. Calcd. for C₃₃H₂₇I (*M_r*: 550.47) (%): C, 72.00; H, 4.94. Found: C, 72.22; H, 4.74. IR (KBr, ν/cm^{-1}): 3083 (m), 3059 (s), 3025 (s), 2919 (m), 1598 (s), 1582 (m), 1493 (vs), 1446 (s), 1410 (m), 1078 (m), 1031 (m), 1002 (s), 783 (m), 765 (m), 699 (vs), 605 (m). ¹H NMR (CDCl₃, 400 MHz): δ 2.11 (s, 3H, CH₃), 6.04 (s, 2H, Ph₂CH), 6.63 (s, 2H, ArH), 7.07–7.10 (m, 8H, ArH), 7.22–7.26 (m, 4H, ArH), 7.28–7.32 (m, 8H, ArH) ppm. ¹³C{¹H} NMR (CDCl₃, 100.6 MHz): δ 21.3 (CH₃), 62.2 (Ph₂CH), 108.2 (C), 126.5 (CH), 128.4 (CH), 130.0 (CH), 130.4 (CH), 137.1 (C), 143.4 (C), 147.2 (C) ppm. ESI-MS: *m/z* calcd.: 573.1055, found: 573.1117 [M + Na]⁺.

2.2b Mono-Schiff base 2: A suspension of **I** (1.00 g, 2.27 mmol) and acetylacetone (0.50 g, 5.00 mmol) in ethanol (50 mL) was heated under reflux for three days. The reaction mixture was concentrated under vacuum to approximately 10 mL, and the resulting white precipitate of **2** was filtered and washed with cold ethanol. Yield: 88% (1.04 g, 2.00 mmol). M.p.: 240–242°C. Anal. Calcd. for C₃₈H₃₅NO (*M_r*: 521.69) (%): C, 87.49; H, 6.76; N, 2.68. Found: C, 87.41; H, 6.58; N, 2.58. IR (KBr, ν/cm^{-1}): 3457 (w, br), 3060 (m), 3024 (m), 2923 (w), 1601 (vs), 1568 (vs), 1494 (m), 1447 (m), 1281 (s), 1189 (m), 1022 (m), 920 (m), 744 (s), 699 (s). ¹H

NMR (CDCl₃, 400 MHz): δ 0.83, 2.04, 2.18 (each s, 3 × 3 H, CH₃), 4.95 (s, 1 H, CH), 5.59 (s, 2 H, Ph₂CH), 6.77 (s, 2 H, ArH), 7.00, 7.10 (each d, *J*_{HH} = 8.0 Hz, 2 × 4 H, ArH), 7.16–7.25 (m, 12 H, ArH), 11.91 (s, 1 H, NH) ppm. ¹³C{¹H} NMR (CDCl₃, 100.6 MHz): δ 18.13, 21.74, 29.04 (each CH₃), 52.20 (Ph₂CH), 96.18 (CH), 126.50 (C), 126.51 (CH), 128.41 (CH), 128.44 (CH), 129.33 (CH), 129.44 (CH), 129.86 (CH), 133.94 (C), 137.17 (C), 142.29 (C), 142.85 (C), 143.40 (C), 163.94 (C), 195.47 (CO) ppm. ESI-MS: *m/z* calcd 560.2356, found 560.2517 [M + K]⁺. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH₂Cl₂–petroleum ether solution (25 mL) over 4–6 days at ambient temperature.

2.2c Bis-Schiff base 3: A suspension of **I** (1.00 g, 2.27 mmol) and 2-hydroxy-5-methylisophthalaldehyde (0.19 g, 1.14 mmol) in ethanol (60 mL) was heated under reflux for two days. The reaction mixture was concentrated to 10 mL under vacuum to obtain compound **3** as a yellow precipitate, which was filtered and washed with cold ethanol. Yield: 82% (0.94 g, 0.93 mmol). M.p.: 177–179°C. Anal. Calcd. for C₇₅H₆₂N₂O (*M_r*: 1007.33) (%): C, 89.43; H, 6.20; N, 2.78. Found: C, 89.23; H, 6.33; N, 3.00. IR (KBr, ν/cm^{-1}): 3445 (m), 3379 (m), 3057 (m), 3024 (m), 2922 (m), 2857 (m), 1627 (s), 1596 (vs), 1490 (m, sh), 1462 (s), 1453 (s), 1255 (w), 1203 (w), 1076 (w, sh), 1032 (m), 747 (w), 700 (vs). ¹H NMR (CDCl₃, 400 MHz): δ 2.04 (s, 6 H, CH₃), 2.18 (s, 3 H, CH₃), 3.30 (s, 2 H, NCH), 5.47 (s, 4 H, Ph₂CH), 5.48 (s, 1 H, OH), 6.40 (s, 4 H, ArH), 6.69 (s, 2 H, ArH), 7.05 (d, *J*_{HH} = 7.2 Hz, 6 H, ArH), 7.11–7.13 (m, 12 H, ArH), 7.15–7.17 (m, 2 H, ArH), 7.20–7.25 (m, 10 H, ArH), 7.28–7.32 (m, 10 H, ArH). ¹³C{¹H} NMR (CDCl₃, 100.6 MHz): δ 20.2 (CH₃), 21.1 (CH₃), 21.5 (CH₃), 52.2 (CH), 52.5 (Ph₂CH), 126.3 (CH), 126.7 (CH), 126.8 (C), 127.2 (C), 128.3 (CH), 128.6 (CH), 129.0 (CH), 129.2 (CH), 129.4 (C), 129.7 (CH), 129.8 (CH), 134.2 (C), 139.8 (C), 142.9 (C), 143.9 (C), 159.1 (C). ESI-MS: *m/z* calcd.: 1007.4935, found: 1007.4975 [M + H]⁺.

2.2d Tris-Schiff base 4: A suspension of **I** (1.00 g, 2.27 mmol) and 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (0.16 g, 0.76 mmol) in ethanol (60 mL) was boiled under reflux for three days and the reaction was concentrated to 10 mL under vacuum to yield an orange precipitate. This solid was filtered and washed with cold ethanol to yield analytically pure **4**. Yield: 85% (0.96 g, 0.65 mmol). M.p.: 218–220°C. Anal. Calcd. for C₁₀₈H₈₇N₃O₃ (*M_r*: 1474.86) (%): C, 87.95; H, 5.95; N, 2.85. Found: C, 87.66; H, 5.90; N, 2.98. IR (KBr, ν/cm^{-1}): 3436 (w, br), 3055 (w), 3026 (w), 2925 (w), 2854 (w), 1602 (s), 1588 (vs), 1494 (w), 1443 (m), 1260 (w), 1029 (w), 1017 (w), 745 (w), 699 (m). ¹H NMR (CDCl₃, 400 MHz): δ 2.17, 2.18, 2.20 (each s, 3 × 3H, CH₃), 5.61 (s, 4H, Ph₂CH), 5.64 (s, 2H, Ph₂CH), 6.70, 6.71, 6.72 (each s, 3 × 2H, ArH), 7.00–7.04 (m, 24H, ArH), 7.06–7.10 (m, 8H, ArH), 7.14–7.19 (m, 18H, ArH), 7.20–7.25 (m, 10H, ArH), 7.47, 7.51, 7.72 (each d, *J*_{HH} = 13.2 Hz, 3 × 1H, HNCH), 11.72, 11.84, 11.28 (each d, *J*_{HH} = 13.2 Hz, 3 × 1H, HNCH). ¹³C{¹H} NMR (CDCl₃, 100.6 MHz): δ 21.77 (CH₃), 21.79 (CH₃),

Table 1. Crystallographic and structure refinement data for **1**, **2** and **4** – **7**.

	1	2	4-2CHCl₃·2CH₃OH	5 H₂O	6-THF·0.5H₂O	7·2THF
Formula	C ₃₃ H ₂₇ I	C ₃₈ H ₃₅ NO	C ₁₁₂ H ₉₇ Cl ₆ N ₃ O ₅	C ₃₄ H ₃₂ F ₃ NO ₄ S	C ₃₇ H ₃₉ BrNO _{0.5}	C ₄₁ H ₄₆ ClNO ₂
Fw	550.44	521.67	1777.62	607.66	601.60	620.24
Temperature (K)	120(2)	150(2)	120(2)	150(2)	150(2)	123(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	8.062(2)	10.953(5)	13.679(3)	9.335(4)	12.4489(4)	12.6014(8)
<i>b</i> /Å	11.954(3)	11.307(5)	18.679(5)	12.939(5)	17.3343(4)	17.3805(9)
<i>c</i> /Å	13.589(4)	13.007(5)	19.446(5)	13.531(5)	31.4789(8)	31.512(2)
α /°	95.558(3)	101.791(5)	84.06(1)	94.272(5)	90	90
β /°	104.187(3)	102.691(5)	73.460(1)	90.732(7)	90	90
γ /°	93.272(5)	107.590(5)	76.00(1)	107.095(6)	90	90
Volume/Å ³	1259.3(6)	1433.1(11)	4637(2)	1556.8(11)	6792.9(3)	6901.7(7)
<i>Z</i>	2	2	2	2	4	8
ρ_{calcd} /g cm ⁻³	1.452	1.209	1.273	1.296	1.176	1.194
μ (Mo K α)/mm ⁻¹	1.291	0.071	0.243	0.160	1.239	0.146
<i>F</i> (000)	556	556	1864	636	2520	2656
θ range/°	2.62–25.00	1.68–25.0	1.79–25.0	2.28–25.0	1.75–25.0	1.74–25.00
No. of reflns collected	9220	11102	35316	11908	51245	55224
<i>R</i> _{int}	0.0238	0.0253	0.1521	0.0410	0.0383	0.1841
Data/restraints/parameters	4368/0/308	5038/0/379	16190/1/1154	5432/0/401	11975/0/734	12145/0/814
<i>R</i> ₁ ^a , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0222/0.0587	0.0449/0.1283	0.1381/0.3460	0.0587/0.1438	0.0497/0.1600	0.1007/0.2222
<i>R</i> ₁ , <i>wR</i> ₂ ^b [all data]	0.0224/0.0589	0.0584/0.1581	0.1596/0.3710	0.0774/0.1556	0.0558/0.1705	0.1819/0.3065
Goof ^c on <i>F</i> ²	1.003	1.117	1.176	1.102	0.927	1.034
Largest diff peak/hole(e, Å ⁻³)	0.395/-0.290	0.315/-0.377	0.874/-1.030	0.432/-0.294	1.013/-0.611	0.945/-0.446

$a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $b wR = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2))]^{1/2}$; $c GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$.

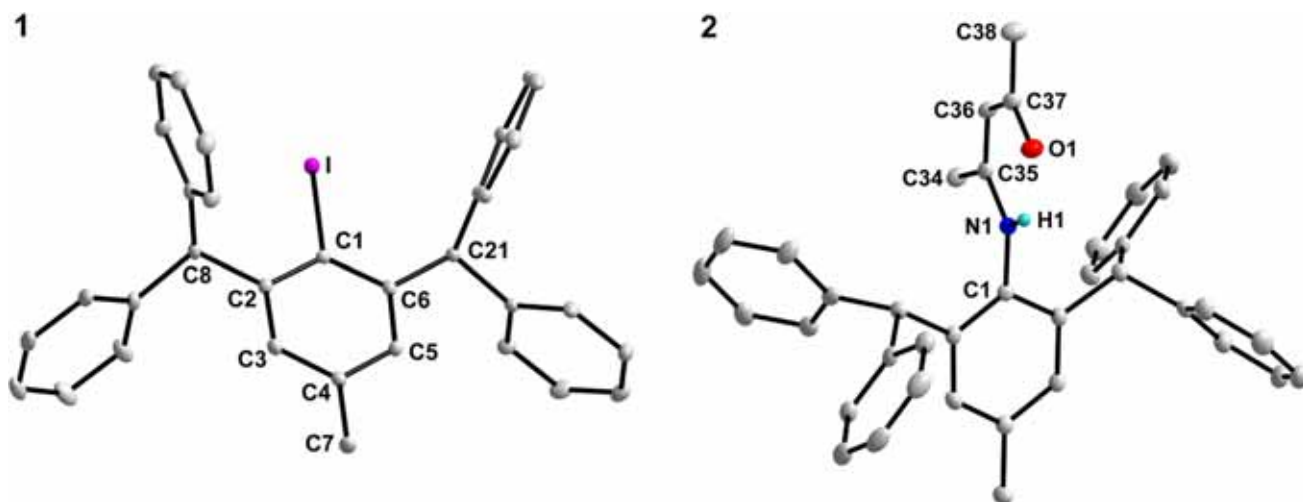


Figure 3. ORTEP representations of **1** and **2** at 30% probability level. Hydrogen atoms, except that on amino nitrogen, have been removed for clarity. Selected bond distances and angles (\AA and deg) for **2**: C(37)-O(1) = 1.245(2), C(36)-C(37) = 1.415(2), C(35)-C(36) = 1.374(2), C(35)-N(1) = 1.337(2), C(1)-N(1) = 1.421(2), C(35)-N(1)-C(1) = 126.67(14).

52.14 (Ph₂CH), 52.19 (Ph₂CH), 52.22 (Ph₂CH), 106.07 (C), 106.10 (C), 106.14 (C), 106.36 (C), 126.62 (CH), 126.65 (CH), 126.66 (CH), 128.53 (CH), 128.55 (CH), 129.54 (CH), 129.57 (CH), 129.61 (CH), 129.63 (CH), 136.01 (C), 136.03 (C), 137.22 (C), 137.24 (C), 137.25 (C), 140.87 (C), 140.88 (C), 141.03 (C), 141.10 (C), 142.66 (C), 142.67 (C), 142.79 (C), 142.80 (C), 156.77 (CH), 157.40 (CH), 157.79 (CH), 158.29 (CH), 181.38 (C), 184.92 (CO), 184.95 (CO), 188.26 (CO). ESI-MS: *m/z* calcd.: 1474.6826, found: 1474.6906 [M + H]⁺. Crystals of **4**·2CHCl₃·2CH₃OH suitable for X-ray diffraction were obtained from a CHCl₃-CH₃OH solution (25 mL) through slow evaporation over 5–7 days at ambient temperature.

2.2e Triflate salt 5: To a solution of **I** (200 mg, 0.46 mmol) in THF (8 mL) was added a solution of triflic acid (730 mg, 4.60 mmol) in THF (4 mL) and the resulting mixture stirred for a while, filtered and kept for crystallization to yield colourless needle-shaped crystals of **5** over 4–6 days at ambient temperature. Yield: 79% (214 mg, 0.36 mmol). Anal. Calcd. for C₃₄H₃₀F₃NO₃S + 1.5 H₂O (*M_r*: 589.67 + 18.02) (%): C, 66.22; H, 5.39; N, 2.27; S 5.20. Found: C, 66.16; H, 5.12; N, 2.28; S, 5.29. IR (KBr, ν/cm^{-1}): 3437 (br, m), 3183 (br, m), 3061 (m), 3028 (m), 2927 (m), 1959 (w), 1894 (w), 1599 (m), 1494 (s), 1449 (s), 1290 (m), 1103 (vs), 1049 (vs), 910 (w), 772 (m), 746 (m), 732 (m), 702 (s), 626 (m), 606 (m), 544 (w), 480 (w). ¹H NMR (CDCl₃, 400 MHz): δ 2.16 (s, 3H, CH₃), 5.88 (s, 2H, Ph₂CH), 6.62 (s, 2H, ArH), 7.08 (d, *J*_{HH} = 7.2 Hz, 8H, ArH), 7.24–7.32 (m, 12H, ArH). ¹³C{¹H} NMR (CDCl₃, 125.7 MHz): δ 21.7 (CH₃), 51.0 (Ph₂CH), 127.5 (CH), 129.0 (CH), 129.7 (CH), 130.5 (CH), 138.2 (C), 140.9 (C).

2.2f I·HBr 6: To a solution of **I** (200 mg, 0.46 mmol) in THF (8 mL) was added a solution of HBr (373 mg, 4.60 mmol)

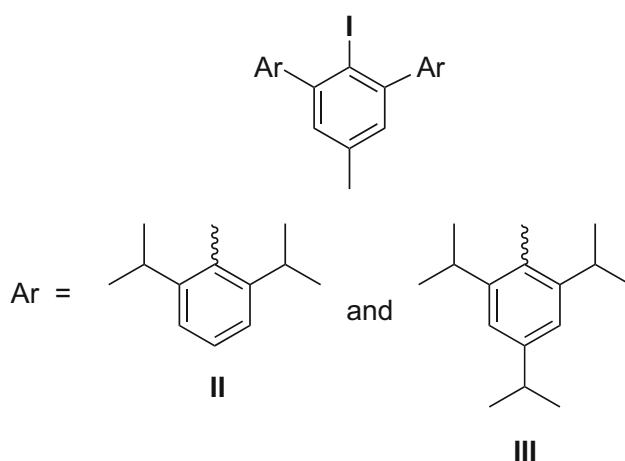


Figure 4. Compounds with structures similar to **1**.

in THF (4 mL), the resulting mixture stirred for a while, filtered and kept for crystallization. Colourless needle shaped crystals of **6** were obtained over 4–6 days at ambient temperature. Yield: 81% (193 mg, 0.37 mmol). Anal. Calcd. for C₃₃H₃₀BrN + THF + 2 H₂O (*M_r*: 520.51 + 72.11 + 36.03) (%): C, 70.69; H, 6.73; N, 2.23. Found: C, 70.33; H, 6.30; N, 2.01. IR (KBr, ν/cm^{-1}): 3433 (br, m), 3060 (m), 3023 (m), 2872 (br, vs), 2600 (m), 1951 (w), 1887 (w), 1813 (w), 1598 (m), 1544 (m), 1494 (m), 1448 (m), 1078 (m), 1049 (m), 1032 (m), 885 (w), 768 (m), 746 (s), 700 (vs), 621 (w), 605 (w), 549 (w). ¹H NMR (CDCl₃, 400 MHz): δ 2.15 (s, 3 H, CH₃), 5.84 (s, 2 H, Ph₂CH), 6.62 (s, 2 H, ArH), 7.09 (d, *J*_{HH} = 6.4 Hz, 8 H, ArH), 7.22–7.31 (m, 12 H, ArH), 7.87 (br, 2 H, NH). (CDCl₃, 125.7 MHz): δ 21.7 (CH₃), 51.1 (Ph₂CH), 123.9 (C), 127.7 (CH), 129.1 (CH), 129.7 (CH), 130.6 (CH), 138.5 (C), 139.7 (C), 140.5 (C).

Table 2. Selected bond distances (Å) and angles (°) for **1**, **II** and **III**.

	I	II	III
C(1)-I(1)	2.118(2)	2.111(4)	2.115(3)
C(1)-C(2)	1.403(2)	1.414(5)	1.398(2)
C(1)-C(6)	1.407(2)	1.394(5)	1.398(2)
C(2)-C(8)	1.525(2)	1.497(5)	1.497(2)
C(6)-C(21)	1.526(2)	1.502(3)	1.497(2)
C(4)-C(7)	1.509(3)	1.497(6)	1.515(4)
C(2)-C(1)-I	119.3(1)	118.7(3)	118.8(1)
C(6)-C(1)-I	118.8(1)	119.5(3)	118.8(1)
C(1)-C(2)-C(8)	121.8(2)	121.9(3)	122.6(2)
C(1)-C(6)-C(21)	121.5(2)	121.8(2)	122.6(2)

2.3 I·HCl 7

To a solution of **I** (200 mg, 0.46 mmol) in THF (8 mL) was added a solution of HCl (166 mg, 4.60 mmol) in THF (4 mL), the resulting mixture stirred for a while, filtered and kept for crystallization to obtain colourless needle-shaped crystals of **7** over 4–6 days at ambient temperature. Yield: 89% (195 mg, 0.41 mmol). Anal. Calcd. for $C_{33}H_{30}ClN$ (M_r : 476.06) (%): C, 83.26; H, 6.35; N, 2.94. Found: C, 83.38; H, 6.40; N, 2.94. IR (KBr, ν/cm^{-1}): 3445 (m), 3379 (m), 3057 (m), 3025 (m), 2917 (m), 2864 (m), 2605 (m), 1953 (w), 1887 (w), 1625 (m), 1599 (m), 1551 (m), 1494 (m), 1465 (m), 1446 (m), 1292 (w), 1237 (w), 1078 (m), 1031 (m), 864 (w), 754 (m), 700 (vs), 605 (m), 557 (w). 1H NMR ($CDCl_3$, 400 MHz): δ 2.10 (s, 3H, CH_3), 6.31 (br, 2H, Ph_2CH), 6.55 (s, 2H, ArH), 7.09 (d, $J_{HH} = 6.8$ Hz, 8H, ArH), 7.15–7.24 (m, 12 H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz): δ 21.4 (CH_3), 51.6 (Ph_2CH),

127.0 (CH), 128.7 (CH), 129.9 (CH), 135.4 (C), 142.0 (C). Cuboidal crystals of $7 \cdot 2THF$ suitable for X-ray diffraction were obtained from $CHCl_3$ -THF in a span of several days.

2.4 Single crystal X-ray diffraction studies

Single crystal X-ray diffraction data of **1**, **2** and **4–6** were collected on a Rigaku Saturn 724+ CCD diffractometer with a Mo- $K\alpha$ radiation source ($\lambda = 0.71075$ Å) at low temperature $\leq 150^\circ C$. Rigaku *Crystal Clear-SM Expert* software was used for data collection. Data integration and indexing were performed with *CrysAlisPro* software suite.⁴² *WinGX* module was used to perform all the calculations.⁴³ The structures were solved by direct methods (*SIR-92*).⁴⁴ The final refinement was carried out using full least-squares methods on F^2 using *SHELXL-2014*.⁴⁵ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically as rigid atoms in their idealized locations. *SQUEEZE* was applied for disordered THF molecules in the crystal lattice of **5** by using the *PLATON* program.⁴⁶

3. Results and Discussion

3.1 Synthesis and Spectral Characterization

2,6-Dibenzhydryl-4-methylaniline, **I** was converted to its diazonium salt by reacting with $H_2SO_4/NaNO_2$ at $\leq 5^\circ C$. The *in situ* generated diazonium salt was reacted with KI followed by work up and column

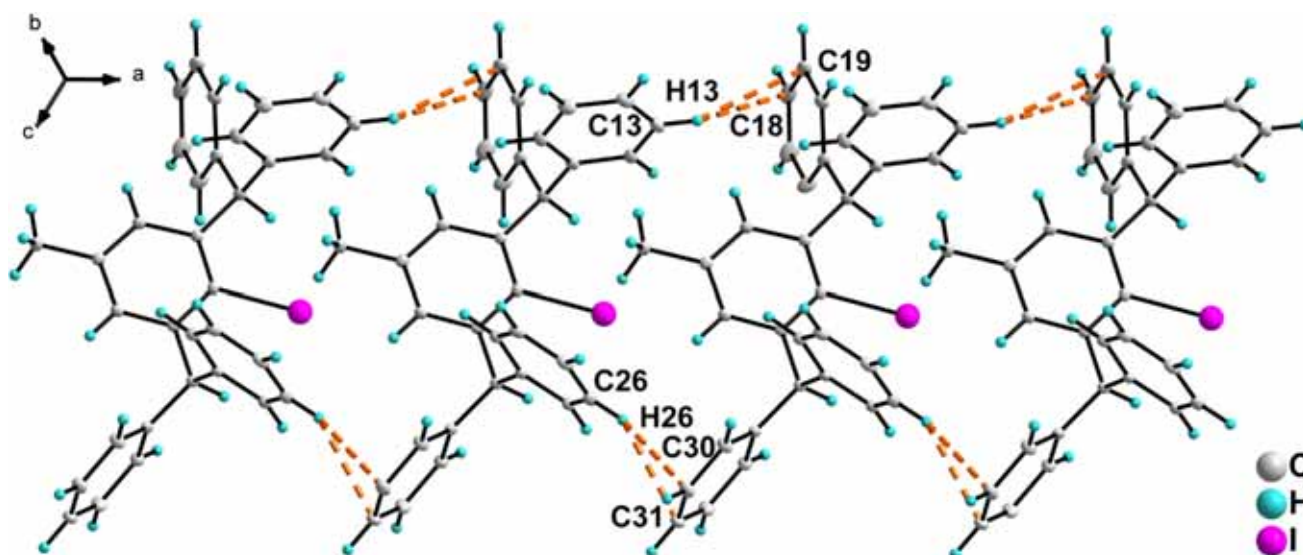


Figure 5. C-H... π interactions present in the crystal lattice of **1**. Hydrogen bond parameters (Å and deg): H13...C18 = 2.826, C13...C18 = 3.622, C13-H13...C18 = 141.94; H13...C19 = 2.857, C13...C19 = 3.754, C13-H13...C19 = 157.94; H26...C30 = 2.728, C26...C30 = 3.623, C26-H26...C30 = 157.14; H26...C31 = 2.764, C26...C31 = 3.626, $\angle C26-H26...C31 = 151.27$.

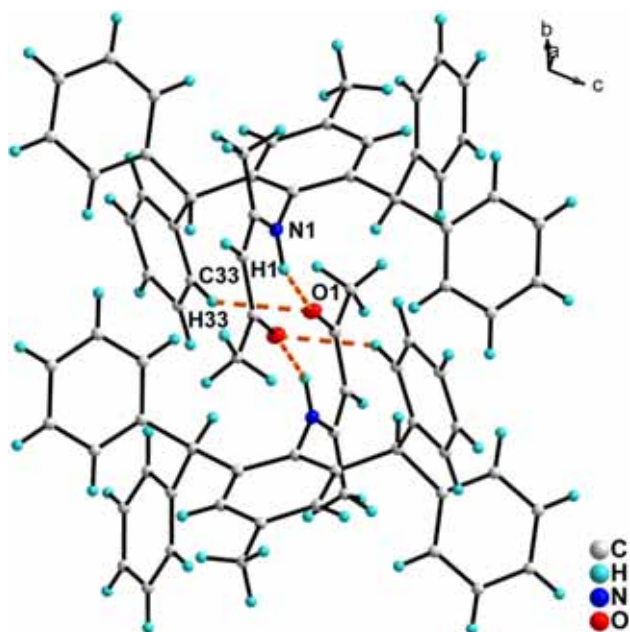


Figure 6. N-H...O and C-H...O interactions present in the crystal lattice of **2**. Hydrogen bond parameters (Å and deg): H1...O1 = 2.215, N1...O1 = 2.863, N1-H1...O1 = 125.21; H33...O1 = 2.524, C33...O1 = 3.318, C33-H33...O1 = 141.24; H36...C13 = 2.790, C36...C13 = 3.618, C36-H36...C13 = 146.10.

chromatography to afford 1-iodo-2,6-dibenzhydryl-4-methylbenzene, **1** in 59% yield (Scheme 1). **1** upon treatment with one equivalent of acetylacetonate (acac) or half equivalent of 2-hydroxy-5-methylisophthalaldehyde or one-third equivalent of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde in ethanol under reflux conditions afforded Schiff bases **2-4** in 88, 82, and 85% yield, respectively (Scheme 1). In each case the final product was obtained as analytically pure solid, through concentration of the reaction mixture followed by separation of the precipitated solid by filtration and subsequent washing with ethanol. **1**, upon treatment with triflic acid in THF followed by crystallization afforded triflate salt, **5** in 79% yield whereas similar reactions carried out with HBr and HCl afforded co-crystals, **1**·HBr and **1**·HCl in 81 and 89% yield, respectively (Scheme 1).

The IR spectra of **2** and **4** show broad bands at 3457 and 3436 cm^{-1} assignable to $\nu(\text{NH})$ while the band observed at 3445 cm^{-1} in the IR spectrum of **3** is assignable to $\nu(\text{OH})$.⁴⁷ Further, the IR spectra of **2,3** and **4** show strong bands at 1601, 1627 and 1602 cm^{-1} , respectively, assignable to $\nu(\text{CO})$.⁴⁷ The IR spectra of **5** and **6** show broad bands at 3437 and 3433 cm^{-1} , respectively and that of **7** shows two bands at 3445 and 3379 cm^{-1} assignable to $\nu(\text{NH})$. Further, the IR spectrum of **5** shows very strong bands at 1103 and 1049 cm^{-1} assignable to $\nu(\text{CF}_3)$ and $\nu(\text{SO}_3)$, respectively.⁴⁷

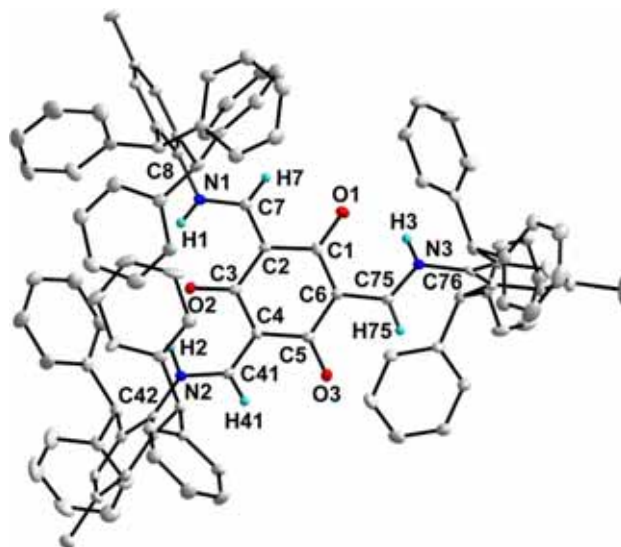


Figure 7. ORTEP representation of **4** at 30% probability level. Hydrogen atoms, except those on amino nitrogens and solvent molecules, have been removed for clarity. Selected bond distances and angles (Å and deg) C(1)-C(2) = 1.459(7), C(2)-C(3) = 1.454(7), C(3)-C(4) = 1.448(7), C(4)-C(5) = 1.458(7), C(5)-C(6) = 1.458(7), C(1)-O(1) = 1.260(6), C(3)-O(2) = 1.275(6), C(5)-O(3) = 1.249(6), C(2)-C(7) = 1.380(7), C(7)-N(1) = 1.323(7), C(8)-N(1) = 1.448(7), C(4)-C(41) = 1.388(7), C(41)-N(2) = 1.335(7), C(42)-N(2) = 1.420(7), C(6)-C(75) = 1.418(7), C(75)-N(3) = 1.311(7), C(76)-N(3) = 1.442(7), N(1)-C(7)-C(2) = 124.0(5), N(2)-C(41)-C(4) = 125.7(5), N(3)-C(75)-C(6) = 124.5(5).

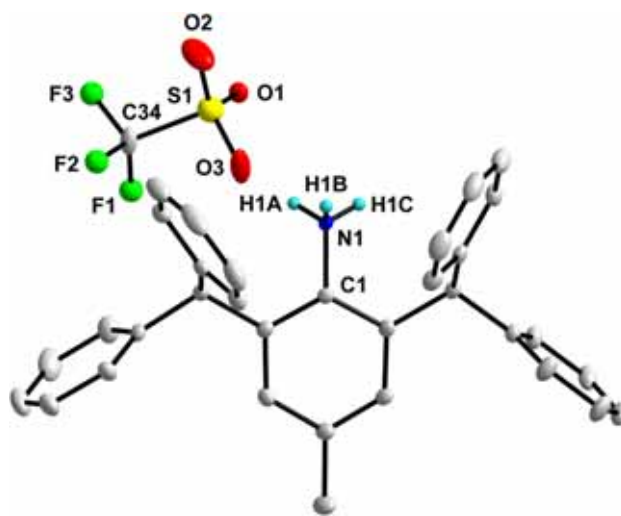


Figure 8. ORTEP representation of **5** at 30% probability level. Hydrogen atoms, except those on amino nitrogen and solvent molecules, have been removed for clarity. Selected bond distances (Å): C(1)-N(1) = 1.474(3), N(1)-H(1A) = 0.85(3), N(1)-H(1B) = 0.98(3), N(1)-H(1C) = 0.84(3), C(34)-F(1) = 1.310(4), C(34)-F(2) = 1.330(3), C(34)-F(3) = 1.327(3), C(34)-S(1) = 1.808(3), O(1)-S(1) = 1.431(2), O(2)-S(1) = 1.419(2), O(3)-S(1) = 1.429(2).

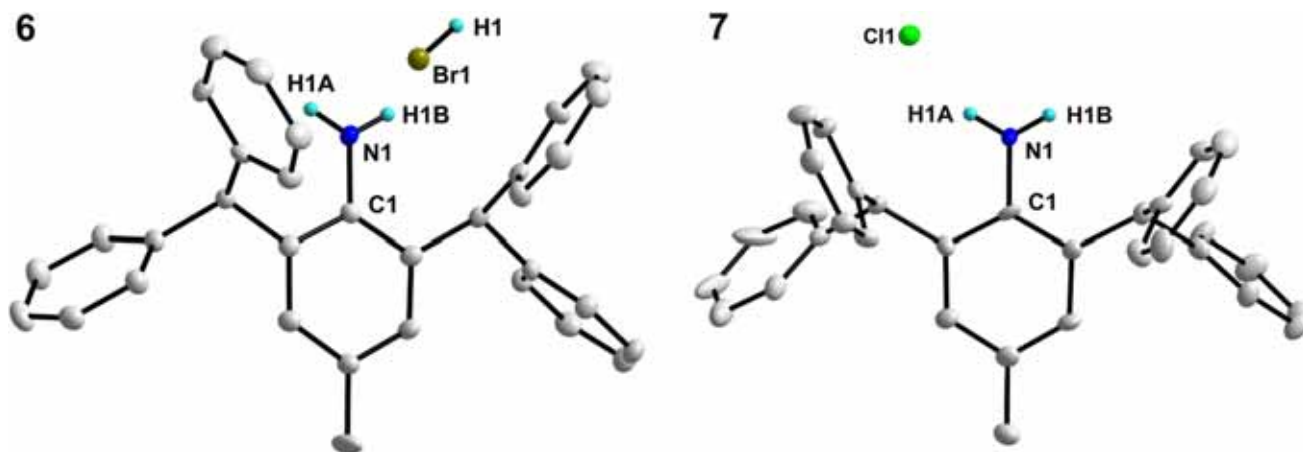


Figure 9. ORTEP representations of **6** and **7** at 30% probability level. Hydrogen atoms, except those on amino nitrogen and solvent molecules, have been removed for clarity. Selected bond distances (Å): C(1)–N(1) = 1.450(8), Br(1)–H(1) = 1.17(11) for **6**; C(1)–N(1) = 1.480(12) for **7**.

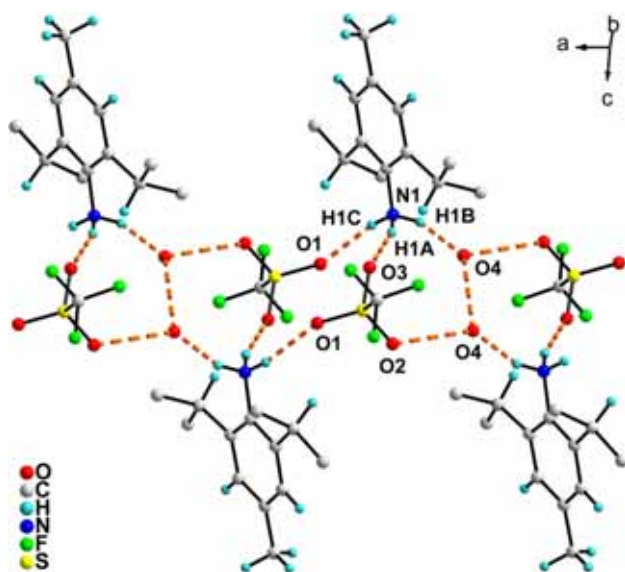


Figure 10. N–H...O and O–H...O interactions present in the crystal lattice of **5**. Benzhydryl phenyl rings have been removed for clarity. Hydrogen bond parameters (Å and deg): N1–H1A = 0.854, H1A...O3 = 1.906, N1...O3 = 2.729, N1–H1A...O3 = 161.45; N1–H1C = 0.844, H1C...O1 = 2.056, N1...O1 = 2.868, N1–H1C...O1 = 161.09; N1–H1B = 0.982, H1B...O4 = 1.836, N1...O4 = 2.774, N1–H1B...O4 = 158.80; O2...O4 = 2.994.

The ^1H and ^{13}C NMR spectra of **1** – **7** are consistent with the structures shown in Scheme 1, which were also confirmed by single crystal X-ray diffraction studies (*vide infra*). Two tautomeric forms *viz.*, enol-imine (OH form) and keto-enamine (NH form) are possible for **4** as shown in Figure 1. However, the ^1H and ^{13}C NMR spectra suggest the presence of exclusively keto-enamine form in solution. The ^1H NMR spectrum of **4** shows three closely spaced peaks for CH_3 protons

(2.17, 2.18 and 2.20 ppm), two closely spaced peaks for six Ph_2CH protons (5.61 and 5.64 ppm) and three closely spaced peaks for the six aryl protons of the central phenyl ring of the three 2,6-dibenzhydryl-4-methylphenyl groups (6.70, 6.71 and 6.72 ppm) (see Experimental section and Figure S10 in the Supplementary Information, SI). The three NH protons and the three HNC H protons are coupled to each other and each is observed as a doublet (total six doublets) with a coupling constant of 13.2 Hz as analogously observed for other tris-salicylideneamines present in the keto-enamine form.^{40,48,49} Similarly, the ^{13}C NMR spectrum of **4** shows two peaks for CH_3 carbons (21.77 and 21.79 ppm), three peaks for Ph_2CH carbons (52.14, 52.19 and 52.22 ppm) of the three 2,6-dibenzhydryl-4-methylphenyl groups and three peaks for CO carbons (184.92, 184.95 and 188.26 ppm) (see Experimental section and Figure S11 in the SI). Two geometrical isomers, **A** (with C_s symmetry) and **B** (with C_3 symmetry) are possible for the keto-enamine tautomeric form of **4**, as shown in Figure 2.⁴⁰ The ^1H and ^{13}C NMR related observations suggest that in solution, compound **4** is present exclusively in the form **A** with C_s symmetry. This contrasts with the presence of a mixture of C_3 and C_s forms for tris-salicylideneamines formed with less bulky amines such as $(\text{PhNH}_2, 4\text{-(MeO)C}_6\text{H}_4\text{NH}_2$ and $3,5\text{-Me}_2\text{C}_6\text{H}_3\text{NH}_2)$ ⁴⁰ and exclusively C_3 form for those employing amines with bulkier substituent such as 2,6-(4-(MeO) C_6H_4) $_2\text{C}_6\text{H}_3\text{NH}_2$ and others.^{48–50}

3.2 Molecular structures

Molecular structures of **1**, **2** and **4–7** were determined by single crystal X-ray diffraction studies. Crystallographic and structure refinement parameters of **1**, **2**

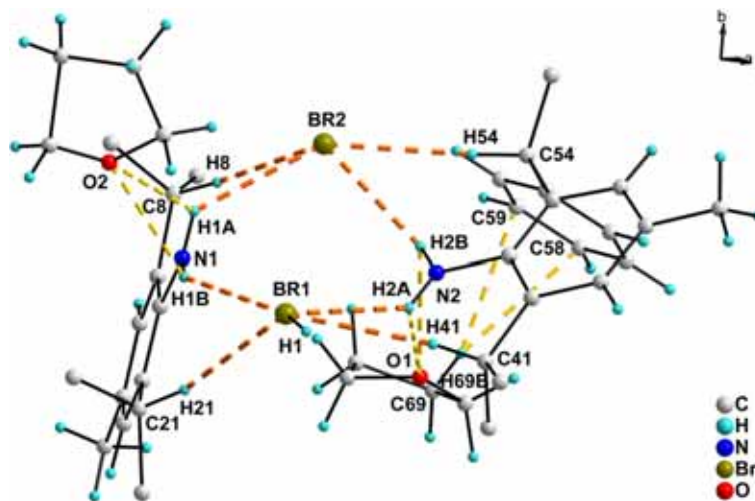


Figure 11. N-H \cdots Br, N-H \cdots O, C-H \cdots Br and C-H \cdots π interactions present in the crystal lattice of **6**. Benzhydryl phenyl rings not involved in hydrogen bonding have been removed for clarity. Hydrogen bond parameters (\AA and deg): H1B \cdots Br1 = 2.585, N1 \cdots Br1 = 3.283, N1-H1B \cdots Br1 = 136.94; H2A \cdots Br1 = 2.604, N2 \cdots Br1 = 3.299, N2-H2A \cdots Br1 = 136.54; H1A \cdots Br2 = 2.660, N1 \cdots Br2 = 3.310, N1-H1A \cdots Br2 = 131.72; H2B \cdots Br2 = 2.577, N2 \cdots Br2 = 3.280, N2-H2B \cdots Br2 = 137.42; H21 \cdots Br1 = 2.730, C21 \cdots Br1 = 3.707, C21-H21 \cdots Br1 = 166.11; H41 \cdots Br1 = 2.726, C41 \cdots Br1 = 3.714, C41-H41 \cdots Br1 = 169.89; H8 \cdots Br2 = 2.623, C8 \cdots Br2 = 3.618, C8-H8 \cdots Br2 = 175.10; H54 \cdots Br1 = 2.655, C54 \cdots Br1 = 3.653, C54-H54 \cdots Br1 = 176.54; H1A \cdots O2 = 2.458, N1 \cdots O2 = 2.675, N1-H1A \cdots O2 = 94.54; H1B \cdots O2 = 2.567, N1 \cdots O2 = 2.675, N1-H1B \cdots O2 = 87.33; H2A \cdots O1 = 2.581, N2 \cdots O1 = 2.687, N2-H2A \cdots O1 = 87.26; H2B \cdots O1 = 2.626, N2 \cdots O1 = 2.687, N2-H2B \cdots O1 = 84.43; H69B \cdots C58 = 2.870, C69 \cdots C58 = 3.777, C69-H69B \cdots C58 = 152.86; H69B \cdots C59 = 2.817, C69 \cdots C59 = 3.688, C69-H69B \cdots C59 = 147.30; H67 \cdots C1 = 2.897, C67 \cdots C1 = 3.656, C67-H67 \cdots C1 = 134.22.

and **4-7** are given in Table 1. The molecular structure of **1** is shown in Figure 3 and selected bond distances and angles for **1** along with those of structurally close compounds shown in Figure 4, are given in Table 2.⁵¹ Compound **1** is an iodo derivative of the bulky amine, **I** and the C-I distance (2.122(2) \AA) in **1** is comparable to that in **II** (2.111(4) \AA) and **III** (2.115(3) \AA) as well as to the C-I distances reported in similar compounds in literature (Figure 1).⁵²⁻⁵⁵ The C(2)–C(8) and C(6)–C(21) distances in **1** (1.529(3) and 1.528(3) \AA) are longer as compared to those in **II** (1.497(5) and 1.502(3) \AA) and **III** (1.497(2) \AA), as in the first compound, they correspond to C(aryl)–C(alkyl) bond whereas in the latter two they correspond to C(aryl)–C(aryl) bond. However, the angles C(1)–C(2)–C(8)/C(1)–C(6)–C(21) are comparable in **1**, **II** and **III** (121.8(2)/121.6(2) (**1**), 121.9(3)/121.8(2) (**II**) and 122.6(2) $^\circ$ (**III**)) which suggest that there is no effect of the substitution of 2,6-diisopropylphenyl group in **II** or 2,4,6-triisopropylphenyl group in **III** by benzhydryl

group in **1**. Schulz *et al.*, have however shown through theoretical calculations that **1** is sterically less bulky than **III** as the cone angle for **1** is 220 $^\circ$ and that for **III** is 238 $^\circ$.⁵⁶ This may have implications in the metal coordination chemistry of derivatives of **1** which needs further investigation in future. 1-D-chains are formed in the crystal lattice of **1** mediated by C-H \cdots π interactions which grow along the *a*-axis (Figure 5). Compound **2** is a mono-Schiff base and exists in enamine form as is evident by the C–O distance of 1.245(2) \AA corresponding to a double bond, C–N distance of 1.337(2) \AA corresponding to a single bond and alternate single and double bond lengths for the Nacac moiety carbons, C(36)–C(37) = 1.415(2) and C(35)–C(36) = 1.374(2) \AA (Figure 3).⁵⁷ The N1–C35–C36–C37–O1 moiety is nearly planar (angle between the mean plane defined by the atoms O1, C37, C36 and N1, C35, C36 is 2.88 $^\circ$). The central phenyl ring of the amino moiety forms an angle of 82.67 $^\circ$ with the mean plane defined by the five atoms of the Nacac moiety. The structural

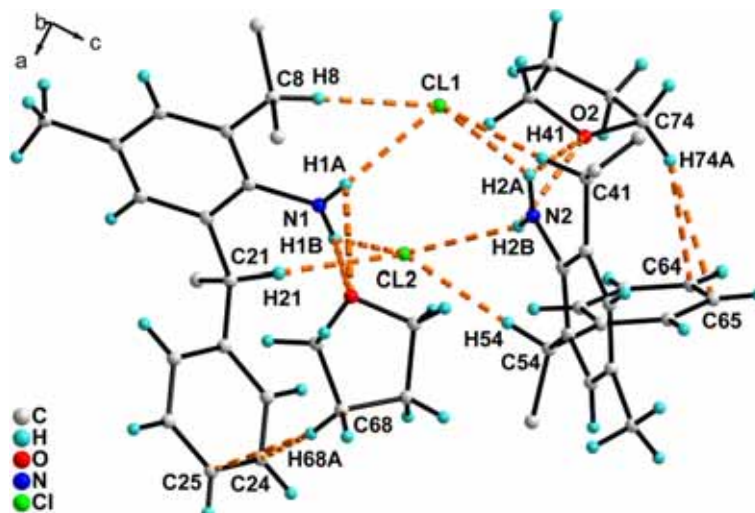


Figure 12. N-H \cdots O, N-H \cdots Cl, C-H \cdots Cl and C-H \cdots π interactions present in the crystal lattice of **7**. Benzhydryl phenyl rings not involved in hydrogen bonding have been removed for clarity. Hydrogen bond parameters (\AA and deg): H1A \cdots C11 = 2.457, N1 \cdots C11 = 3.164, N1-H1A \cdots C11 = 135.54; H2A \cdots C11 = 2.432, N2 \cdots C11 = 3.123, N2-H2A \cdots C11 = 136.03; H1B \cdots Cl2 = 2.412, N1 \cdots Cl2 = 3.118, N1-H1B \cdots Cl2 = 137.48; H2B \cdots Cl2 = 2.513, N2 \cdots Cl2 = 3.170, N2-H2B \cdots Cl2 = 131.62; H8 \cdots C11 = 2.591, C8 \cdots C11 = 3.587, C8-H8 \cdots C11 = 175.52; H41 \cdots C11 = 2.609, C41 \cdots C11 = 3.587, C41-H41 \cdots C11 = 166.05; H21 \cdots Cl2 = 2.572, C21 \cdots Cl2 = 3.572, C21-H21 \cdots Cl2 = 179.13; H54 \cdots Cl2 = 2.508, C54 \cdots Cl2 = 3.508, C54-H54 \cdots Cl2 = 176.94; H1A \cdots O1 = 2.612, N1 \cdots O1 = 2.726, N1-H1A \cdots O1 = 87.91; H1B \cdots O1 = 2.693, N1 \cdots O1 = 2.726, N1-H1B \cdots O1 = 82.76; H2A \cdots O2 = 2.599, N2 \cdots O2 = 2.705, N2-H2A \cdots O2 = 87.31; H2B \cdots O2 = 2.500, N2 \cdots O2 = 2.705, N2-H2B \cdots O2 = 93.80; H68A \cdots C24 = 2.898, C68 \cdots C24 = 3.792, C68-H68A \cdots C24 = 150.55; H68A \cdots C25 = 2.745, C68 \cdots C25 = 3.716, C68-H68A \cdots C25 = 166.59; H74A \cdots C64 = 2.784, C74 \cdots C64 = 3.676, C74-H74A \cdots C64 = 149.95; H74A \cdots C65 = 2.889, C74 \cdots C65 = 3.833, C74-H74A \cdots C65 = 159.43.

parameters of **2** match well with the mono-Schiff bases formed by the condensation of acac with amines such as 2,4,6-[CH(SiMe₃)₂]C₆H₂NH₂, 2,4,6-Me₃C₆H₂NH₂, 2-(MeS)C₆H₄NH₂, 2-(HO)C₆H₄NH₂ and 2-(HO)C₁₀H₆NH₂, reported in the literature.^{58–62} Adjacent molecules of **2** in the crystal lattice are connected by N-H \cdots O and C-H \cdots O interactions (Figure 6).

Compound **4** is a tris-Schiff base which exists in keto-enamine form in the solid state as also found in the solution (*vide supra* and Figure 7). The reported examples in the literature also show that the condensation of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde with three equivalent of amine results in the formation of a tris-Schiff base existing in the keto-enamine form.^{40,48–50,63–65} This is also evident by the observed short C-O bond distances in the range of a C-O double bond (1.249(6), 1.260(6) and 1.275(6) \AA) and nearly equal bond distances between the six carbons

of the central core ring in the range of C-C single bond (1.438(8)–1.460(7) \AA).⁵⁷ Thus, the central core of **4** is made up of cyclohexanetrione unit but the C₆ ring remains flat.^{40,48–50,63–65} It is suggested that the loss of aromaticity in the formation of cyclohexanetrione core in compounds such as **5** is accompanied by a net stabilization from the relatively large basicity of the nitrogen versus the phenolic oxygen.⁴⁰ In the past, MacLachlan and co-workers have shown that the NH form of the tris-salicylideneanilines is more stable than the OH form by -75 kJ/mol.⁴⁰ Further, from the crystal structure we find that **4** exists in the C_s form in the solid state, as also found in the solution state. This contrasts with the exclusive C₃ form observed in the hitherto reported tris-salicylideneamines.^{40,48–50,63–65} The structural parameters of **4** compare well with the tris-salicylideneamines involving a bulky amine.^{48,50} The central aryl ring

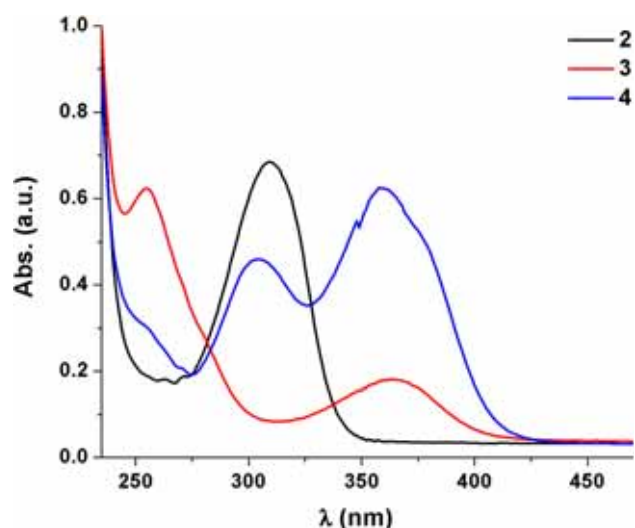


Figure 13. UV-Vis spectra of **2–4** in dichloromethane (0.5×10^{-4} M).

of the three amino moieties in **4** form an angle of 56.13° , 80.53° and 87.56° with the cyclohexanetrione core of the molecule.

The molecular structure of **5** shows that it is an ary-lammonium salt of triflic acid, as three amino hydrogen atoms could be located from the difference Fourier map (Figure 8). On the other hand, **6** and **7** are co-crystals of the bulky amine and HBr or HCl, respectively (Figure 9). The two amino hydrogen atom in both **6** and **7** could not be located and have been fixed whereas hydrogen atom could be located only on one of the two Br atoms present in an asymmetric unit of **6** while it was not be possible to locate hydrogen atom on any of the two Cl atoms in the asymmetric unit of **7**. N-H...O interactions involving amino hydrogens and triflate or crystal lattice water oxygen atoms and O-H...O interactions between the trilate oxygen and lattice water molecule as well as between the lattice water molecules lead to the formation of a 1D-chain along *a*-axis (Figure 10).

On the other hand, N-H...Br/Cl and C-H...Br/Cl interactions connect two amino molecules in the crystal lattice of **6** and **7** in the form of a dimer and THF molecules present in the crystal lattice form N-H...O and C-H... π interactions with these molecules (Figures 11 and 12).

3.3 UV-Vis absorption studies

The UV-Vis absorption spectra of **2–4** were recorded in dichloromethane and are shown in Figure 13. The absorption spectrum of **2** exhibited a band at 310 nm ($\epsilon = 13720 \text{ M}^{-1}\text{cm}^{-1}$) assignable to π - π^* transitions of the benzene rings and C=O. On the other hand, the

absorption spectrum of **3** showed bands at 255 nm ($\epsilon = 12460 \text{ M}^{-1}\text{cm}^{-1}$) and 363 nm ($\epsilon = 3640 \text{ M}^{-1}\text{cm}^{-1}$) assignable to π - π^* transitions of the aryl rings and C=N and that of **4** showed two bands at 303 nm ($\epsilon = 9220 \text{ M}^{-1}\text{cm}^{-1}$) and 358 nm ($\epsilon = 12500 \text{ M}^{-1}\text{cm}^{-1}$) assignable to π - π^* transitions of the aryl rings and C=O.

4. Conclusions

2,6-Dibenzhydryl-4-methylaniline was employed to synthesise a series of bulky compounds containing 2,6-dibenzhydrylphenyl moiety. These include a bulky iodo-derivative, one mono-, one bis- and one tris-Schiff base, one triflate salt of the bulky amine and two co-crystals of the bulky amine with HBr or HCl. The compounds have been structurally and spectroscopically characterised. This work shows various pathways of incorporating a bulky group in new compounds and opens up the possibility for the use of iodo-derivative and the three Schiff bases for further applications, including complexation. These studies are underway.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1553976-1553981 (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>). The ^1H , ^{13}C and DEPT 135 spectra of **1–7** and combined checkcif file are given in the Supplementary Information, which are available at www.ias.ac.in/chemsci.

Acknowledgements

R. M. is grateful to SERB, New Delhi for a J. C. Bose Fellowship (SB/S2/JCB-85/2014) through which this research work was carried out. P. S. thanks IIT Bombay for a Post-doctoral Fellowship. IIT Bombay is greatly acknowledged for providing analytical and instrumental facilities.

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