X-ray Crystal Structure of Hetaryl Leuco-TAM Dyes, (2Z,2'E)-2,2'-(2-Phenyl Propane-1,3-diylidene) Bis(1,3,3-trimethyl indoline) Derivatives

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The unequivocal solid-state structure and stereochemistry of the hetaryl leuco-TAM dye, 2,2'-(2-phenyl propane-1,3-diylidene) bis(1,3,3- trimethylindoline) derivatives were established using X-ray single crystal analysis. The X-ray crystal analysis showed that the (Z, E)-isomers only formed stereoselectively, with a so-called "three-bladed propeller" conformation, from the reaction of a Fischer base and benzaldehyde derivatives. These isomers were stacked in a juxtaposition to form a dimer or a double dimer, adopting either a triclinic, with P-1, or monoclinic crystal system with a space group P21/n in the unit cell of the crystal.

Introduction

Triarymethane (TAM) compounds are known as an important group of intermediates in the synthesis of various functional organic compounds. These molecules are sometimes called "Leuco bases" and are precursors of cationic TAM⁻ dye molecules.[1-4]

TAM compounds have traditionally been used in various chemical and industrial applications. Triarylmethane dyes have potentially numerous applications in the chemical, pharmaceutical and life science industries including staining agents, ink dyes, thermal imaging and carbonless copying materials, drugs, leather, *etc.*[5,6] These dyes are also used in medicinal applications such as photochemotheraphy agents, particularly in eye protection devices *etc.*[7,8]

The group of triarylmethane (TAM⁻) dyes includes a wide range of substances with an absorption maxima between 450 and 650 nm. A number of TAM⁺ dye molecules, such as Malachite green (MG), Crystal violet, Pararosanilin, *etc.*, are well known. Among them, MG is one of the most commonly used chemicals in dye chemistry. MG is a common green dye, but it is absorbed into the human body in other forms such as carbinol and leuco forms. MG is very active with the fungus Saprolegnia, which infects fish eggs in commercial aquacul-

ture and is also known to be a good treatment against ichthyophthirius in freshwater aquaria. However, the use of this substance has been restricted in many countries because of its toxicity.[9,10]

Very recently, novel hetaryl leuco-TAM molecules were synthesized from the reaction of excess Fischer base and substituted salicylaldehydes. The chemical structures of these molecule in solution were tentatively determined using 1H & 13C NMR spectroscopy and chemical analysis.[11]

The hetaryl leuco-TAM molecules in the solid state must be structurally identified. To the best of knowledge, the X-ray crystal analysis of these leuco-TAM dyes bearing two FB (Fischer base) moieties has never been described in the literature so far. This work described the solid state structure of the heteroaryl leuco-TAM dyes, **1-3**, in Scheme 1.

Experimental Section

General procedures. The melting points were determined on a Fischer-Johns block and were uncorrected. The ¹H NMR spectra were taken using a Bruker CXP-400 FT-NMR spectrophotometer. The electron-impact (EI) mass spectra were recorded on a VG Quattro mass spectrometer at Queen's University.

Materials. The Fischer base (2-methylene-1,3,3-trimethyl-indoline) and salicylaldehyde derivatives were obtained from the Aldrich Chemical Co. and used without further purification. A mixture of 5-substituted salicylaldehyde and excess (2-3 fold) Fischer base in ethanol was stirred at room temperature for 2-4 hours to prepare the heteroaryl leuco-TAM dye {2,2'-(2-phenylpropane-1,3-diylidene)bis(1,3,3-trimethyl-indoline)} derivatives. The white precipitate was filtered from the reaction mixture and washed thoroughly with cold diethyl ether. Purification was carried out through precipitation from chloroform/hexane. The product was identified using ¹H NMR, X-ray crystal structure ananlysis and EI-mass spectroscopy, and it exhibited the appropriate elemental behavior.

(2Z,2'E)-2,2'-(2-Phenylpropane-1,3-diylidene)bis(1,3,3-
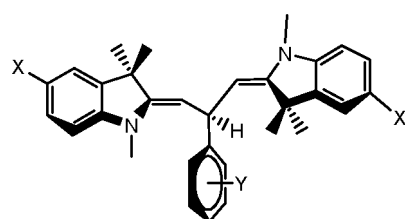
Compounds	X	Y
1 bis-(FB)PP	H	H
2 bis-(5-ClFB)PP	Cl	H
3 bis-(5-ClFB)(2-Cl-5-NO₂P)P	Cl	2-Cl, 5-NO₂

Scheme 1. Chemical structures of the hetaryl leuco-TAM bis-(FB)PP molecules examined.

trimethyl indoline) bis-(FB)PP, 1: White, Yield 75%, m.p. 146.4 °C. ^{1}H NMR(300 MHz, CDCl$_3$) δ 1.35 (s, 3H), 1.44 (s, 3H), 1.54 (s, 3H), 1.71 (s, 3H), 2.99 (s, 3H), 3.31 (s, 3H), 4.38 (d, J = 9.3 Hz, 1H), 4.45 (d, J = 9.9 Hz, 1H), 5.30 (t, J = 9.0, 10.2 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 6.79 (t, J = 8.7 Hz, 1H), 7.07 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.22 (t, J = 8.7 Hz, 1H), 7.34 (t, J = 7.2, 7.5 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 28.5, 28.9, 29.3, 30.5, 30.7, 33.7, 38.6, 44.3, 44.9, 97.7, 101.9, 105.3, 106.3, 122.0, 122.4, 122.5, 123.5, 126.0, 127.3, 127.4, 127.8, 128.5, 139.6, 139.9, 145.0, 146.7, 147.7, 151.5, 151.8; EI-Mass for C$_{31}$H$_{34}$N$_2$, Mw: 434.6; 158(26), 173(32), 260(72), 262(44), 263(24), 358(38), 420 (58), 434(100), 435(34) *m/z* (%): C, 85.67; H, 7.89; N, 6.45 obtained C, 84.54; H, 8.09; N, 6.34.

(2Z,2'E)-2,2'-(2-Phenylpropane-1,3-diylidene)bis(5-chloro-1,3,3-trimethyl indoline), bis-(5-ClFB)PP, 2: White, Yield 82%, m.p. 189 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.32 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 1.68 (s, 3H), 2.95 (s, 3H), 3.26 (s, 3H), 4.36 (d, J = 9.2, 1H), 4.42 (d, J = 10.2 Hz, 1H), 5.22 (t, J = 9.6 Hz, 1H), 6.35 (d, J = 8.5 Hz, 1H), 6.42 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 2.1 Hz, 1H), 7.02 (d, J = 2.3 Hz, 1H), 7.05 (dd, J = 8.3, 2.1 Hz, 1H), 7.09 (dd, J = 8.3, 2.3 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 28.1, 28.5, 28.9, 30.1, 30.4, 33.3, 38.3, 44.0, 44.6, 97.5, 101.6, 105.0, 106.0, 121.6, 122.0, 125.7, 127.0, 127.1, 127.5, 128.2, 139.4, 139.6, 144.8, 146.4, 145.0, 147.4, 151.3, 151.6; EI-Mass for C$_{31}$H$_{32}$Cl$_2$N$_2$, Mw: 503.5; 192(46), 207(52), 280(40), 294(98), 297(34), 309 (26), 425(34), 427(24), 487(70), 502(100), 504(66), 506(10) *m/z* (%): C, 73.95; H, 6.41; Cl, 14.08; N, 5.56 obtained C, 74.14; H, 6.52; Cl, 13.94; N, 5.84.

(2Z,2'E)-2,2'-(2-(2-Chloro-5-nitrophenyl)propane-1,3-diylidene)bis(5-chloro-1,3,3-trimethyl indoline), bis-(5-ClFB) (2Cl-5-NO$_2$-P)P, 3: Orange, Yield 65%, m.p. 201.5 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (s, 3H), 1.31 (s, 3H), 1.49 (s, 3H), 1.55 (s, 3H), 2.95 (s, 3H), 3.28 (s, 3H), 4.31 (d, J = 9.0, 1H), 4.37 (d, J = 10.2 Hz, 1H), 5.52 (t, J = 9.0, 10.5 Hz, 1H), 6.34 (d, J = 9.0 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 2.1 Hz, 1H), 6.95 (d, J = 2.7 Hz, 1H), 7.06 (dd, J = 9.0, 2.1 Hz, 1H), 7.09 (dd, J = 8.4, 2.7 Hz, 1H), 7.52 (d, J = 9.0 Hz, 1H), 8.02 (d, J = 2.1 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 28.5, 28.9, 29.6, 30.4, 30.6, 33.5, 38.6, 43.7, 44.4, 100.4, 103.9, 104.6, 105.6, 118.0, 118.2, 126.3, 126.6, 126.7, 127.6, 128.9, 138.3, 138.5, 140.5, 146.1, 151.1, 151.3, 151.4, 152.8; EI-Mass for C$_{31}$H$_{30}$Cl$_3$N$_3$O$_2$, Mw: 582.9; 192(100), 194(58), 207(26), 339(78), 373(74), 374(70), 375(60), 425 (82), 427(58), 566(44), 568(48), 581(58), 583(56), 585(17.7), 587(2) *m/z* (%): C, 63.87; H, 5.19; O, 5.49; N, 7.21; Cl, 18.25 obtained C, 64.21; H, 5.23; O, 5.41; N, 7.15; Cl, 18.37.

X-ray Crystallography. Crystal data for C$_{31}$ H$_{32}$ N$_2$ Cl$_2$, M = 503.49, monoclinic, a = 9.7043(8), b = 22.8136(18), c = 12.0760(10) Å, U = 2667.5(4) Å, T = 293(2) K, space group $P2(1)/n$, Z = 4, μ(Mo-K$_\alpha$) = 0.266 mm^{-1}, 27341 reflections measured, 6598 unique (R$_{int}$ = 0.0327) which were used in all calculations. Data for C$_{31}$H$_{34}$N$_2$, M = 474.60, triclinic, a = 8.3642(5), b = 13.0783(7), c = 13.2056(7) Å, U = 1352.44

(13)(4) Å, T = 233(2) K. space group P-1, Z = 2, μ(Mo-K$_\alpha$) = 0.074 mm^{-1}, 18774 reflections measured, 6747 unique (R$_{int}$ = 0.0305) which were used in all calculations.

The final wR(F^2) was 0.0433 (all data). The intensity data for **1-2** were collected using a Siemens SMART ccd area detector mounted on a Siemen P4 diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) source and a CCD detector. The total multi frames of the two-dimensional diffraction images were collected. The frame' data were processed to determine the structure factors using the program SAINT.^{12} The structure was found using direct methods and refined with full matrix least-squares on F^2 for all of the data using the SHELXTL software.^{13} The hydrogen atom position was initially determined geometrically and refined using a driding model. The non-hydrogen atoms were refined using the anisotropic displacement parameters.

Results and Discussion

From the reaction of the Fisher base, 2-methylene-1,3,3-trimethylindoline with substituted benzaldehydes in a 2.5:1 ratio in methylene chloride, the corresponding hetaryl leuco-TAM molecules, and 5-substituted (2Z,2'E)-2,2'-(2-phenylpropane-1,3-diylidene)bis(1,3,3-trimethylindoline) **1-3** were obtained.

The stereochemistry of the diastereomer for the prepared hetaryl leuco-TAM molecules in organic solvents was tentatively determined using ^{1}H and ^{13}C NMR spectroscopy. The (Z, E)-isomer was obtained as a major product in all of the cases examined. The other diastereomers could not be found and isolated in the solid state without any clear reason.

Table 1 shows the crystal data, structure refinement, atomic coordinates (× 104), and equivalent isotropic displacement parameters (Å2 × 103) for the bishetarylarylmethanes **1-3**. Selected bond lengths and bond angles were collected in Table 2.

A comparative analysis of the X-ray crystal structures of the hetaryl leuco-TAM dyes **1 - 3** revealed that, while bis-(FB)PP, **1** and bis(5-ClFB)(2-Cl-5-NO$_2$-P)P, **3** adopted a triclinic crystal system with the space group P-1, bis-(5-ClFB)PP, **2** displayed a monoclinic crystal system with the space group $P2_1/n$. An ORTEP diagram of bis-(5-ClFB)PP **2** showing the atom numbering scheme is included in Figure 1 as a representative example.

The prepared molecules **1-3** crystallized from acetone. Unfortunately, crystal growth was unsuccessful for molecule **4**.

For compound **1**, the C(7)-C(8) and C(7)-C(20) distances were 1.523 and 1.504 Å, respectively, which were typical lengths of C-C single bonds. The enamine C(8)-C(9) and C(20)-C(21) bonds were 1.335 and 1.329 Å, respectively, which were typical lengths of C=C bonds. Similar C-C single and C=C double bond characteristics were observed for compounds **2** and **3**.

In the crystals, three aromatic rings of the heteroaryl TAM leuco dyes **1-3** were linked into three different layers. Namely, these molecules had so-called "three-bladed propeller" conformations, as reported earlier for various nonheteroaryl TAM dyes.^{14,15}

The inter-planes angles of the aromatic ring A-B, A-C & B-C were 79.8, 84.8 & 74.9; 60.1, 83.2 & 75.7; and 77.9, 80.2 & 85.6° for **1**, **2** and **3**, respectively, in Figure 2. The NMR

Table 1. Crystal data and structure refinement for bis-(FB)PP **1**, bis-(5-ClFB)PP **2** and bis-(5-ClFB)(2-Cl-5-NO₂P)P **3**.

Identification code	bis-(FB)PP	bis-(5-ClFB)PP	bis-(5-ClFB)(2-Cl-5-NO₂P)P
Empirical formula	$C_{31} H_{34} N_2$	$C_{31} H_{32} Cl_2 N_2$	$C_{31} H_{29} Cl_3 N_3 O_2$
Formula weight	434.60	503.49	582.95
Temperature	233(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic,	Monoclinic	Triclinic
space group	*P*-1	*P*21/n	*P*-1
Unit cell dimensions	$a = 8.3642(5)$ Å	$a = 9.7043(8)$ Å	$a = 10.4953(9)$Å
	$\alpha = 106.1230(10)°$	$\alpha = 90°$	$\alpha = 69.255(2)°$
	$b = 13.0783(7)$ Å	$b = 22.8136(18)$ Å	$b = 12.4987(11)$ Å
	$\beta = 100.7900(2)°$	$\beta = 93.839(2)°$	$\beta = 68.635(2)°$
	$c = 13.2056(7)$ Å	$c = 12.0760(10)$ Å	$c = 12.7481(11)$ Å
	$\gamma = 93.8030(10)°$	$\gamma = 90°$	$\gamma = 79.762(2)°$
Volume	1352.44(13)(4) Å	2667.5(4) Å	1454.1(2) Å
Z	2	4	2
Calculated density	1.165 Mg/m³	1.254 Mg/m³	1.329 Mg/m³
μ	0.074 mm⁻¹	0.266 mm⁻¹	0.348 mm⁻¹
F(000)	508	1064	612
Crystal size	0.22 × 0.14 × 0.10 mm	0.22 × 0.14 × 0.10 mm	0.25 × 0.16 × 0.07 mm
Θrangefordata collection	1.63 to 28.42 deg.	1.79 to 28.29 deg.	1.74 to 28.33 deg.
Limiting indices	$-11 \le h \le 11, -17 \le k \le 17,$ $-17 \le l \le 17$	$-12 \le h \le 12, -29 \le k \le 30,$ $-16 \le l \le 16$	$-13 \le h \le 13, -16 \le k \le 16,$ $-16 \le l \le 16$
Reflections collected / unique	18774/6747 [R_{int} = 0.0305]	27341 / 6598 [R_{int} = 0.0327]	15159 / 7154 [R_{int}= 0.0493]
Completeness to θ = 28.43	99.1%	99.8%	98.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix LS on F^2	Full-matrix LS on F^2
Data/restraints/ parameters	6747 / 0 / 329	6598 / 0 / 322	7154 / 0 / 358
Goodness-of-fit on F^2	1.033	1.010	0.861
Final R indices [I > 2σ(I)]	$R1 = 0.0622, wR2 = 0.1805$	$R1 = 0.0433, wR2 = 0.1052$	$R1 = 0.0639, wR2 = 0.1891$
R indices (all data)	$R1 = 0.1206, wR2 = 0.2304$	$R1 = 0.0760, wR2 = 0.1269$	$R1 = 0.1691, wR2 = 0.2776$
Largest diff. peak and hole	0.517 and -0.386 e.A³	0.245 and -0.301 e.A³	0.501 and -0.514 e.A³

$^{a}R_1 = \Sigma |F_o|-|F_c|$ (based on reflections with $F_o^2 > 2\sigma F^2$). $^{b}wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$(also with $F_o^2 > 2\sigma F^2$).

Table 2. Selected bond distances (Å), and bond angles (°) for **1 - 3**.

Ring	Bond length (Å) & Bond angle (°)	Bis compounds		
		1	**2**	**3**
A	C8-C7	1.523	1.513	1.508
A	C9-C8	1.335	1.330	1.326
B	C7-C20	1.504	1.506	1.511
B	C20-C21	1.329	1.332	1.327
A	N1-C9-C8	129.7	129.4	129.4
A	C9-C8-C7	130.9	131.0	132.8
B	C7-C20-C21	128.3	127.4	128.2
B	C20-C21-N2	124.2	123.0	122.7
A	C15-N1-C9	127.0	126.6	126.6
A	C12-N1-C15	121.5	121.1	122.4
A	C10-C9-C8	122.9	122.9	123.5
	C8-C7-C20	110.4	110.0	110.8
	C8-C7-C1	115.0	113.8	112.4
	C1-C7-C20	108.5	109.7	107.9
A	N1-C9-C10	107.4	107.5	107.2
A	C9-N1-C12	111.3	110.3	110.9
B	C24-N2-C21	112.2	111.4	111.7
B	C24-N2-C27	125.5	124.0	124.6
B	C21-N2-C27	122.1	123.8	123.6

spectra indicated that these compounds are rigid in solution.[11] The conformations of these compounds were energetically favored in the solid and solution states and therefore, of major interest for stereochemistry.

The dihedral angles of H7-C7-C8-H8 (θ_1) and H7-C7-C20-H20 (θ_2), were 149.8 & 164.1, 158.9 & 178.9, and 139.8 & 152.9° for bis-(FB)PP **1** and bis-(5-ClFB)PP **2** and bis-(5-ClFB)(2-Cl-5-NO₂p)p **3**, respectively.

The dihedral angles of these molecules in the solution state have been calculated using the modified Karplus equation from the ¹H NMR vicinal coupling constant values of 1-3.[16] As an example, the calculated coupling constants of **1** were 9.32 and 10.9 Hz for H7-C7-C8-H8 and H7-C7-C20-H20, respectively. These values were in excellent agreement with the experimental values (9.30 and 10.2 Hz),[11] which may imply that the stuctures of the newly synthesized bishetarylaryl methane molecules were very similar to those in the solution state.

The inter-planes angles and dihedral angles for **1-3** are given in Table 3.

The double bonds C(8)=C(9), C(20)=C(21) of the two Fischer base moieties had (*Z, E*) configurations. The (*Z, E*) isomers of the hetaryl leuco-TAM dyes 1-4 formed as the sole product in each case, even though three isomers, (*Z, E*), (*E, E*) & (*Z, Z*), were possible for these dyes from the reaction of excess Fischer
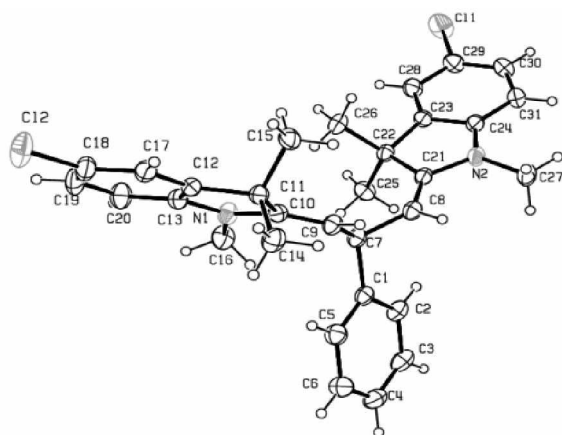
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Figure 1. ORTEP diagram of bis-(5-ClFB)PP 2, showing the atom numbering scheme.
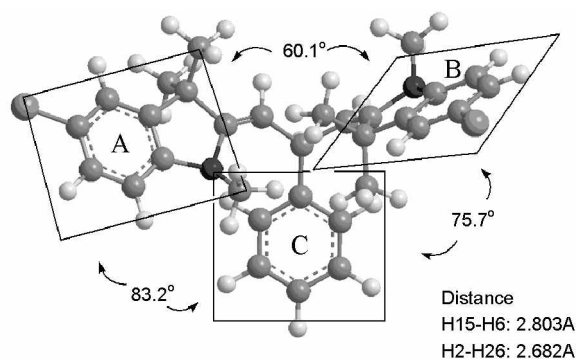
Figure 2. Propeller shape of bis-(5-ClFB)PP, 2, showing the inter-planes angles.

Figure 3. Molecular packing diagram of the bis-FB molecules, showing the formation of the dimer and double dimer, for 1 (A) & 2 (B), respectively. The intermolecular distances are depicted by dotted lines.

Figure 4. UV-Vis spectral data of bis(5-ClFB)PP 2 in EtOH, showing the various forms such as the leuco (2a, solid), TAM⁺ (2b, dashed), carbinol (2c, short-dashed) and decomposed forms (2d, dotted).

base and benzaldehydes. The distances between the gem-methyl proton, H26, and the ortho-proton, H2, of the phenyl ring were 3.133 and 2.803 Å, and distances between the N1-Me group and the ortho-proton, H6, of the phenyl ring were 2.977 and 2.682 Å, for the compound 1 and 2, respectively. The former was longer than the latter, which implied that the *E*-configuration was favored over the *Z*-isomer. Therefore, the presence of the (*E*, *E*) isomer was expected to be minor, and the (*Z*, *Z*) isomer was expected to be extremly minor if any formed at all. The stereoselective formation of the (*Z*, *E*) isomer of these dyes from the reaction of excess Fischer base and benzaldehydes requires further examination.

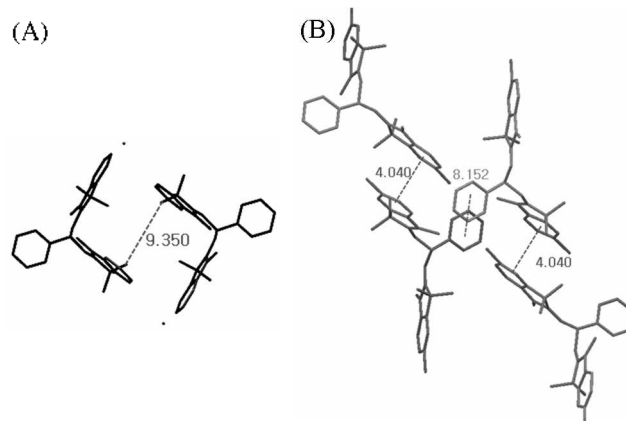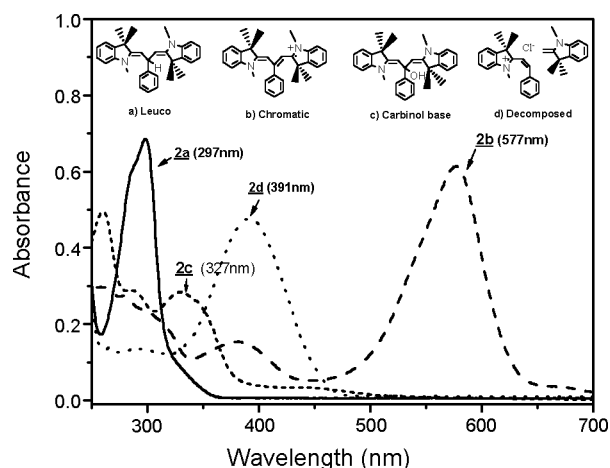Compound 1 was stacked in a juxtaposed manner to form a dimer in the unit cell of the crystal. Whereas bis-(5-ClFB)PP

2 was stacked to form double dimers in the unit cell of the crystal. This interesting conformation was stabilized for both cases *via* intermolecular dispersive interactions between two aromatic rings in the crystal packing. However, the distances between molecules in 1 and 2 differed, and also, the crystal packing in the unit cells of the two compounds were distinct as shown in Figures 3A and 3B. The indole unit of one molecule was parallel to the indole unit of the second molecule. The distances between the two indole planes were 9.350 and 4.040

Table 3. Inter-planes angles and dihedral angles (°) for the hetaryl leuco-TAM 1, 2 & 3.

Angles		Major (Z, E) isomer		
		bis-(FB)PP, 1	bis-(5-ClFB)PP, 2	bis-(5-ClFB)(2-Cl-5-NO₂P)P, 3
Inter-plane of	Ring A - Ring B	79.8	60.1	77.9
	Ring A - Ring C	84.8	83.2	80.2
	Ring B - Ring C	74.9	75.7	85.6
Dihedral	H7-C7 - C8-H8	149.8	158.9	139.8
	H7-C7 - C20-H20	164.1	178.9	152.9

Table 4. UV-Vis spectral data of the various forms of the hetaryl leuco-TAM **1**, **2** & **3**.

Compounds				Various Structural Forms[a] (λ_{max})				Solid Colour
Names	Aryl	Aryl'	Aryl"	Leuco (a)	Carbinol (b)	TAM⁻ (c)	Decompd.(d)	
Crystal Violet[b]	4-N(Me)₂	4-N(Me)₂	4-N(Me)₂	265	266	585	-	blue violet
Malachite Green[c]	H	4-N(Me)₂	4-N(Me)₂	265	265, 620	620, 430	-	green
bis-(FB)PP **1**	H	FB	FB	284	343	609, 426	385	blue
bis-(5-ClFB)PP **2**	H	5-ClFB	5-ClFB	296	327	578, 370	391	blue
bis-(5-ClFB)(2-Cl, 5-NO₂P)P **3**	2-Cl, 5-NO₂	5-ClFB	5-ClFB	290	-	-	379	yellow

[a]Symbols (a)-(d) are denoted as indicated in Figure 4. [b]Data in acetonitrile from the ref. 18. [c]Data in acetonitrile from the ref. 19.

A for **1** and **2**, respectively. The molecules in **2** were stacked well and the intermolecular interaction in **2** was stronger than in **1**. These unique structural features of **1** & **2** explained the ease of formation and the relatively high stability of the crystalline phase.

The UV-Vis spectral data of the heteroaryl leuco-TAM dye showed various structural forms such as the (a) leuco-, (b) carbinol-, (c) chromatic and (d) decomposed conjugated forms, in Figure 4.

The chromatic form (b) was obtained from the reaction of the leuco form (a) of the bis-(FB)PP materials with DDQ/HCl, except in the case of compound **3**. The chromatic forms of the prepared leuco-TAM molecules had an absorption maxima at 550 ~ 650 nm in organic solvents. The compound, bis-(5-ClFB)(2-Cl-5-NO₂P)P **3**, had an ortho-Cl substituent, which may have prevented the molecules from adopting a planar structure through the so-called steric inhibition of resonance.[17] In a basic media, the carbinol form (b) was detected at 327 ~ 346 nm in acetonitrile. The leuco form of these molecules decomposed in acid to form conjugated molecules at 369 ~ 391 nm. UV-Vis spectral behavior of the various forms of the bis-FB compounds **1-3** are summarized in Table 4 in comparison to those of well-known TAM dyes.

Conclusions

The unequivocal solid-state structure and stereochemistry of novel hetaryl leuco-TAM dye 2,2'-(2-phenyl propane-1,3-diylidene) bis(1,3,3-trimethylindoline) derivatives was established using X-ray single crystal analysis. The X-ray crystal analysis showed that the (Z, E)-isomers formed stereoselectively, with a so-called "three-bladed propeller" conformation. These isomers stacked in a juxtaposition to form a dimer or a double dimer, adopting either a triclinic, with P-1, or monoclinic crystal system with a space group P21/n in the unit cell of the crystal.

The UV-Vis spectral behaviors showed various structural forms for bis-(FB)PP, such as the leuco-, carbinol-, chromatic TAM⁻ and decomposed conjugated forms, for typical TAM dyes such as Malachite green and Crystal violet. A detailed discussion and theoretical calculation for the stability of (E, Z) isomer will be presented in a future work, in comparison to other two isomers (E, E) and (Z, Z).

Supplementary Material. The crystallographic data for the structural analysis was provided to the Cambridge Crystallo-

graphic Data Center as supplementary publication numbers CCDC 703443, 703444 & 703445 for **1-3**, respectively. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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