# Crystal structure of p-formylphenyl, di(p-methylphenyl)amine, and p-bromophenyl, di(o-bromo-p-methylphenyl)amine

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p-Formylphenyl, di(p-methylphenyl)amine (1), and p-bromophenyl, di(o-bromo-p-methylphenyl)amine (2) were prepared and characterized by X-ray crystallography. Formyl-substituted triphenylamine(1) crystallizes in the monoclinic space group  $P2_1/c$  with a = 9.068(1), b = 17.115(2), c = 11.297(2) Å,  $\beta = 106.73(1)^\circ$ , V = 1679.0(5) Å<sup>3</sup> and Z = 4. Bromo -substituted compound 2 crystallizes in the monoclinic space group  $P2_1/n$  with a = 16.170(4), b = 7.9477(8), c = 16.906(4) Å,  $\beta = 117.67(2)^\circ$ , V = 1924.1(7) Å<sup>3</sup> and Z = 4. The N atoms deviate slightly from the plane of the bonded C atoms and the benzene ring planes are rotated by 25–67° to avoid overlap of the *ortho*-substituted atoms. The major force of crystal formation comes from the multiple phenyl embraces (MPE).

**KEY WORDS:** Electroluminescence; triphenylamine; multiple phenyl embraces.

## Introduction

Considerable effort has been made in the last decade in the synthesis of nonlinear optical (NLO) and electroluminescence (EL) chromophores and their incorporation into a polymer matrix to develop new organic polymer-based electrooptic materials.<sup>1–3</sup> Introduction of diarylamino functionalities to NLO chromophore molecules has been shown to enhance the thermal stability dramatically.<sup>4,5</sup> EL devices have been found to possess high performance when triphenylamine containing chromophores were incorporated into the active layer.<sup>6,7</sup> Triphenylamine derivatives are also the compounds necessary for the preparation of ammonium salt-free radicals.<sup>8,9</sup>

Molecules carrying triphenyl groups, -XPh<sub>3</sub> often engage in so-called multiple phenyl embraces (MPE), in which the phenyl rings of two groups are interleaved in such a way that six and/or four edge-to-face (ef) phenyl—phenyl interactions are established.<sup>10</sup> A prevalent MPE is the sextuple phenyl embrace (SPE), which occurs for compounds containing  $Ph_3P$  or  $Ph_4P^+$  and is a dominant factor in their crystal packing.<sup>11,12</sup> SPE have net attractive energies in the range 60 to 85 kJ mol<sup>-1</sup> and P...P separations in the range 6.4–7.4 Å. Another MPE engaged by  $Ph_4P^+$  and  $Ph_4As^+$  groups is the quadruple phenyl embrace (QPE) involving two phenyl groups on each partner.<sup>12,13</sup> QPEs frequently occur at relatively longer P...P (or As...As) separations and have lower attractive energies. Triphenylamine and trip-tolylamine have been presented.<sup>14,15</sup> In this paper, we reported the intramolecular electronic interaction in two  $Ph_3N$  containing compounds and the MPE between  $Ph_3N$  moieties.

#### Experimental

#### Syntheses and identification

All reagents were purified by distillation or recrystallization. <sup>1</sup>H-NMR measurements with shifts relative to internal TMS were recorded on a Bruker AC-500 NMR spectrometer; FT-IR spectra were

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taken using KBr mulls pressed into pellets, on a Perkin-Elmer PRA-1000 spectrometer.

Formyl-substituted compound 1 was prepared by Vilsmerier–Haack formylation of 4,4'-dimethyltriphenylamine: 2.2 g DMF (30 mmol) and 4.6 g POCl<sub>3</sub> (30 mmol) were stirred at  $0^{\circ}$ C under N<sub>2</sub> atmosphere. A solution of 5.5 g (20 mmol) 4,4'dimethyltriphenylamine dissolved in 20 ml 1,2dichloroenthane was added. The mixture was kept at 80-90°C for 6 h, then cooled to room temperature, poured into ice-water, and neutralized with 2MNaOH solution. The solid was collected, washed with water, dried, and purified by recrystallizing from ethanol. The compound obtained, 4,4'-dimethyl-4"formyl-triphenylamine (1), was a yellow solid; m.p. : 105–106°C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 8.50 (1 H), 6.90-7.60 (12 H), 2,30 (6 H); IR (KBr): 2750, 1690, 1590, 1500, 1320, 1290, 1220, 845 cm<sup>-1</sup>. Compound 1 was dissolved in petroleum ether/acetone (volume, 3/1), and the resulting clear solution was evaporated at room temperature to yield yellow prismatic crystal.

Treatment of 4,4'-dimethyltriphenylamine (10 mmol) with NBS (35 mmol) in CCl<sub>4</sub> at 70°C for 3 h gave compound **2** a 70% yield. Further purified by recrystallizing from THF/methanol (volume, 1/1). The pale-yellow product 4,4'-methyl-2,2',4"-tribromo-triphenylamine melts at 138–140°C. <sup>1</sup>H-NMR: (500 MHz, CDCl<sub>3</sub>): 6.75–7.45 (10 H), 2,30 (6 H); IR (KBr): 2850, 1590, 1510, 1490, 1330, 1070, 810 cm<sup>-1</sup>. Single crystals suitable for crystal analyses were grown from THF solution by slow evaporation.

### Crystal determination

Single crystals of the two compounds, each having approximate dimensions of 0.20\*0.20\*0.30, were mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$  radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement. Hydrogen atoms were not refined. The crystal structures were solved by direct methods<sup>16</sup> and expanded using Fourier technique.<sup>17</sup> A summary of data collection and structure refinement is given in Table 1; final atomic positional parameters, selected bond lengths, and bond angles are given in Tables 2 and 3, respectively.

Table 1. Crystal Data and Structure Refinement

Molecule	1	2
Formula	$C_{21}H_{19}NO$	C <sub>20</sub> H <sub>16</sub> NBr <sub>3</sub>
CCDC no.	CCDC-1003/5970	CCDC-1003/5971
Color/shape	Yellow, prismatic	Yellow, prismatic
Formula weight	301.39	510.07
Temperature	293 K	293 K
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1}/c$ (#14)	$P2_1/n$ (#14)
Unit cell		
dimensions (Å)		
a = 9.068(1)		a = 16.170(4)
b = 11.115(2)		b = 7.9477(8)
c = 11.297(2)		c = 16.906(4)
$\beta = 106.73(1)^{\circ}$		$\beta = 117.67(2)^{\circ}$
Volume Å <sup>3</sup>	1679.0(5)	1924.17(7)
Ζ	4	4
Density (calculated)	1.192 g/cm <sup>3</sup>	1.761 g/cm <sup>3</sup>
$\mu$ (Mo $K\alpha$ ), cm <sup>-1</sup>	0.73	63.10
$2\theta_{\rm max}$	$50^{\circ}$	$50^{\circ}$
No. of reflections	Total: 3152	Total: 3497
measured		
	Unique: 2953	Unique: 3355
	$(R_{\rm int} = 0.059)$	$(R_{\rm int} = 0.036)$
No. of observations	$(I > 3.00\sigma(I))$ 1980	$(I > 2.5\sigma(I))$ 2094
No. variables	210	218
Reflection/ para-	9.43	9.61
meter ratio		
Residuals: $R/R_w$	0.051; 0.065	0.045; 0.054
Goodness of	2.29	1.94
fit indicator		
Max. shift/error	0.01	0.00
in final cycle		
Max. peak in final	$0.24 \text{ e}^{-}/\text{Å}^{3}$	$0.48 \text{ e}^{-}/\text{Å}^{3}$
diff. map		
Min. peak in final	$-0.17 \text{ e}^{-}/\text{Å}^{3}$	$-0.58 \text{ e}^{-}/\text{Å}^{3}$
diff. map		

# **Results and discussion**

Thermal ellipsoid plots of the two compounds are shown in Fig. 1. In compound 1, one of the N-bonded benzene rings is substituted by formyl at the para position. This result suggests that the formylation of 4,4'-dimethyltriphenylamine led to the para-positionsubstituted product; electrophilic substitution at the ortho-position may be sterically inhibited. For compound 2, the bromine atoms substituted not only at the para position of one benzene ring but also at the ortho position of the other two benzene rings. In an early report, Baker and his co-workers claimed that bromination of tripenylamine in organic solvent stopped at the para-substitution stage.<sup>18</sup> Our result is in disagreement. The free radical mechanism substitution can obviously take place at the ortho position when the para positions were occupied.

		Compound 1				Compound 2			
Atom	X	у	Z,	B(eq)	Atom	x	у	z	B(eq)
0	-0.5604(3)	0.7892(2)	0.0535(2)	7.22(9)	Br(1)	1.36840(6)	-0.4860(1)	0.92169(7)	6.17(3)
N	0.0549(2)	0.6282(1)	-0.0063(2)	4.01(5)	Br(2)	0.93612(5)	0.1921(1)	0.89924(6)	5.24(2)
C(1)	0.0542(3)	0.6277(1)	-0.1337(2)	3.66(5)	Br(3)	0.97627(6)	-0.0623(1)	0.72200(7)	6.42(2)
C(2)	-0.0602(3)	0.5891(2)	-0.2209(2)	4.37(6)	Ň	1.1243(4)	0.1128(6)	0.8988(4)	3.4(1)
C(3)	-0.0580(3)	0.5887(2)	-0.3430(2)	4.85(6)	C(1)	1.2220(5)	-0.0369(8)	0.8465(5)	3.6(2)
C(4)	0.0574(3)	0.6239(1)	-0.3800(2)	4.36(6)	C(2)	1.2775(5)	-0.1769(9)	0.8511(5)	3.7(2)
C(5)	0.1705(3)	0.6622(2)	-0.2912(2)	4.72(7)	C(3)	1.2924(4)	-0.2984(8)	0.9140(4)	3.4(2)
C(6)	0.1692(3)	0.6653(2)	-0.1692(2)	4.47(6)	C(4)	1.2545(4)	-0.2873(8)	0.9714(4)	3.3(2)
C(7)	0.0616(4)	0.6204(2)	-0.5121(2)	6.50(8)	C(5)	1.1977(4)	-0.1524(8)	0.9649(4)	3.4(2)
C(8)	0.1863(3)	0.5972(1)	0.0832(2)	3.51(5)	C(6)	1.1820(4)	-0.0251(7)	0.9030(4)	3.1(2)
C(9)	0.2326(3)	0.6250(1)	0.2042(2)	4.03(6)	C(7)	1.0585(5)	0.2299(7)	0.9923(4)	3.4(2)
C(10)	0.3604(3)	0.5932(2)	0.2894(2)	4.51(6)	C(8)	1.1360(5)	0.1857(8)	0.9800(5)	3.4(2)
C(11)	0.4466(3)	0.5344(2)	0.2571(2)	4.70(7)	C(9)	1.2236(5)	0.2144(9)	1.0507(5)	4.2(2)
C(12)	0.4016(3)	0.5084(2)	0.1359(2)	4.80(7)	C(10)	1.2350(5)	0.2818(9)	1.1294(5)	4.4(2)
C(13)	0.2732(3)	0.5391(1)	0.0495(2)	4.17(6)	C(11)	1.1576(6)	0.3278(8)	1.1414(5)	4.6(2)
C(14)	0.5867(4)	0.5030(2)	0.3532(3)	8.1(1)	C(12)	1.0703(5)	0.3025(9)	1.0705(5)	4.1(2)
C(15)	-0.0752(3)	0.6550(1)	0.0240(2)	3.55(5)	C(13)	1.1736(5)	0.4012(9)	1.2349(5)	4.2(2)
C(16)	-0.1713(3)	0.7106(2)	-0.0516(2)	4.37(6)	C(14)	1.0214(5)	0.1605(8)	0.7375(5)	3.7(2)
C(17)	-0.2978(3)	0.7387(2)	-0.0233(2)	4.70(6)	C(15)	1.0854(4)	0.2165(8)	0.8211(4)	3.2(2)
C(18)	-0.3367(3)	0.7127(2)	0.0804(2)	4.19(6)	C(16)	1.1102(5)	0.3871(8)	0.8292(4)	3.7(2)
C(19)	-0.2435(3)	0.6568(2)	0.1540(2)	4.20(6)	C(17)	1.0731(5)	0.494(1)	0.7561(5)	4.3(2)
C(20)	-0.1147(3)	0.6280(1)	0.1274(2)	3.95(6)	C(18)	1.0109(5)	0.432(1)	0.6721(5)	4.3(2)
C(21)	-0.4709(4)	0.7432(2)	0.1128(3)	5.85(8)	C(19)	0.9856(5)	0.264(1)	0.6647(5)	4.4(2)
					C(20)	0.9659(5)	0.553(1)	0.5884(5)	4.7(2)

Table 2. Atomic Parameters and Equivalent Isotropic Thermal Parameters

**Table 3.** Selected Interatomic Distances and Bonds Angles

	Bond	Angles (°)								
Molecule 1										
O-C(21)	1.189(4)	N-C(8)	1.425(3)	C(1) - N - C(8)	118.0(2)					
N-C(1)	1.438(3)	N-C(15)	1.397(3)	C(1) - N - C(15)	119.1(2)					
C(1) - C(2)	1.377(3)	C(15) - C(16)	1.402(3)	C(8) - N - C(15)	122.8(2)					
C(1) - C(6)	1.379(3)	C(15) - C(20)	1.395(3)	N-C(1)-C(2)	120.3(2)					
C(2) - C(3)	1.386(3)	C(16) - C(17)	1.364(3)	N-C(1)-C(6)	120.1(2)					
C(3) - C(4)	1.373(3)	C(17) - C(18)	1.389(3)	C(2) - C(1) - C(6)	119.6(2)					
C(4) - C(5)	1.377(4)	C(18) - C(19)	1.385(3)	N-C(15)-C(16)	119.6(2)					
C(4) - C(7)	1.504(3)	C(18) - C(21)	1.463(4)	N-C(15)-C(20)	122.3(2)					
C(5) - C(6)	1.383(3)	C(19) - C(20)	1.377(3)	N-C(8)-C(9)	121.6(2)					
		Molecu	ile 2							
Br(1) - C(3)	1.897(6)	N-C(6)	1.419(8)	C(6) - N - C(8)	118.5(5)					
Br(2) - C(7)	1.894(7)	N-C(8)	1.420(8)	C(6) - N - C(15)	119.4(5)					
Br(3) - C(14)	1.887(7)	N-C(15)	1.426(8)	C(8) - N - C(15)	117.3(5)					
C(1) - C(2)	1.409(9)	C(7) - C(12)	1.373(9)	N-C(15)-C(14)	123.9(6)					
C(1) - C(6)	1.383(9)	C(8) - C(9)	1.384(9)	N - C(6) - C(1)	121.7(6)					
C(2) - C(3)	1.372(9)	C(9) - C(10)	1.37(1)	N-C(15)-C(16)	119.0(6)					
C(3) - C(4)	1.371(9)	C(10) - C(11)	1.41(1)	N - C(6) - C(5)	119.0(6)					
C(4) - C(5)	1.383(9)	C(11) - C(12)	1.38(1)	N - C(8) - C(7)	121.1(6)					
C(5) - C(6)	1.392(9)	C(11) - C(13)	1.59(1)	N-C(8)-C(9)	121.6(6)					
C(7) - C(8)	1.406(9)			Br(1) - C(3) - C(2)	118.8(5)					
				Br(1) - C(3) - C(4)	119.4(5)					
				Br(2) - C(7) - C(8)	119.8(5)					
				Br(2) - C(7) - C(12)	119.4(5)					



Fig. 1. Thermal ellipsoid plots of compounds 1 and 2 (30% probability ellipsoids).

The C-N bond lengths (Table 3) of compound 1 are 1.438(3) and 1.425(3) Å for p-methyl-substituted benzene rings and 1.396(3) Å for the formylsubstituted benzene ring, respectively. The decrease of the C-N bond length related to the formylsubstituted benzene ring may be due to the electronwithdrawing power of p-formyl group. CNC bond angles are 118.0°(2), 119.1°(2), and 122.8°(2). The C-N bond length of compund 2 is 1.419(8) Å for the p-bromo-substituted benzene. The others are 1.420(8) Åand 1.426(8) Å, and the CNC bond angles are  $118.5^{\circ}(5)$  (C6–N–C8),  $119.4^{\circ}(5)$  (C6–N–C15) and  $117.3^{\circ}(5)$  (C8–N–C15). The CNC bond angles of the two compounds are close to 120°, which corresponding to the sp<sup>2</sup> hybridization of the N-bonding orbits. The N atom deviates slightly from the plane of the bonded C atoms by about 15°. The benzene rings in each molecule are planar and their geometry is unexceptional. The value of the dihedral angles (deposited) showed that the dihedral angles between phenyl-ring planes and the plane of N-bonded C atoms vary from 25 to 55° for compound 1 and from 43 to  $67^{\circ}$  for compound **2**. The dihedral angles of compound 2 (in which two bromide atoms substituted at the ortho position of two benzene rings) are larger than those of compound **1** (in which the *ortho* positions are unoccupied). Hence, it can be inferred from the previous discussion that the N atom and adjacent C atoms are coplanar, whereas the three phenyl rings rotated some angles to avoid overlap of the ortho-substituted atoms. Substitutions at the para



Fig. 2. Quadruple phenyl embrace (QPE) and sextuple phenyl embrace (SPE) in the crystal structure of compound 1 (a) and compound 2 (b). The connecting lines identify the intermolecular interactions by their  $N \cdots N$  distance marked (Å).

## Crystal structure of substituted triphenyl amines

and *ortho* positions of benzene rings do not greatly influence the geometry of the central fragment. Introduction of substitutions to the *ortho* positions result in the large rotation angels of benzene rings. The molecule geometry of triphenylamines shows that the lone electron pair of the N atom occupies the p orbit, which favors the realization of the intramolecular p- $\pi$  interaction. The interaction may be interrupted to some extent when the *ortho* positions are substituted.

Compound 1 crystallized in space group  $P2_1/c$ . The characteristic of lattice is something like the MPE. As shown in Fig. 2(a), two molecules form a dimer with the N···N separation 7.02 Å. This N···N separation is a typical geometry for QPE which has been observed in Ph<sub>4</sub>P<sup>+</sup> and Ph<sub>4</sub>As<sup>+</sup>.<sup>12,14</sup> The 9.15 Å interactions between dimers (see Fig. 2(a)) suggest the occurrence of weak QPE (involving four rings from two dimers, two edge-to-face (ef) and one offsetface-to-face (off) attraction). For compound 2, the phenyl rings of two molecules are interweaved in such a way that total of six ef phenyl-phenyl interaction are established. The geometry (Fig. 2(b)) and the N···N separation of 6.62 Å are similar to those of SPE. This interaction could be defined as a SPE dimer. Each dimer is in contact with two neighboring molecules at N···N separation 8.84 Å. This interaction is a weak QPE. The geometry and the calculated energies of MPE motifs for the -Ph<sub>3</sub>N group will be presented in a separate paper, as well as the patterns of their occurrence and formation of networks in molecular crystals.

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