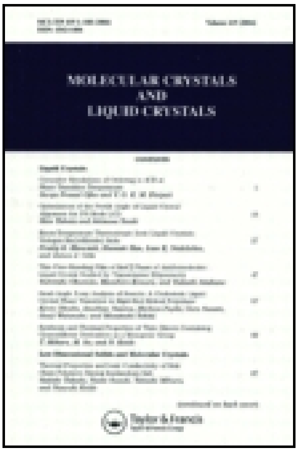

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Starburst Molecules for Amorphous Molecular Materials: Synthesis and Morphology of 1,3,5-Tris(diphenylamino)benzene and Its Methyl-substituted Derivatives

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STARBURST MOLECULES FOR AMORPHOUS MOLECULAR MATERIALS : SYNTHESIS AND MORPHOLOGY OF 1,3,5-TRIS(DIPHENYLAMINO)BENZENE AND ITS METHYL-SUBSTITUTED DERIVATIVES

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Abstract Methyl-substituted derivatives of 1,3,5-tris(diphenylamino)benzene are found to constitute a novel class of amorphous molecular materials, as characterized by differential scanning calorimetry and X-ray diffraction. These compounds readily form stable amorphous glasses having glass-transition temperatures of ca. 50 °C on cooling from the melt. The methyl substituent exerts a great influence on the formation of the glassy state.

***Keywords:** starburst molecule, amorphous molecular material, 1,3,5-tris(diphenylamino)benzene, methyl substituted 1,3,5-tris(diphenylamino)benzene, amorphous glassy state, glass-transition temperature*

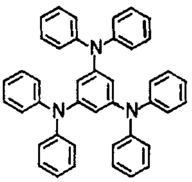
INTRODUCTION

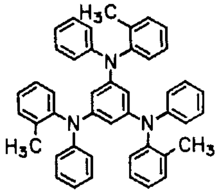
There has been a growing interest in amorphous materials. They are attractive because of their excellent processability, transparency, inexistence of grain boundaries and isotropic properties. Amorphous inorganic materials and amorphous metals have recently received attention. Amorphous organic materials such as polymers and molecularly-doped systems, where low-molcular weight compounds are dispersed in polymer binders, have also received attention from both fundamental and practical viewpoints.[1-3]

However, little attention has been directed to low-molecular weight materials that form stable amorphous glassy states, because low molecular weight organic crystals generally tend to form crystals. Only limited numbers of low molecular weight compounds (e.g. β-carotene, 1,3,5-tri(α-naphthyl)benzene, oligophenylenes) are known to form amorphous glassy states,[4-7] although amorphous or quasi-amorphous films of certain organic compounds can be formed by vapor deposition onto a substrate maintained at low temperature.[8]

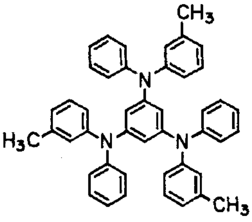
It is of interest to develop amorphous molecular materials for potential uses in electronic devices. For the purpose of developing photo- and electro-active amorphous molecular materials with glass-transition temperatures higher than room temperature, we have been studying the synthesis and properties of novel starburst molecules consisting of π-electron systems. We have reported the synthesis and properties of a novel class of starburst molecules for photo- and electro-active amorphous molecular materials, 4,4',4"-tris(diphenylamino)triphenylamine and 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine.[6] These compounds are found to form readily stable amorphous glasses having glass-transition temperatures of 89 °C and 75 °C, respectively.

In the present study, we have found that methyl-substituted derivatives of 1,3,5-tris(diphenylamino)benzene (TDAB) constitute a novel class of amorphous molecular materials. We report here the synthesis and glass-forming properties of starburst molecules consisting of a conjugated π-electron system, TDAB and its methyl-substituted derivatives, 1,3,5-tris(2-methylphenylphenylamino)-benzene (o-MTDAB), 1,3,5-tris(3-methylphenylphenylamino)benzene (m-MTDAB), and 1,3,5-tris(4-methylphenylphenylamino)benzene (p-MTDAB).

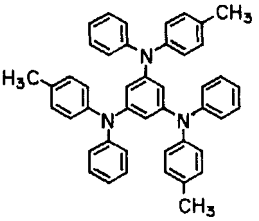

TDAB



o-MTDAB



m-MTDAB



p-MTDAB

EXPERIMENTAL

Synthesis of 1,3,5-Tris(diphenylamino)benzene (TDAB)

Method a: 1,3,5-Tris(phenylamino)benzene (4.39 g, 12.5 mmol), which was prepared from phloroglucinol and aniline according to the method in the literature,[9] was reacted with iodobenzene (15.3 g, 75 mmol) in decalin (5 ml) at 160 °C for 6 h in the presence of copper powder (3.0 g, 47 mmol) and potassium hydroxide (8.4 g, 0.15 mol) under nitrogen atmosphere. The resulting reaction mixture was extracted with hot benzene. After evaporation of benzene, the residue was chromatographed on silica gel using a mixed solvent of benzene and hexane (1:1) as an eluent to give **a colorless powder of** TDAB (3.86 g, 63 % yield).

Method b: 1,3,5-Triiodobenzene (0.43 g, 1.0 mmol), prepared starting from trimesic acid, was reacted with diphenylamine (1.01 g, 6.0 mmol) in decalin (4 ml) at 170 °C for 10 h in the presence of copper powder (1.0 g, 16 mmol) and potassium hydroxide (0.56 g, 10 mmol) under nitrogen atmosphere. The resulting reaction mixture was extracted with hot benzene. After evaporation of benzene, the residue was chromatographed on silica gel using a mixed solvent of benzene and hexane (1:1) as an eluent to give colorless powder of TDAB (0.15 g, 26 % yield).

Recrystallization from benzene/hexane gave colorless needles. MS: m/e 579(M^+). Found: C, 86.85; H, 5.67; N, 7.20%. Calcd for $C_{42}H_{33}N_3$: C, 87.01; H, 5.74; N, 7.25%. UV (λ_{max}, log ε): 301 nm, 4.8. ^{1}H NMR (C_6D_6): δ 6.73 (6H, m), 6.77 (3H, s), 6.95 (12H, m), 7.08 (12H, m).

Synthesis of o-, m-, and p-MTDAB

Likewise, o-, m-, and p-MTDAB were synthesized by the reaction of o-, m-, or p-iodotoluene with 1,3,5-tris(phenylamino)benzene (Method a). m-MTDAB was also synthesized using 1,3,5-triiodobenzene and 3-methylphenyl phenylamine (Method b). o-MTDAB (Recryst. from benzene/hexane, colorless prisms) yield: 22 %. MS: m/e 621(M^+). Found: C, 86.98; H, 6.26; N, 6.64%. Calcd for $C_{45}H_{39}N_3$: C, 86.92; H, 6.32; N, 6.76%. UV (λ_{max}, log ε): 300 nm, 4.9. ^{1}H NMR (C_6D_6): δ 2.01 (9H, s), 6.49 (3H, s), 6.68 (3H, m), 6.87-7.00 (21H, m), 7.06 (3H, m). m-MTDAB (Recryst. from benzene/hexane, colorless powder) yield: 35 % (Method a), 24 % (Method b). MS: m/e 621(M^+). Found: C, 86.51; H, 6.32; N, 6.65%. Calcd for $C_{45}H_{39}N_3$: C, 86.92; H, 6.32; N, 6.76%. UV (λ_{max}, log ε): 301 nm, 4.9. ^{1}H NMR (C_6D_6): δ 1.93 (9H, s), 6.59 (3H, d), 6.75 (3H, m), 6.83 (3H, s), 6.90-7.00 (15H, m), 7.13 (6H, m). p-MTDAB (Recryst. from benzene/hexane, colorless powder) yield: 46 %. MS: m/e 621(M^+). Found: C, 87.19; H, 6.32; N, 6.70%. Calcd for $C_{45}H_{39}N_3$: C, 86.92; H, 6.32; N, 6.76%. UV (λ_{max}, log ε): 301 nm, 4.9. ^{1}H NMR (C_6D_6): δ 2.00 (9H, s), 6.73 (3H, m), 6.78 (6H, m), 6.81 (3H, s), 6.97 (6H, m), 7.05 (6H, m), 7.13 (6H, m).

Measurements

Morphological changes were characterized by differential scanning calorimetry (DSC) and X-ray diffraction. The oxidation potentials were determined by cyclic voltammetry using platinum plates as the working and counter electrodes and $Ag/AgNO_3$ (0.01 M) as the reference electrode in dichloromethane containing tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte (scan rate: 100 mV sec^{-1}).

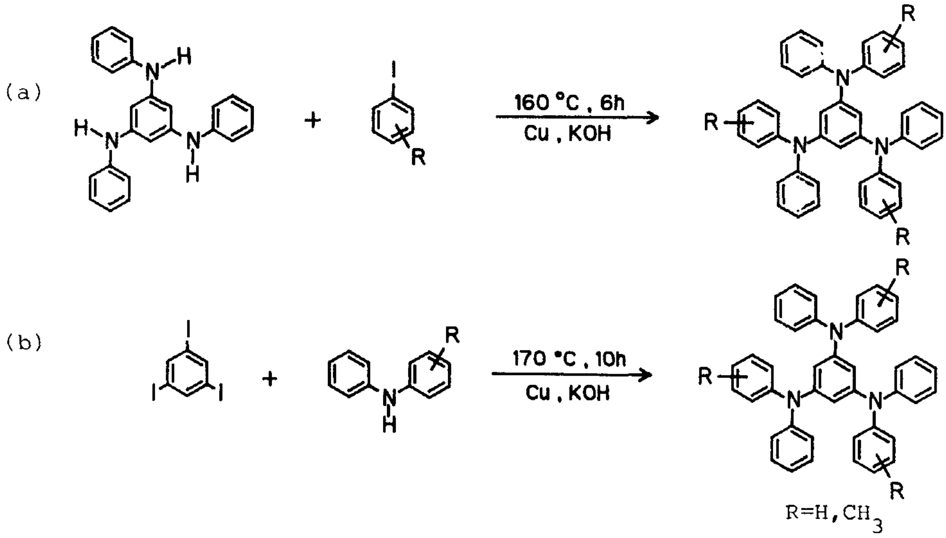
Apparatus

DSC measurements were made with a DSC 20 (SEIKO I&E). X-Ray diffraction was carried out with a Rotaflex RU200 (Rigaku). Cyclic voltammetry was carried out with a HA-501 Potentiostat and a HB-104 Function Generator (Hokuto Denko).

RESULTS AND DISCUSSION

Synthesis of Starburst Molecules, TDAB and o-, m-, and p-MTDAB

The new compounds, TDAB and its methyl-substituted derivatives, o-, m-, and p-MTDAB, were synthesized by the following two routes; (a) Ullmann reaction of 1,3,5-tris(phenylamino)benzene with iodobenzene or the corresponding iodotoluenes, and (b) Ullmann reaction of



SCHEME 1 Synthesis of TDAB and o-, m-, p-MTDAB

1,3,5-triiodobenzene with the corresponding amines (Scheme 1). The overall product yields were much higher for the former reactions. The yield in the former reactions increased in the order of o-MTDAB < m-MTDAB < p-MTDAB < TDAB. Steric hindrance by the methyl group in the starting aryliodides may be responsible for this.

The oxidation potentials ($E^{ox}_{p/2}$) of TDAB, o-MTDAB, m-MTDAB, and p-MTDAB are 0.57, 0.55, 0.55, and 0.50 V vs. Ag/Ag$^+$, respectively, as determined by cyclic voltammetry. These values are lower than that for triphenylamine ($E^{ox}_{p/2}$ = 0.73 V vs. Ag/Ag$^+$).

Formation of the Amorphous Glassy State

Figure 1 shows DSC thermograms of TDAB and m-MTDAB, respectively. The parent compound TDAB does not form a glassy state. When the crystalline sample of TDAB obtained by recrystallization from benzene/hexane is heated, an endothermic peak due to melting is observed at 257 °C. Even when the melted sample of TDAB is rapidly cooled down with liquid nitrogen, it instantly crystallizes, and the same DSC trace as Figure 1(a) is reproduced. By contrast, as Fig. 1(b) shows, when the melted sample of m-MTDAB is cooled down

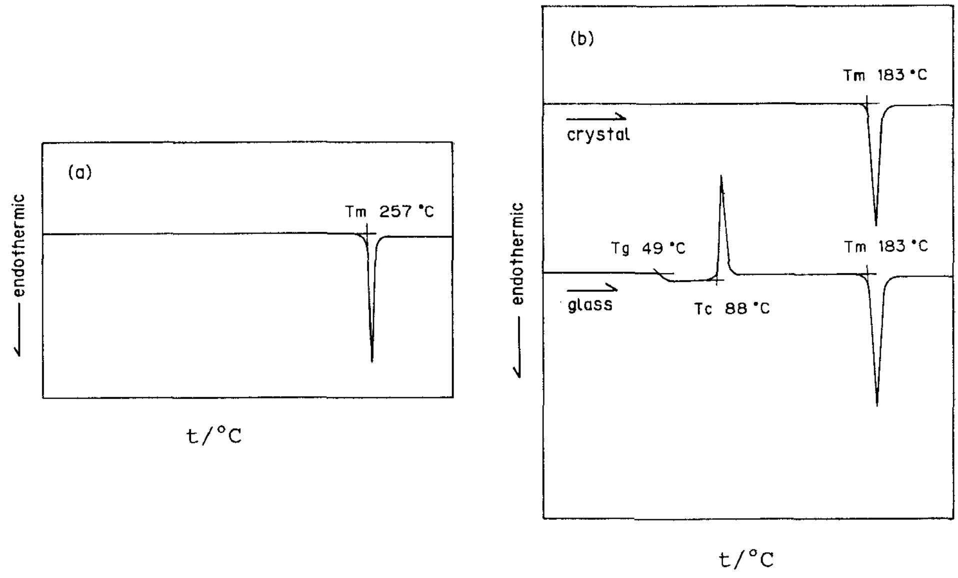


FIGURE 1 DSC thermograms of (a) TDAB and (b) m-MTDAB. Heating rate: 10 °C min^{-1}.

with liquid nitrogen or on standing in air, it spontaneously forms a supercooled liquid state and then changes into an amorphous glassy state. When the amorphous glassy sample is again heated, a glass transition is observed at 49 °C. Then an exothermic peak due to crystallization is observed around 88 °C, which is followed by an endothermic peak due to melting at 183 °C. The enthalpy changes for the crystallization and for the melting were -28 and 47 kJ mol^{-1}, respectively.

Similarly, o- and p-MTDAB were found to form readily stable amorphous glasses when the melt samples were cooled down with liquid nitrogen or on standing in air. When the amorphous glassy samples of o- and p-MTDAB are again heated, glass-transition phenomena are observed at 46 and 58 °C, respectively, and then crystallization follows.

Table I summarizes the glass-transition temperatures, crystallization temperatures, and melting points for TDAB and o-, m-, and p-MTDAB, as determined from DSC thermograms. The glass-transition temperature (Tg) increases in the order of o-MTDAB < m-MTDAB < p-MTDAB. The order of increasing Tg is in parallel with that of the melting point. The transparent, amorphous glassy states of o-, m-, and p-MTDAB are quite stable at room temperature, and no crystallization has been noticed for over one year for m- and p-MTDAB. For o-MTDAB, no crystallization has been noticed over three months up to this time. The glassy state of o-MTDAB appears to be very stable.

The formation of the amorphous glassy state and the crystalline state for o-, m-, and p-MTDAB is evidenced by X-ray diffraction. The X-ray diffraction patterns of the amorphous glassy samples of o-, m-, and p-MTDAB obtained by cooling the melt samples show no sharp peak characteristic of the crystal. By contrast, when the amorphous glassy samples of o-, m-, and p-MTDAB are again heated above the crystallization temperature, characteristic sharp peaks due to the crystal appear in the X-ray diffraction patterns. Figure 2 shows the X-ray diffraction patterns of the glassy state and the crystalline state of m-MTDAB.

TABLE I The glass-transition temperatures, crystallization temperatures, and melting points of TDAB and o-, m-, and p-MTDAB

Compound	Glass-transition temperature Tg(°C)	Crystallization temperature Tc(°C)	Melting point[b] Tm(°C)
TDAB	—	—	257
o-MTDAB[a]	46	120	173
m-MTDAB	49	88	183
p-MTDAB[a]	58	88	198

a) These compounds show solid polymorphism.

b) Melting point of crystals obtained by recrystallization from benzene/hexane.

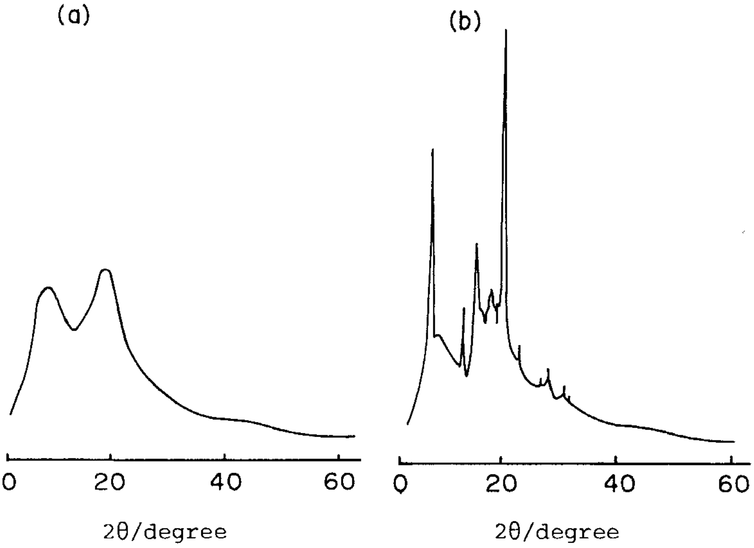


FIGURE 2 X-Ray diffraction patterns of m-MTDAB.
(a) Amorphous glass obtained by cooling the melt.
(b) Crystals formed on heating the amorphous glass above 90 °C.

As described above, while TDAB does not form an amorphous glass, the methyl-substituted derivatives of TDAB, o-, m-, and p-MTDAB, readily form stable amorphous glasses when cooled down from the melt. The present results indicate that the methyl substituent exerts a great influence on the formation of the glassy state. It is thought that incorporation of the methyl group at the o-, m-, or p-position of the phenyl group in TDAB increases the number of conformers of the molecules and the mode of packing of molecules, thus preventing crystallization.

The present study will enable various molecular design based on TDAB for developing novel photo- and electro-active amorphous molecular materials for potential use in electronic devices.

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