Methoxycarbonyl Group as a Conformational Regulator for The Benzene Ring of Triphenylamines

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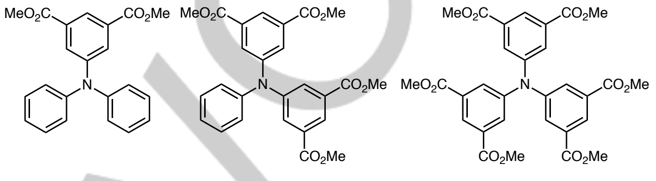
Abstract: A series of triphenylamine derivatives bearing a methoxycarbonyl group on the benzene ring was synthesized. The structural and physical properties based on the introduction of the methoxycarbonyl group into benzene ring were investigated by single crystal X-ray diffraction, computational studies and spectroscopic methods. It was revealed that the methoxycarbonyl group has not only structural control but also a definite electronic effect on the triphenylamine structure.

Triarylamines are one of the most extensively studied organic molecules with potential applications for photoelectrical properties. They have been much use in the fabrication of various types of electronic devices based primarily or partly on organic electroactive components.[1] Varying the structure of attached aryl units allows tuning of the electronic properties of triarylamines. As part of such tuning, utilizing the properties of twisted geometry chromophores to generate charge-separated states are potentially useful for various organic optoelectronic applications including light-harvesting and photoconductivity technologies.[2] To induce a twisted triphenylamine conformation, some examples using various methods have been reported. Lahti et al. reported the highly twisted triarylamine derivatives which one of the benzene rings are substituted with bulky anthracene moieties and their electronic effect or aggregation-induced enhanced emission (AIEE) properties.[3] Tang and coworkers reported 9-aryl substituted carbazole derivatives and investigated their optical properties based on the twisted angle of the structures between the substituted benzene ring and carbazole moiety.[4]

In this paper, we report on the synthesis, structural and photophysical properties of triphenylamine derivatives **1**-**3** bearing methoxycarbonyl groups on benzene rings as a conformational regulator (Scheme 1). Although the structures of those compounds are simple, triphenylamines **1**-**3** bearing methoxycarbonyl groups on the *meta*-position to the amino-nitrogen atom were not reported for their structural and electronic properties. Through the synthetic report of compound **1** by Portnaya and his colleague is existed,[5] triphenylamines **2** and **3** are novel compounds.



1 **2** **3**

Scheme 1. Triphenylamine derivatives **1, 2** and **3**.

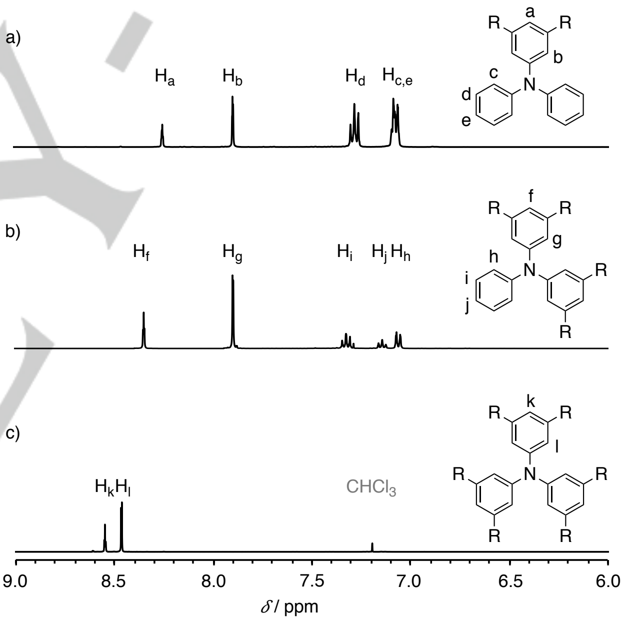


Figure 1. Expansion of the aromatic region of ^{1}H NMR spectra (400 MHz) of tripheylamines **1** (a), **2** (b) and **3** (c) in CDCl$_3$. (R = CO$_2$Me)

The triphenylamine derivative **1** was synthesized by the palladium-catalyzed coupling reaction of dimethyl 5-aminoisophthalate with an excess amount of iodobenzene. Triphenylamines **2** and **3** were also prepared from aniline or dimethyl 5-aminoisophthalate with dimethyl 5-iodoisophthalate under palladium catalysis, and thus-obtained triphenylamines **1**-**3** were fully characterized spectroscopically.

In the ^{1}H NMR spectrum of triphenylamine **3** in CDCl$_3$, the C*H* protons on the benzene rings were obviously downfield shifted than those of aromatic protons of other triphenylamine derivatives **1** and **2** (Figure 1). From the result of ^{1}H-NMR studies of bulky triarylamines in previous reports,[3b, 6] it is suggested that the twisted angle of benzene rings of triphenylamine **3** were larger than those of the other two derivatives.

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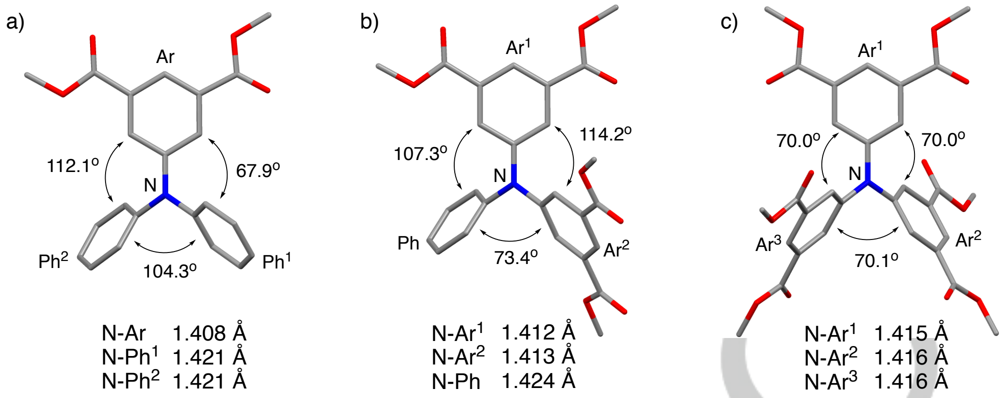

Figure 2. Optimized structures of (a) **1**, (b) **2** and (c) **3** calculated at CAM-BYLYP/6-31G** level.

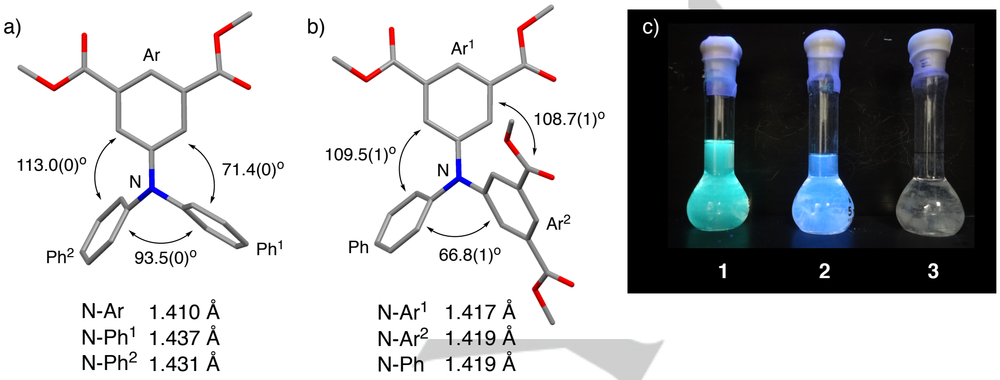

Figure 3. Crystal structures of (a) **1** and (b) **2**. (c) Photograph (under 365 nm) of triphenylamines **1-3** in dichloromethane (1.0 × 10^{-3} M).

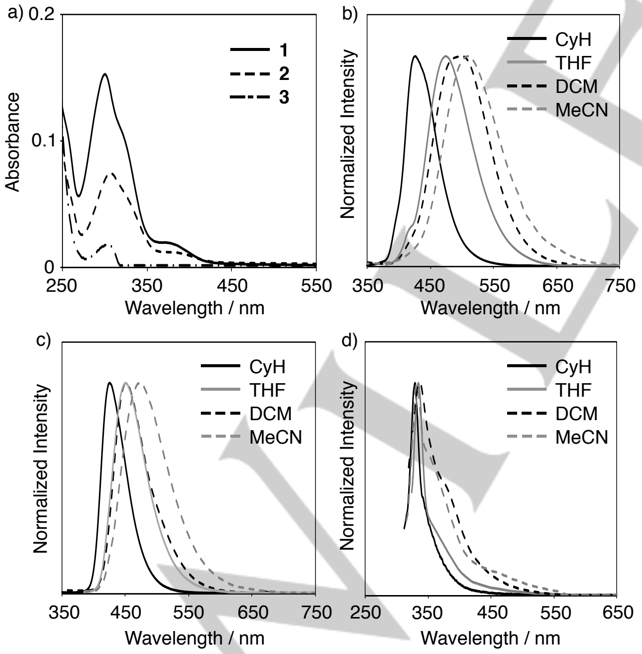

Figure 4. (a) The electronic spectra of **1**, **2** and **3** in CH_2Cl_2 (1.0 × 10^{-5} M). The emission spectra of (b) **1** (λ_{ex} = 301 nm), (c) **2** (λ_{ex} = 308 nm) and (d) **3** (λ_{ex} = 305 nm) in cyclohexane (CyH), tetrahydrofuran (THF), dichloromethane (DCM) and acetonitrile (MeCN) (1.0 × 10^{-5} M) at ambient temperature.

To estimate the torsion angles of triphenylamines **1-3**, their ground-state geometries were optimized by the density functional theory (DFT) calculations. As shown in Figure 2, the optimized structures for triphenylamines **1-3** calculated at [CAM-B3LYP/6-31G**] level.[7] Since single crystal X-ray diffraction analyses of triphenylamines **1** and **2**, were able to be performed,[8] the torsion angles of benzene ring were compared with the calculated results. Figure 2 and 3a and 3b were shown that the values of the torsion angle for each compound have good correlation (112.1 and 113.0°, 104.3 and 93.5°, 67.9 and 71.4° for compound **1**; 107.3 and 109.5°, 73.4 and 66.8°, 114.2 and 108.7° for compound **2**). From the results in **1** and **2**, the level of the basis set is considered to be sufficient to predict the conformation of triphenylamine **3**. In triphenylamine **3**, it is considered that the torsion angle of each benzene ring is almost 70°, and the conformation also might be regulated by the steric effect by the introduction of methoxycarbonyl groups in the solid state (Figure 2). On the other hand, it was found that the carbon-nitrogen bond length is shortened by the introduction of methoxycarbonyl group which is an electron-withdrawing group (Figure 2). The average bond length between aryl carbon and the nitrogen atom (1.408 Å for compound **1**; 1.413 Å for compound **2**; 1.416 Å for compound **3**) is larger as it is substituted by more methoxycarbonyl groups, which is considered to be due to the steric repulsions in the molecule. The similar tendency was also observed for the carbon-nitrogen bond length in the obtained crystal structure (Figures 3a and 3b), indicating the validity of the DFT calculation results.

Table 1. Solvatochromic emission data for **1**-**3**.

	CyH		THF		DCM		MeCN	
	λ_{max}[a] (nm)	Φ[b] (%)	λ_{max}[a] (nm)	Φ[b] (%)	λ_{max}[a] (nm)	Φ[b] (%)	λ_{max}[a] (nm)	Φ[b] (%)
1	426	7	474	6	500	6	510	3
2	425	4	451	6	452	6	474	4
3	329	<0.6	335	<0.7	336	<0.7	332	<0.5

[a] measured in 1.0×10^{-5} M solution.

[b] measured by using quinine sulfate as a reference standard.

The electronic properties of triphenylamines **1**, **2** and **3** were investigated by UV-Vis and emission spectroscopy. As shown in Figure 4a, compounds **1** and **2** exhibit strong absorption at 300-350 nm and a minor absorption at 350-450 nm. According to the previous report, the strong absorption is caused to π-π* transition between the aromatic rings and nitrogen atoms,[9] and the minor absorption might be attributed to the push-pull nature of triphenylamines with increasing acceptor strength.[10] On the other hand, for triphenylamine **3**, the absorption band in the region over 300 nm was smaller than those of compounds **1** and **2**, and almost no absorption was found around 350-400 nm (Figure 4a). This phenomenon is considered to be due to the fact that the degree of freedom of the pitch angle of the benzene ring is restricted by the steric repulsion of the methoxycarbonyl group introduced to each benzene ring and the lack of orbital overlap has occurred.

Another interesting feature of the designed triphenylamines **1** and **2** is their luminescent properties in dichloromethane (Figure 2c and Table 1). Green luminescence at 500 nm was observed in the emission spectrum of the triphenylamine **1** (Φ = 0.06). In compound **2**, blue luminescence having a peak at 452 nm was observed (Φ = 0.06). However, feeble emission was observed for triphenylamine **3** ($\Phi = < 7 \times 10^{-3}$). According to the previous reports,[3a, 11] it might be considered that some twisted triphenylamines show luminescent behavior based on twisted-intramolecular-charge-transfer (TICT), therefore triphenylamine **3** with restricted conformation would show weak luminescence. Additionally, solvatochromic emission behavior was shown in triphenylamine **1** and **2**; increasing the solvent polarity from cyclohexane to acetonitrile results in large red shifts and spectral broadening indicative of polarized excited states associated with the push-pull effect of the chromophore (Figures 4a, 4b and Table 1). Contrastively, emission from compound **3** was structured in both polar and non-polar solvents and non-solvatochromic (Figure 4d and Table 1).

The redox properties of triphenylamines **1**-**3** were also investigated by cyclic voltammetry in acetonitrile (Figure S6). The compounds showed one oxidation wave (**1**: E_{pc} = 0.74 V vs. Fc/Fc$^+$; **2**: E_{pc} = 0.86 V vs. Fc/Fc$^+$; **3**: E_{pc} = 1.98 V vs. Fc/Fc$^+$), respectively, which might be assigned to the successive oxidation of the triphenylamine moiety. From the result, as the number of methoxycarbonyl group introduced into the benzene ring, the substantial negative shift of the oxidation wave was observed. Although negligible changes were observed in the reduction waves of compound **1** and **2** (**1**: E_{pc} = 0.50 V vs. Fc/Fc$^+$; **2**: E_{pc} = 0.61 V vs. Fc/Fc$^+$), the reduction wave of compound **3** was largely shifted to the reduction side (E_{pc} = 0.25 V vs. Fc/Fc$^+$). Those results may support the push-pull effect due to the introduction of methoxycarbonyl groups to the benzene ring.

In conclusion, the structure electronic and redox properties of the triphenylamine moiety based on the introduction of a methoxycarbonyl group at the *meta*-position of the benzene ring were investigated. Spectroscopic, computational studies and the obtained X-ray crystal structures revealed that methoxycarbonyl group at the *meta*-position on the benzene ring of triphenylamine is effective for promoting the twist angle between each benzene ring. On the other hand, the push-pull effect based on the property as the electron withdrawing group possessed by the methoxycarbonyl group also revealed that substantial influence emission solvatochromism and redox potential occurs. This study suggests that even simple functional groups are sufficiently effective to induce steric and electronic effects. Further investigation is currently underway to study the influence on the electronic and structural properties based on functional group conversion of methoxycarbonyl group.

Supporting Information Summary

General procedures, synthesis and characterization data for **1**-**3**, crystallographic data and packing diagrams of **1**-**2**, copies of ^{1}H NMR, selected computational results and CV for compounds **1**-**3**.

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Keywords: triphenylamine • luminescence • substitutional effect • methoxycarbonyl groups

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[8] Crystal data for **1**: $C_{22}H_{19}NO_4$, M = 361.40 orthorombic, space group *Pbca* (no. 61), a = 9.06083(16) Å, b = 18.9250(3) Å, c = 21.8017(12) Å, V = 3738.47(12) Å^3, Z = 8, T = 275 K, D_{calc} = 1.284 g cm^{-1}, μ(CuKα) = 8.500 cm^{-1}, CuKα radiation (λ = 1.54187 Å) R_1 = 0.0464, wR_2 = 0.1330 Crystal data for **2**: $C_{26}H_{23}NO_8$, M = 477.47, monoclinic, space group P-$2_1/c$ (no. 14), a = 11.1950(2) Å, b = 9.64979(19) Å, c = 21.6893(4) Å, β = 93.2833(4)°, V = 2339.23(8) Å^3, Z = 4, T = 277 K, D_{calc} = 1.356 g cm^{-3}, μ(CuKα) = 8.500 cm^{-1}, CuKα radiation (λ = 1.54187 Å) R_1 = 0.0631, wR_2 = 0.2287. Crystallographic Data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1889282 for **1**, CCDC-1889281 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:(internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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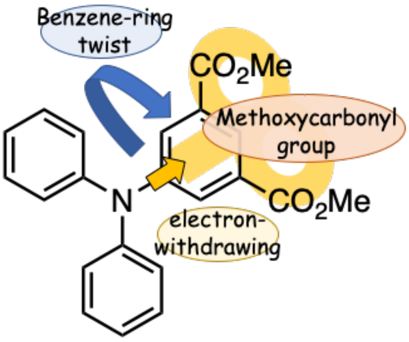

A small and simple methoxycarbonyl group was introduced at the meta-position of the benzene ring to control the π-conjugated moiety of triphenylamine. As the number of methoxycarbonyl group increased, the angle of the benzene ring was regulated based on the steric effect of the substituent. Moreover, the electronic properties were changed by the substituent effect of methoxycarbonyl group.