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3,6-Disubstituted carbazole chromophores containing thiazole and benzothiazole units: Synthesis, characterization and first-order hyperpolarizabilities

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Abstract

3,6-Disubstituted carbazole chromophores containing thiazole and benzothiazole units were synthesized and characterized by NMR, IR, and UV. The first-order hyperpolarizabilities (β) were calculated via solvatochromic method. Our experiments suggest that the incorporation of thiazole and benzothiazole into carbazole-based chromophores can allow for significant enhancement of molecular hyperpolarizabilities. Nonlinear optical properties of AπDπA carbazole chromophores are superior to those of the corresponding DπA aryl compounds.

Keywords: Nonlinear optical chromophores; The first-order hyperpolarizabilities; Heteroaromatic compounds

1. Introduction

Significant interest exists in the design and development of NLO materials because of the potential applications in telecommunications, optical computing, and optical signal processing [1–3]. In the past decade, considerable effort focused on the development of organic materials with large molecular hyperpolarizabilities, improved optical transparency, and good thermal stability. Heteroaromatic compounds have attracted widespread interest because their linear and nonlinear optical properties are superior to those of the corresponding aryl analogues.

We now present several NLO chromophores containing heteroaromatic ring such as thiazole, benzothiazole, and carbazole. It is well known that carbazole compounds exhibit good charge transfer and hole transporting properties, which have already played an important role in NLO materials. In this paper, disubstituted carbazole derivatives are selected as the building blocks for the molecular design of novel nonlinear optical materials. These chromophores both with AπDπA structure consist of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing nitro-substituted units. Fig. 1 shows the backbone of 3,6-disubstituted carbazole chromophores. Our results reveal that the hyperpolarizabilities of thiazole-containing chromophores exceed those of their phenyl analogues.

2. Experimental

2.1. Materials

The *N*-ethyl carbazole, 2-amino-5-nitrothiazole and 2-amino-6-nitrobenzothiazole were obtained from Aldrich Chemical Co. *N*,*N*-Dimethylformamide (DMF) was dried over molecular sieves. All other solvents and chemical reagents were obtained commercially and were used as received without further purification.

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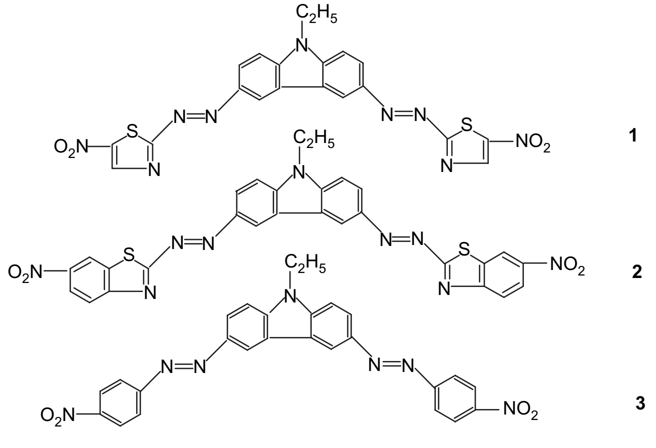


Fig. 1. 3,6-Disubstituted carbazole chromophores **1**–**3**.

2.2. 9-Ethyl-3,6-bis[(5-nitrothiazole-2-yl)azo] carbazole, *1*

2-Amino-5-nitrothiazole (2.9 g, 20 mmol) was dissolved in 10 ml concentrated sulfuric acid and 20 ml mixture of acetic acid and propanoic acid (5:1) at 0–5 °C. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stiring. The mixture was stirred vigorously for 2 h in an ice-bath for temperature control. Freshly prepared 2-amino-5-nitrothiazole diazonium salt (0–5 °C) was added dropwise for 1 h to the solution of *N*-ethyl carbazole (1.95 g, 10 mmol) in 20 ml acetic acid under vigorous mechanical stiring. After stirring the mixture for a further 6 h, the mixture was neutralized with ammonia water to pH 5–6 while stirring for 0.5 h. The precipitate was filtered and dried after repeatedly washed with water and ethanol. The crude product was recrystallized and purified crystals was obtained. Further purification was performed by column chromatography.

Chromophore **1**. Melting point: 219–221 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.61$ (3H, $-CH_3$), 4.40 (2H, $-CH_2$), 7.39 (dd, 2H, carbazole-H *meta* to *N*-ethyl), 7.49 (d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.55 (d, 2H, carbazole-H *meta* to *N*-ethyl), 8.81 (d, 2H, thiazole-H *ortho* to nitro group). IR: γ (cm^{-1}) = 1625 (C=N), 1594 (N=N), 1328, 1513 (nitro group), 3050, 1473, 750 (thiazole group), 628 (C–S).

2.3. 9-Ethyl-3,6-bis[(6-nitrobenzothiazole-2-yl)azo] carbazole, *2*

2-Amino-6-nitrobenzothiazole (3.9 g, 20 mmol) was dissolved in concentrated sulfuric acid and glacial acetic acid at 0–5 °C. The reaction flask was immersed in an ice-bath for temperature control. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stiring. The mixture was stirred vigorously for 2 h, diazonium salt was obtained and used for coupling reaction. Freshly prepared 2-amino-6-nitrobenzothiazole diazonium salt (0–5 °C) was added dropwise for 1 h to the solution of *N*-ethyl carbazole (1.95 g, 10 mmol) in 20 ml acetic acid under vigorous mechanical stiring. After stirring the mixture for a further 5 h, the mixture was neutralized with ammonia water to pH 5–6 while stirring for 0.5 h. The precipitate was filtered and dried after repeatedly washed with water and ethanol. The crude product was recrystallized and purified crystals were obtained. Further purification was performed by column chromatography.

Chromophore **2**. Melting point: 226–228 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.55$ (3H, $-CH_3$), 4.45 (2H, $-CH_2$), 7.58 (d, 2H, carbazole-H *meta* to *N*-ethyl), 7.49 (d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.40 (dd, 2H, carbazole-H *meta* to *N*-ethyl), 8.88 (d, 2H, benzthiazole-H *ortho* to nitro group), 8.29 (d, 2H, benzthiazole), 8.38 (d, 2H, benzthiazole). IR: γ (cm^{-1}) = 1625(C=N), 1594 (N=N), 1334, 1513 (nitro group), 3060, 1473, 748 (benzthiazole ring), 621 (C–S).

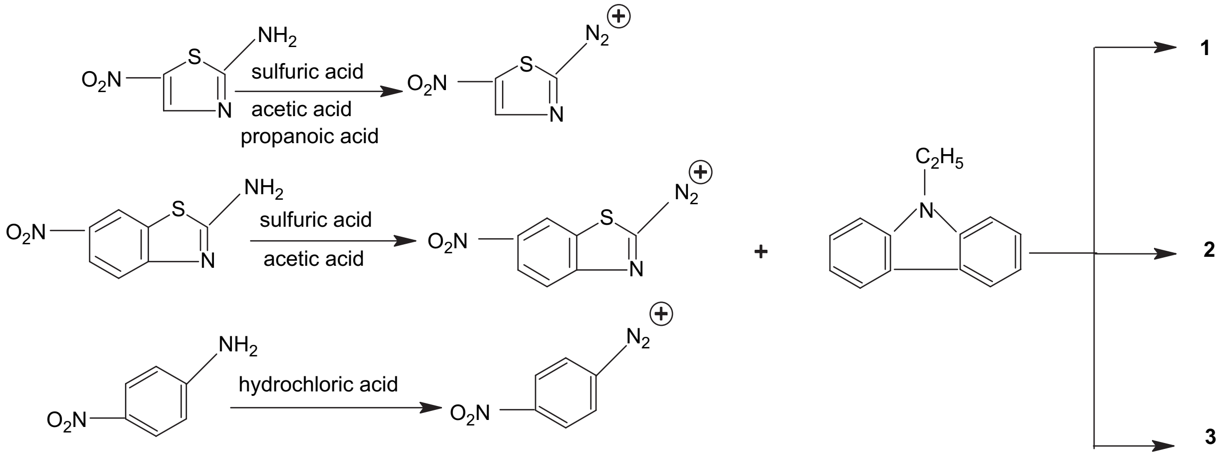
2.4. 9-Ethyl-3,6-bis(4′-nitrophenyl-1′-azo) carbazole, *3*

4-Nitroaniline (2.76 g, 20 mmol) was dissolved in 18% hydrochloride solution (20 ml) at 0–5 °C. The reaction flask was immersed in an ice-bath for temperature control. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stiring. Freshly prepared 4-nitroaniline diazonium salt (0–5 °C) was added dropwise for 1 h to the solution of *N*-ethyl carbazole (1.95 g, 10 mmol) in 20 ml acetic acid under vigorous mechanical stiring. After stirring the mixture for a further 4 h, the mixture was neutralized with sodium acetate to pH 5–6. After stirring further for 0.5 h, the mixture was filtered and the precipitate was dried after repeatedly washed with water and ethanol. The crude product was recrystallized and purified crystals were obtained. Further purification was performed by column chromatography.

Chromophore **3**. Melting point: 189–190 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.45$ (t, 3H, $-CH_3$), 4.38 (qua, 2H, $-CH_2$), 7.21 (d, 2H, carbazole-H *ortho* to *N*-ethyl), 7.40 (dd, 2H, carbazole-H *meta* to *N*-ethyl), 7.45 (d, 2H, carbazole-H *meta* to *N*-ethyl), 7.48 (d, 2H, benzene-H *meta* to NO_2), 7.82 (d, 2H, benzene-H meta to NO_2), 8.11 (d, 2H, benzene-H *ortho* to NO_2), 8.17 (d, 2H, benzene-H *ortho* to NO_2). IR: γ (cm^{-1}) = 1597 (N=N), 1332, 1517 (nitro group).

2.5. Characterization

Chemical structures were identified by Fourier transform infrared spectra (FTIR) and ^{1}H NMR spectra. FTIR spectra were recorded on a Nicolet 750 series in the region of 4000–400 cm^{-1} using KBr pellets. ^{1}H NMR measurements were determined with a Brucker 500 MHz apparatus, with TMS (tetramethyl silane) as internal standard and chloroform as solvent. Linear optical properties were measured by a Shimadzu UV-2201 UV–vis spectra in solution.



Scheme 1. Synthesis of the carbazole-containing NLO chromophores **1–3**.

3. Results and discussion

3.1. Synthesis and characterization of chromophores

Three carbozole-based NLO chromophores were prepared by azo-coupling reaction. These chromophores both with AπDπA structure consist of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing nitro-substituted aryl units. The synthetic procedure of chromophores **1–3** is shown in Scheme 1. The reaction was performed in azo-coupling process under mild circumstances. We developed a useful synthetic method for bifunctional conjugated chain formation in which the core is generated from carbazole by a mild reaction.

The resonance corresponding to carbazole moieties can be observed nearly at the same points in ^{1}H NMR spectrum of the chromophores. The FTIR spectrum of **1** and **2** is shown in Figs. 2 and 3. For example in chromophore **2**, the clear appearance of ~1594 cm^{-1} bands characteristic of N=N stretching, the ~3060 cm^{-1}, 1473 cm^{-1}, and 748 cm^{-1} bands, characteristic of benzthiazole ring, indicated the chemical structure of chromophore **1**. The characteristic absorption of the –C–S– stretching in the ring was observed at 621 cm^{-1}. The characteristic absorption peaks at ~1513 cm^{-1} and 1334 cm^{-1} bands indicated the existence of the nitro group.

Fig. 4 shows these solvatochromic phenomena in different solvents, which is the solvent dependence of the UV–vis absorption spectrum of molecules. In particular, the effect of solvent on position, shape, or intensity of the absorption bands of a molecule can be determined from the UV–vis spectrum. This result suggests that absorption changes with the polarity of different solvents. The UV–vis spectrum of the chromophores show the absorption bands at 225–350 nm attributed to the carbazole moiety and at 350–700 nm attributed to the π–π* transition of the azo conjugated unit.

3.2. The first-order hyperpolarizabilities of chromophores *1–3*

An alternative approach for determining the first-order hyperpolarizabilities of organic chromophores is the solvatochromic method. The method is based on the two-level

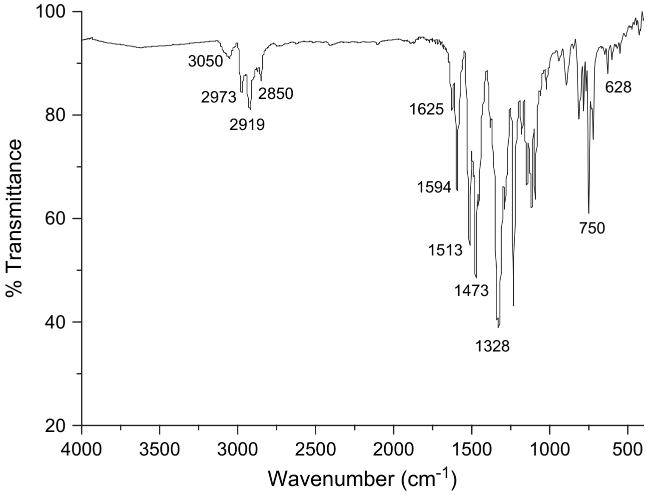


Fig. 2. FTIR spectrum of chromophore **1**.

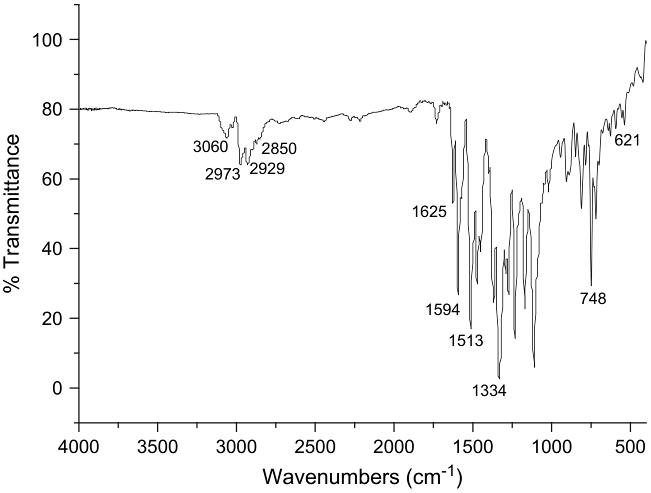


Fig. 3. FTIR spectrum of chromophore **2**.

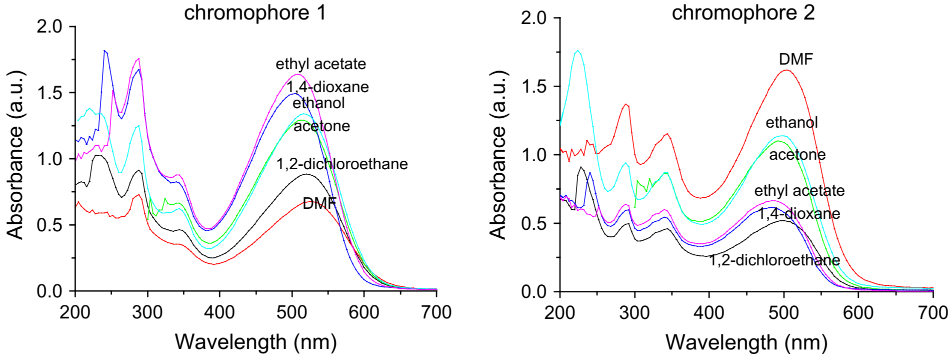


Fig. 4. UV–vis spectra of chromophores **1** and **2** in different solvents.

quantum-mechanical model where only terms that involve either the ground or the first excited single state are considered. As a consequence the dominant component of the first-order hyperpolarizability β_{ijk} is β_{xxx}, often referred as β_{CT}. For the determination of the excited-state dipole moment, the solvatochromic effect is used. It describes the fact that the spectrum of a molecule in a solution is changed depending on the solvent polarity.

The quantum-mechanical two-level model yields the following expression for the first-order hyperpolarizability [4,5]:

$$\beta_{xxx}(2\omega)=\frac{3}{2\hbar}\frac{\mu_{\mathrm{eg}}^2\left(\mu_{\mathrm{e}}-\mu_{\mathrm{g}}\right)\omega_{\mathrm{eg}}^2}{\left(\omega_{\mathrm{eg}}^2-\omega_0^2\right)\left(\omega_{\mathrm{eg}}^2-4\omega_0^2\right)} \tag{1}$$

where ω_{eg} is the frequency of transition from the ground state to the first excited state, μ_{eg} is the transition dipole moment between the ground and excited states, μ_{g} is the permanent dipole moment of the ground state, μ_{e} is the permanent dipole moment of the excited state, and ω_0 is the laser frequency.

Often, another expression β_{xxx} is used [6–8],

$$\begin{aligned}\beta_{xxx}&=C\frac{\omega_{\mathrm{eg}}}{\left(\omega_{\mathrm{eg}}^2-\omega_0^2\right)\left(\omega_{\mathrm{eg}}^2-4\omega_0^2\right)}f\left(\mu_{\mathrm{e}}-\mu_{\mathrm{g}}\right)\\&=CF(\omega)f\Delta\mu_{\mathrm{eg}}\end{aligned} \tag{2}$$

where f is the oscillator strength and $F(\omega)=\omega_{\mathrm{eg}}/[(\omega_{\mathrm{eg}}^2-\omega_0^2)(\omega_{\mathrm{eg}}^2-4\omega_0^2)]$, $\Delta\mu_{\mathrm{eg}}=\mu_{\mathrm{e}}-\mu_{\mathrm{g}}$.

The oscillator strength f is related to the intensity of transition and can be gotten from the area under the band by means of Eq. (3) [4,5,8]:

$$f=4.32\times10^{-9}\times\text{area} \tag{3}$$

$$\text{Area}=\int\xi M\,\mathrm{d}\omega=\frac{2\pi\omega_{\mathrm{eg}}N_0n\mu_{\mathrm{eg}}^2M}{3(2.303)\varepsilon_0ch} \tag{4}$$

where M is the concentration of the chromophore, N_0 is Avogadro's number, n is the solvent refractive index, ξ is the molar extinction coefficient, ε_0 is the permittivity of vacuum, c is speed of light in vacuum, and h is Planck's constant.

Various theoretical treatments of solvatochromic shifts in absorption frequency of a molecule have been developed and a useful expression is that of McRae equation [8].

$$\left(\omega_{\mathrm{eg}}\right)_{\mathrm{s}}-\omega_{\mathrm{eg}}=A\times\frac{n^2-1}{2n^2+1}+B\times\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right] \tag{5}$$

$$B=\frac{2}{4\pi\varepsilon_0\hbar a_0^3}\mu_{\mathrm{g}}\left(\mu_{\mathrm{g}}-\mu_{\mathrm{e}}\right) \tag{6}$$

where $(\omega_{\mathrm{eg}})_{\mathrm{s}}$ is the frequency of the transition in a solvent, ω_{eg} is the frequency of the transition in a vacuum, ε is the relative permittivity of the solvent, n is the refractive index of the solvent, A and B are constants, and a_0 is the radius of a spherical cavity in the solvent occupied by the chromophore. The term $\Delta\mu_{\mathrm{eg}}=\mu_{\mathrm{e}}-\mu_{\mathrm{g}}$ is obtained from the McRae equation. Hence, β_{xxx} can be gotten by means of Eq. (2). Table 1 summarizes these solvatochromic data and the first-order hyperpolarizabilities of the carbazole-based chromophores **1–3**.

The key findings revealed in Table 1 are as follows: (1) AπDπA structure consists of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing nitro-substituted units exhibit large hyperpolarizabilities; (2) bis-thiazole and

Table 1
Solvatochromic data and first-order hyperpolarizabilities of chromophores **1–3**

Chromophores	ω_{eg} (cm^{-1})	f	$\Delta\mu_{\mathrm{eg}}\times10^{-18}$ esu	$\beta_{1064}\times10^{-30}$ esu	$\beta_{1907}\times10^{-30}$ esu
1	19 608	0.76	6.46	323.1	90.4
2	20 040	0.46	6.59	341.2	91.8
3	17 182	0.45	5.75	166.5	82.5

β_{1064} is defined as β_{xxx} at wavelength 1064 nm, and β_{1907} is defined as β_{xxx} at wavelength 1907 nm. Solvatochromic data were measured in DMF solvent. $\Delta\mu_{\mathrm{eg}}=\mu_{\mathrm{e}}-\mu_{\mathrm{g}}$. μ_{g} is molecular ground state dipole moment, which was obtained from molecular simulation using the MOPAC-AM1 geometry method.

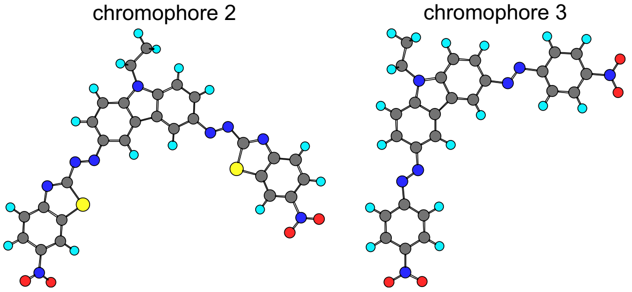


Fig. 5. Molecular structures of chromophores **2** and **3**.

bis-benzothiazole chromophores display larger hyperpolarizabilities than their diphenyl analogues (cf. **1** and **2** vs **3**).

These chromophores **1**–**3** with AπDπA structure consists of an electron-donating *N*-ethyl carbazole unit and two electron-withdrawing units, and is considered to have efficient intramolecular charge transfer (CT) from donor to acceptor across a π-conjugated linker both in the ground and excited states. Their nonlinear optical properties are superior to those of the corresponding aryl compounds of DπA structure.

The aromatic delocalization energies of benzene and thiazole are 36 kcal/mol and 25 kcal/mol, respectively. As the aromatic delocalization energy of the bridge decreases, the mixing of the ground state and charge-transfer state increases, leading to increased hyperpolarizability. Hence, bis-thiazole and bis-benzothiazole chromophores display larger hyperpolarizabilities than their diphenyl analogues.

It is clear that the differences in aromatic delocalization energies must not be the only factors influencing the NLO properties; heteroaromatic ring can influence the strength of the donor or acceptor through inductive effects. Thiazole is adjacent to the electron acceptor rather than adjacent to the electron donor as in case of **1** and **2**, the dipole of the thiazole moiety reinforces the molecular dipole, so the hyperpolarizability is increased. Experiments and calculations of chromophores containing heteroaromatics such as thiazole, benzothiazole, and carbazole have shown that the incorporation of these ring systems into the π-electron bridge can enhance the hyperpolarizability significantly.

In addition to electronic factors, it is clear that steric factors also play an important role. In most instances, heterocyclic rings enable the attainment of planar, or nearly planar, geometries (shown in Fig. 5), which translate into larger hyperpolarizabilities.

These factors working synergistically afford enhanced NLO properties. The incorporation of heteroaromatic rings, with careful consideration of steric and electronic factors, can allow for significant enhancement of molecular NLO properties.

4. Conclusions

3,6-Disubstituted carbazole-cored chromophores were synthesized and characterized by NMR, IR, and UV. In an effort to better understand the NLO properties of heteroaromatic derivatives of AπDπA carbozole chromophores, we utilized the solvatochromic method to calculate molecular hyperpolarizabilities (β).

When substituted at the acceptor end, thiazole and benzothiazole enhance hyperpolarizability to a greater extent than phenyl ring. Our experiments suggest that the incorporation of thiazole and benzothiazole into nonlinear optical carbazole chromophores, with careful consideration of steric and electronic factors, can allow for significant enhancement of molecular hyperpolarizabilities.

Acknowledgements

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