

Experimental Section

All experiments were carried out under argon using standard Schlenk techniques. Degassed and dry solvents were used throughout. Borosilicate columns (3 × 50 mm, 3 × 150 mm) silanized with bicyclo[2.2.1]hept-5-en-2-yltrichlorosilane were used. Monoliths **I–VIII** were prepared as follows: Solution A (chilled to –20 °C, NBE/Q1/2-propanol 25/25/40 (in wt %)) and solution B (toluene/[Cl₂(PCy₃)₂Ru(=CHPh)] 9.995/0.005 (in wt %))^[13] were mixed and rapidly transferred to the prechilled borosilicate column. Polymerization was allowed to proceed at 0 °C for 30 min and then at room temperature overnight. The initiator was cleaved off by passing 1-hexene/toluene (10/90) over the column. For functionalization of monoliths **I–VII**, 1 h after polymerization was started the column was purged with toluene to remove unchanged initiator. An aliquot (1 mL) of a 10 % solution of monomer **1–7** in toluene or dimethylformamide was passed over the column. The HPLC columns were sealed and kept at 60 °C overnight. The catalyst was removed as described above. The total amount of ruthenium that remained within the monolith was determined by atom absorption spectroscopy (AAS) to be less than 10 µg^{–1}. Use of the stoichiometry described here allows the preparation of monoliths whose microstructure consists of microglobules that are 4 ± 1 µm. Nevertheless, the microstructure may be varied within 0.5–30 µm by changing the stoichiometry of the reactants and the porogenic solvents. For scanning electron microscopy (SEM), samples were sputtered with Au/Pd under high vacuum. The specific surface (σ), the pore porosity (ε_p), and the interparticle porosity (ε_z) were determined by inverse gel permeation chromatography (GPC).^[15] The in situ derivatization did not cause any significant changes in these values.

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Optimized Two-Dimensional NLO Chromophores with a Threefold Symmetry Axis**

J. Jens Wolff,* Fred Siegler, Ralf Matschiner, and Rüdiger Wortmann*

Dedicated to Professor Dieter Hellwinkel on the occasion of his 65th birthday

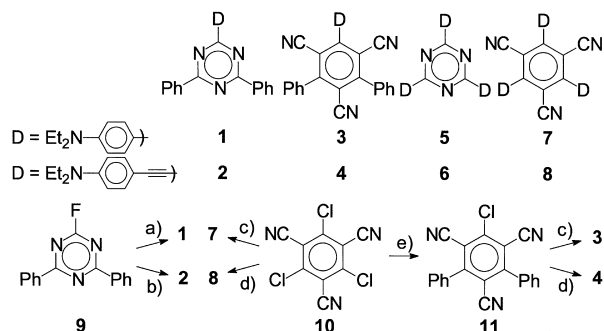
The design of nonlinear optical (NLO) chromophores without dipole moment is a current area of research in molecular nonlinear optics.^[1] Such molecules can be used for processes such as frequency doubling, frequency mixing, parametric oscillation, and electrooptical modulation. This seems to be in contradiction to the traditional opinion that efficient NLO chromophores should be designed as dipolar π systems substituted with one donor and one acceptor—like the prototype *p*-nitroaniline (*p*NA). However, in contrast to one-dimensional (1D) chromophores of the *p*NA type, non-dipolar NLO chromophores with multiple donor–acceptor substitution generally show several significant tensor elements of the second-order polarizability (β). New NLO processes where electrical fields of different polarizations can be efficiently coupled with each other only become possible through two- and three-dimensional (2D and 3D) chromophores. So far, however, effective strategies for the optimization of such nondipolar chromophores have not been found. Thus, it is still uncertain whether they are really superior to their dipolar analogues with respect to the general efficiency–transparency problem—as has been stated several times.^[2] For example, in planar, conjugated chromophores with a threefold symmetry axis, several efficient donor and acceptor groups have to be coupled to a central π system without great steric hindrance. Here we describe the most active 2D chromophores found so far and present the first systematic comparison between 2D chromophores of symmetry D_{3h} and analogous 1D chromophores of symmetry C_{2v} .

Four 1,3,5-triazine derivatives with the donor groups 4-*N,N*-diethylaminophenyl and 4-*N,N*-diethylaminophenylethynyl (**1**, **2**, **5**, **6**) were synthesized by nucleophilic aromatic substitutions of cyanuric fluoride (Scheme 1). As representatives of the second new class of compounds, 1,3,5-tricyanobenzenes **3**, **4**, **7**, and **8** with single and triple substitution were obtained starting from 1,3,5-tricyano-2,4,6-trichlorobenzene. All UV/Vis spectra are shown in Figure 1.

These two structural types were chosen after a careful analysis^[1a] of the nondipolar NLO chromophores published so

[*] Priv.-Doz. Dr. J. J. Wolff, Dr. F. Siegler
Organisch-chemisches Institut der Ruprecht-Karls-Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-544205
E-mail: wolff@donar.oci.uni-heidelberg.de
Prof. Dr. R. Wortmann, Dipl.-Phys. R. Matschiner
Physikalische Chemie der Universität Kaiserslautern
Erwin-Schrödinger-Weg, 67663 Kaiserslautern (Germany)
Fax: (+49) 631-2052536
E-mail: rworkman@rhrk.uni-kl.de

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Scheme 1. a) 4-Iodo-*N,N*-diethylaniline, *t*BuLi; b) 4-*N,N*-diethylaminophenylacetylene, *n*BuLi; c) 4-*N,N*-diethylaminophenyltributyltin, Pd⁰, CuO; d) 4-*N,N*-diethylaminophenylacetylene, Pd⁰, CuI; e) Bu₃SnPh, Pd⁰, CuO.

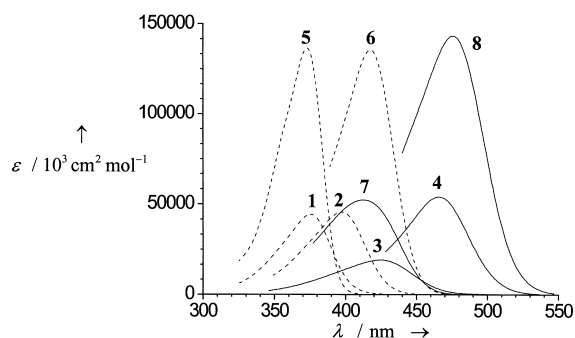


Figure 1. Optical absorption spectra of the triazine derivatives **1**, **2**, **5**, **6** (---) and the tricyanobenzene derivatives **3**, **4**, **7**, **8** (—) in dioxane.

far. Structural types that have already been investigated—such as tris-donor-substituted trinitrobenzenes,^[3] triphenyl-carbenium ions,^[4] and tris-acceptor-substituted triphenylamine derivatives^[5]—show structural deformations caused by electronic and/or steric effects, which reduce their symmetries and π conjugations, and as a consequence also their NLO efficiencies. In tetrahedral structures,^[14] like tetrasubstituted tin and phosphonium compounds, conjugation through the central element is equally insufficient. The NLO figures of merit β_0/M of the chromophores mentioned are in almost all cases^[5c] lower than that of *p*NA.^[1a] The triazines and elongated tricyanobenzenes of this work are mostly planar

(with the exception of **3** and **7**), as could be proven by X-ray determinations and semiempirical calculations. Thus, negative effects of sterically caused deformations can be avoided.

Compounds **5–8** were carefully characterized by hyper Rayleigh scattering (HRS).^[1b, 6] In contrast to the traditional method of field-induced frequency doubling (EFISH),^[7] no external electric field for poling is needed. The study of ionic and nondipolar chromophores thus becomes possible.

In addition, the dipolar 1D NLO chromophores **1–4** were characterized by electrooptical absorption measurements (EOAM).^[9] The importance of the EOAM method for the investigation of 1D NLO chromophores follows from their low-lying, intensive charge transfer (CT) bands, which mostly determine the second-order polarizability β . An analysis of the band forms yields the electrical dipole moments in the electronic ground state (μ_g), the dipole difference between ground and excited states ($\Delta\mu$), and the transition dipole moment (μ_{ag}). According to a two-level model,^[10] β is proportional to the product $(\mu_{ag})^2\Delta\mu$.^[11] The approximate validity of this model has been proven experimentally for a large number of NLO chromophores.^[11a, 10b] The second-order polarizabilities of 1D systems are associated with a main component β_{zzz} along the CT direction (z axis).

However, NLO chromophores with multiple donor–acceptor substitution often show several significant tensor elements of β , which for molecules with C_{2v} symmetry can be related to CT bands with a transition dipole moment that lies perpendicular to the electronic CT direction.^[10c, 10d] Four significant tensor elements are present in planar, π -conjugated NLO chromophores **5–8**: $\beta_{zzz} = -\beta_{zyy} = -\beta_{yzy} = -\beta_{yyz}$.

All compounds investigated show intense absorption bands in the visible range which correspond to single CT bands for the 1D structures **1–4** and to degenerate transitions for the 2D structures **5–8**. The absorptivity of the 2D structures is approximately three times that of the 1D structures. For the latter, a longer wavelength absorption is expected on the basis of solvatochromic effects associated with their dipole moments. However, Scheme 1 and Table 1 show that with the exception of **3** and **7** there is a bathochromic shift for the 2D structures. One reason for this effect is provided by the small dipole moments of **1–4**, which cause a low solvatochromism.

Table 1. Molecular properties of chromophores **1–8** and the reference *p*NA, determined by electrooptical absorption measurements and hyper Rayleigh scattering in dioxane.^[a]

	<i>p</i> NA	1	2	3	4	5	6	7	8
M [g mol ^{−1}]	138.1	380.5	404.5	452.6	476.6	522.7	549.8	549.8	666.9
λ_{ag} [nm]	354	375	397	425	466	373	418	413	476
ϵ_{max} [10 ³ cm ² mol ^{−1}]	15900	44200	45500	18950	53900	136500	135500	52200	143300
μ_g [10 ^{−30} Cm]	21	11	12	9	14	—	—	—	—
μ_{ag} [10 ^{−30} Cm]	16	24	26	18	28	28	31	22	34
$\Delta\mu$ [10 ^{−30} Cm]	31	36	51	47	55	—	—	—	—
$\beta_0^{(ag)}$ [10 ^{−50} Cm ³ V ^{−2}]	16	44	80	42	137	—	—	—	—
β [10 ^{−50} Cm ³ V ^{−2}]	27	96	166	—	1520	142	423	128	2680
β_0 [10 ^{−50} Cm ³ V ^{−2}]	15	42	63	—	285	63	138	43	428
$(\beta_0/M)_{rel}$	≡ 1	1.01	1.43	0.85	5.50	1.11	2.30	0.72	5.89

[a] Conversion of units: 10^{−30} Cm = 0.2998 Debye; 10^{−50} Cm³ V^{−2} = 2.694 × 10^{−30} esu. β is given according to the Taylor series convention^[12] relative to quartz $d_{11}(1064 \text{ nm}) = 0.50 \text{ pm V}^{-1}$. $\beta = \beta_{zzz}$ for chromophores **1–4** (z axis in the direction of the dipole moment); $\beta = \beta_{zzz} = -\beta_{yyz} = -\beta_{yzy} = -\beta_{zyy}$ for the D_{3h} -symmetric chromophores **5–8**. $\beta_0^{(ag)}$ is the two-level value of the second-order polarizability calculated from the EOAM experiments. The transition dipole moment given for **1–4** is related to the CT transition, for **5–8** only for one of the two degenerate transitions. Experimental deviations: 3–5 % for μ_g , μ_{ag} and $\Delta\mu$; 5–10 % for β .

In addition, the unusually effective conjugation in the planar systems **5**, **6**, and **8** leads to a reduction of the HOMO–LUMO distance. Only in the distorted structures **3** and **7** can the expected bathochromic shift of the dipolar 1D structure really be observed.

The changes of dipole moments $\Delta\mu$ in the CT bands detected for **1–4** by EOAM experiments are in some cases quite large; for **4** almost twice as large as for *p*NA. Together with the transition dipole moments derived from integration of the absorption signals, μ_{ag} , the strength of a donor–acceptor pair can be determined.^[1a] Especially tricyanobenzene, but also triazine, show acceptor strengths comparable to that of a nitrophenyl group. Consequently, even the 1D chromophores **2** and **4** lie close to the optimum region for second-order nonlinearities (Table 1). At 1064 nm the values of β for **2** and **4** are 6- and 56-fold larger than that of *p*NA. Even after dispersion correction (wavelength extrapolation to infinite value) to give β_0 values and standardization to the molecular mass of *p*NA, an NLO figure of merit β_0/M for **4** is obtained which is almost six times larger than that of *p*NA. The second-order polarizabilities calculated from μ_{ag} and $\Delta\mu$ on the basis of the two-level model are quite close to the data from HRS measurements. Greater deviations are only observed for **4**, and these are possibly caused by multilevel contributions.

Even greater values for the second-order polarizabilities are observed for the threefold-donor-substituted compounds **6** and **8**. The measured β value of **8** is 100 times and the figure of merit six times larger than the corresponding value of *p*NA. This is the largest value ever obtained for nondipolar NLO chromophores with a threefold symmetry axis. In contrast, the second-order polarizabilities of the sterically hindered systems **3** and **7**, with drastically reduced transition dipole moments, are clearly smaller and below that of *p*NA.

Figure 2 proves a clear correlation between the NLO figures of merits of the 1D and 2D NLO chromophores. For the optimization of β_{zzz} of dipolar and nondipolar NLO

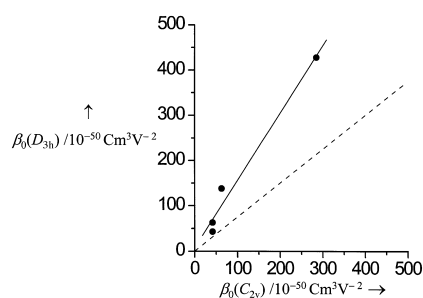


Figure 2. Correlation of β_0 for the one-dimensional and the analogous two-dimensional NLO phores with threefold symmetry (—). The slope expected for three independent subchromophores is 0.75 (---).

chromophores with a threefold symmetry axis, similar design criteria have to be used—at least for the systems shown here. This result, which is at first surprising, has recently been theoretically predicted by us on the basis of a simple two-electron, three–center system.^[1a]

In conclusion, the new structural types offer an important contribution to the optimization of nonlinear optical chromophores with threefold symmetry. In contrast to the often

expressed opinion that dipolar two-level contributions are unimportant in these compounds lacking dipole moments, a clear correlation between the second-order polarizabilities β of threefold-acceptor-substituted nonpolar chromophores with D_{3h} symmetry and the analogous C_{2v} -symmetric dipolar chromophores with substitution by a single acceptor has been proven experimentally. Even after corrections with respect to absorption and molecular mass, compound **8**, with a carefully adjusted donor–acceptor strength and minimized steric hindrance, is several times more active than the NLO prototype *p*NA and therefore gives a new upper limit for this type of NLO-active compound.

Experimental Section

Purities of the compound samples used for measurements were secured by NMR spectroscopy (Bruker, 300 MHz for ^1H NMR; CDCl_3 as solvent, unless noted otherwise) and elemental analysis (deviations of less than 0.2% C, H, N).

1-Chloro-3,5-diphenyl-2,4,6-tricyanobenzene (**11**): Compound **10**^[13] (1026 mg, 4.000 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (116 mg, 0.100 mmol), and CuO (278 mg, 3.50 mmol) in DMF^[14] (20 mL) were stirred at 50 °C for 30 min. After the addition of tributylphenyltin^[15] (1285 mg, 3.500 mmol), heating was continued at 90 °C for 90 min. Dilution with CH_2Cl_2 (100 mL), extraction with a 10% solution of KF, treatment with water (8 ×), drying over MgSO_4 , and chromatography (silica gel, toluene) yielded starting material (16%), 1,3-dichloro-5-phenyl-2,4,6-tricyanobenzene (45%, m.p. 258–259 °C from heptane/toluene), and **11** (210 mg, 0.620 mmol, 35%), m.p. 235 °C (colorless prisms from heptane/toluene). ^1H NMR: δ = 7.51–7.56 (m, 4H), 7.57–7.62 (m, 6H); ^{13}C NMR: δ = 112.74, 113.94, 114.33, 115.70, 128.79, 129.29, 131.45, 133.13, 144.82, 154.27.

2-(4-*N,N*-Diethylaminophenyl)-4,6-diphenyl-1,3,5-triazine (**1**): *t*BuLi (1.7 M in *n*-pentane, 1.3 mL, 2.2 mmol) was added at –78 °C to a solution of 4-iodo-*N,N*-diethylaniline^[16] (550 mg, 2.00 mmol) in THF (10 mL). The temperature was raised to –45 °C and then lowered again to –78 °C to give a colorless suspension. Over 20 min, a solution of **9**^[17] (502 mg, 2.00 mmol) in THF (25 mL) was added; a yellow color formed immediately. The mixture was allowed to warm to room temperature, and the suspension gave a clear, yellow solution. Addition of diethyl ether (100 mL), extraction with half-concentrated NaCl, drying over MgSO_4 , chromatography (silica gel, CH_2Cl_2 /light petroleum 1/4), and concentration of the product fraction yielded **1** as yellow needles (235 mg, 0.618 mmol, 31%), m.p. 165 °C. ^1H NMR: δ = 1.23 (t, 3J = 7.0 Hz, 6H), 3.46 (q, 3J = 7.0 Hz, 4H), 6.77 (pseudo d, J = 9.2 Hz, 2H), 7.52–7.61 (m, 6H), 8.63 (pseudo d, J = 9.2 Hz, 2H), 8.74–8.77 (m, 4H); ^{13}C NMR δ = 12.62, 44.57, 110.80, 122.53, 128.44, 128.78, 130.91, 131.94, 136.89, 151.06, 170.93, 171.37.

2-(4-*N,N*-Diethylaminophenylethynyl)-4,6-diphenyl-1,3,5-triazine (**2**): *n*BuLi (1.6 M, 1.5 mL, 2.4 mmol) was added at –78 °C to a solution of 4-*N,N*-diethylaminophenylacetylene^[18] (433 mg, 2.50 mmol) in THF (25 mL). The temperature was then raised to 0 °C and lowered again to –78 °C. A solution of **9**^[17] (502 mg, 2.00 mmol) in THF (25 mL) was added, and an intensive orange-yellow color developed. The mixture was allowed to warm to room temperature, and Et_2O (100 mL) was added. The resulting solution was extracted with half-saturated solutions of NaCl, dried with MgSO_4 , filtered, and purified by chromatography over aluminum oxide (neutral, activity II; CH_2Cl_2 /light petroleum 1/4). Concentration gave **2** as bright yellow platelets (525 mg, 1.30 mmol, 65%), m.p. 184–186 °C. ^1H NMR: δ = 1.18 (t, 3J = 7.1 Hz, 6H), 3.38 (q, 3J = 7.1 Hz, 4H), 6.63 (pseudo d, J = 9.5 Hz, 2H), 7.50–7.64 (m, 8H), 8.65–8.69 (m, 4H); ^{13}C NMR: δ = 12.49, 44.38, 87.56, 95.14, 105.71, 110.95, 128.57, 129.01, 132.56, 135.10, 135.65, 149.05, 161.45, 171.32.

1-(4-*N,N*-Diethylaminophenyl)-3,5-diphenyl-2,4,6-tricyanobenzene (**3**): Prepared from **11** (235 mg, 0.692 mmol) in analogy to the synthesis of **7**. Chromatography (CH_2Cl_2 /light petroleum 7/3) gave pure **3** (226 mg, 0.499 mmol, 72%); orange-yellow needles from heptane/toluene (130 mg), m.p. 237–238 °C. ^1H NMR: δ = 1.23 (t, J = 7.1 Hz, 6H), 3.40 (q, J = 7.1 Hz, 4H), 6.78 (pseudo d, 2H), 7.53 (pseudo d, 2H), 7.59 (brs, 10H);

^{13}C NMR: $\delta = 12.49, 44.28, 110.92, 112.89, 114.01, 114.84, 115.45, 119.22, 128.88, 128.96, 130.63, 131.09, 134.48, 149.66, 153.72$.

1-(4-*N,N*-Diethylaminophenylethynyl)-3,5-diphenyl-2,4,6-tricyanobenzene (**4**): Prepared from **11** (221 mg, 0.650 mmol) in analogy to the synthesis of **8**; orange microneedles (215 mg, 0.451 mmol, 69%), m.p. 273–275 °C (formation of a deep red polymorph at ca. 266 °C). ^1H NMR: $\delta = 1.18$ (t, $^3J = 7.0$ Hz, 6H), 3.40 (q, $^3J = 7.0$ Hz, 4H), 6.61 (pseudo d, $J = 9.2$ Hz, 2H), 7.51–7.58 (m, 12H); ^{13}C NMR: $\delta = 12.49, 44.56, 85.07, 105.24, 111.23, 111.62, 112.89, 114.69, 114.81, 114.94, 128.88, 129.08, 130.82, 134.04, 135.20, 136.15, 149.82, 152.92$.

1,3,5-Tricyano-2,4,6-tris(4-*N,N*-diethylaminophenyl)benzene (**7**): A suspension of **10** (256 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (162 mg, 0.140 mmol), and CuO (254 mg, 3.20 mmol) in DMF (15 mL) was heated for 10 min to 80 °C and then cooled to room temperature. 4-*N,N*-Diethylaminophenyltributyltin^[9] (1403 mg, 3.200 mmol) in DMF (8 mL) was added, and the mixture heated again to 85 °C for 8 h. After cooling, the mixture was diluted with CH_2Cl_2 (100 mL). It was extracted with a 10% solution of KF ($3 \times$) and water ($5 \times$) and then dried (MgSO_4). Chromatography (silica gel, CH_2Cl_2) gave a yellow product (395 mg), which was dissolved in CH_2Cl_2 /light petroleum (1/4). The solution was filtered and concentrated to provide yellow needles (295 mg, 0.496 mmol, 50%), m.p. 280–284 °C. ^1H NMR: $\delta = 1.20$ (t, $^3J = 7.1$ Hz, 18H), 3.40 (q, $^3J = 7.1$ Hz, 12H), 6.74 (pseudo d, $J = 9.0$ Hz, 6H), 7.47 (pseudo d, $J = 9.0$ Hz, 6H); ^{13}C NMR: $\delta = 12.57, 44.25, 110.84, 111.99, 116.71, 120.41, 130.98, 149.32, 154.34$.

1,3,5-Tricyano-2,4,6-tris(4-*N,N*-diethylaminophenylethynyl)benzene (**8**): A solution of **10** (256 mg, 1.00 mmol), 4-*N,N*-diethylaminophenylacetylene (693 mg, 4.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (116 mg, 0.100 mmol), and CuI^[18] (19 mg, 0.10 mmol) in NEt_3 (3 mL) was heated to 85 °C for 6 h. Formation of red crystals began after about 30 min, and a viscous, deep red suspension was formed. Chromatography on neutral alumina (activity II; CH_2Cl_2 /light petroleum 1/1) yielded **8** (535 mg, 0.802 mmol, 80%); red prisms from heptane/toluene (375 mg, 0.562 mmol, 56%), m.p. > 230 °C (decomp). ^1H NMR (CD_2Cl_2): $\delta = 1.20$ (t, $^3J = 7.2$ Hz, 18H), 3.43 (q, $^3J = 7.2$ Hz, 12H), 6.67 (pseudo d, $J = 8.9$ Hz, 6H), 7.54 (pseudo d, $J = 8.9$ Hz, 6H); ^{13}C NMR (CD_2Cl_2): $\delta = 12.66, 44.94, 84.39, 105.56, 111.01, 111.68, 112.73, 115.64, 135.11, 150.18$. One signal expected on the basis of the structure could not be detected.

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- $$\beta_{zzz}^{(ag)}(-2\omega; \omega, \omega) = \beta_{zzz}^{(ag)}(0) \frac{\omega_a^4}{(\omega_a^2 - \omega^2)(\omega_a^2 - 4\omega^2)} \quad (1)$$
- $$\beta_{zzz}^{(ag)}(0) = \lim_{\omega \rightarrow 0} (-2\omega; \omega, \omega) = \frac{6\Delta\mu_z^{ag}(\mu_z^{ag})^2}{(\hbar\omega_a)^2} \quad (2)$$
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