

Octupolar (C_3 and S_4) Symmetric Cyclized Indole Derivatives: Syntheses, Structures, and NLO Properties

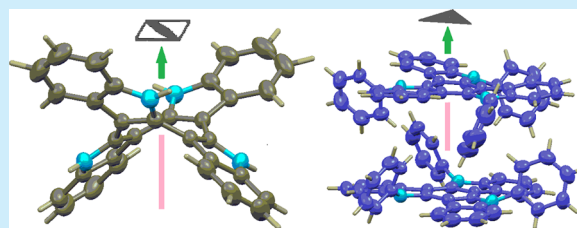
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S Supporting Information

ABSTRACT: Several cyclized indole derivatives have been synthesized, and their structures been determined. The C_3 -symmetric single-chiral *N*-phenyltriindole (Tr-Ph3) crystallized in the $P1$ space group, and the S_4 -symmetric saddle-like tetraindole (TTr) crystallized in the $I\bar{4}$ space group. The Tr-Ph3 and TTr crystals exhibit remarkable powder SHG intensities 5 and 11 times that of KH_2PO_4 (KDP), respectively. TTr is a useful octupolar core to build S_4 -symmetric molecules and crystals for second-NLO materials.



In the traditional organic second-order nonlinear optics (second-NLO), the donor- π -acceptor dipole molecular model has acquired great success.¹ However, many 1-D intramolecular charge-transfer (ICT) dipolar compounds, which have large molecular second-order polarizability (β), failed to exhibit macroscopic second-NLO effects (such as the second harmonic generation, SHG) due to their centrosymmetric packing in crystals.

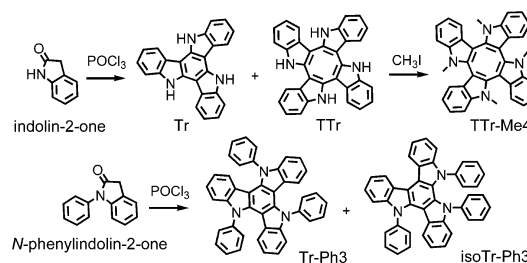
In the early 1990s, Zyss et al. introduced the concept of octupole to organic NLO.² Since then, numerous second-NLO active octupolar compounds have been reported, including pure organic compounds,³ organic salt,⁴ metal-organic complexes,⁵ etc. In a narrow sense, an octupolar molecule is such a nondipolar and noncentrosymmetric ICT molecule that contains C_3 or S_4 point group as its subgroup. The octupolar compounds can be classified as a trigonal C_3 family (characterized by 2-D ICT) and tetragonal S_4 family (with 3-D ICT). For the pure organic octupolar compounds, many reported works are related to molecular β only, while the reports concerning the noncentrosymmetric crystal structures and the useful macroscopic SHG properties are relatively few.

The C_3 -symmetric 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, see the Supporting Information (SI)) is a pioneer octupolar compound.⁶ Its remarkable powder SHG intensity is not compatible with the centrosymmetric $P\bar{1}$ space group but compatible with the noncentrosymmetric polymorph of the crystal.⁷ 2,4,6-Triphenoxy-1,3,5-triazine (see the SI, point group C_3 , space group Cc)⁸ and 2,4,6-tris(benzyloxy)-1,3,5-triazine (see the SI, point group C_3 , space group $Pca2_1$) exhibited a SHG intensity comparable to that of KDP.⁹ 2,4,6-Tris(*p*-methylstyryl)-1,3,5-triazine (see the SI, space group $Pmn2_1$) exhibited a higher powder SHG intensity.¹⁰ As an excellent example, the quasi- C_3 -symmetric 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminostyryl)benzene (see the SI, $P3_1$ space group) exhibited a powder SHG intensity of 45-fold larger than that of urea.¹¹

The second-NLO active S_4 -symmetric octupolar organic compounds are very limited. Several biphenyl compounds were supposed to be of D_{2d} symmetry without X-ray structures.¹² The β value of the 3-D ICT compound 4,4',6,6'-tetrakis(*p*-diethylaminostryl)[2,2']bipyrimidine (see the SI) is large, but its crystal is centrosymmetric ($P2/n$).¹³ A series of 3-D ICT non- S_4 -symmetric compounds, characterized by so-called through-space delocalization, exhibited large β values but no detectable bulk SHG.¹⁴ Recently, an interesting 3-D charge-transfer complex bis(phthalocyaninato)lutetium was reported to have exceptionally large β value.¹⁵ The only example that has noncentrosymmetric S_4 symmetry both for the molecule and crystal is a kind of calixarene (see the SI), but it has no macroscopic SHG.¹⁶

Triindole (Tr, see Scheme 1) is an aromatic and C_{3h} -symmetric planar octupolar compound. Several novel Tr

Scheme 1. Synthetic Route



derivatives have been synthesized in recent years, including the σ -bonded piedfort dimer,¹⁷ π -bridged dimer,¹⁸ conjugated microporous polymer,¹⁹ and azafullerene precursor.²⁰ Tr derivatives have also acquired versatile applications in discotic

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liquid crystals,²¹ organic light-emitting diodes,²² two-photon absorption,²³ organic solar cells,²⁴ etc. The molecular β coefficients of several Tr derivatives are large.²⁵ However, to our knowledge, the macroscopic second-NLO properties of Tr derivatives and the X-ray structure of Tr itself have not been reported.

The chemistry of tetraindole (TTr, see Scheme 1) can be thought of as beginning in 2006.²⁶ TTr was first synthesized in 2010²⁷ and followed by several tetraindoles of large size.²⁸ The only reported X-ray structure is a bromo-substituted TTr with the S_4 molecular point group and the centrosymmetric $Ia\bar{3}d$ space group.²⁹ In this paper, we mainly report the syntheses, structures, and the second-NLO properties of several C_3 - and S_4 -symmetric cyclized indole derivatives.

As shown in Scheme 1, we synthesized the Tr (yield 18.2%) and TTr (yield 5.5%) by trimerizing and tetramerizing the indolin-2-one monomer in the presence of POCl₃ in a one-pot reaction at 100 °C for 8 h under Ar atmosphere. The low yield of TTr may be the reason why TTr failed to be noticed in the previous synthesis of Tr.³⁰ We successfully grew the crystal of Tr, and the X-ray structure (Figure 1 and Table 1) demonstrated the C_{3h} -symmetric octupolar skeleton of the Tr molecule, but its crystal is centrosymmetric ($P2_1/c$).

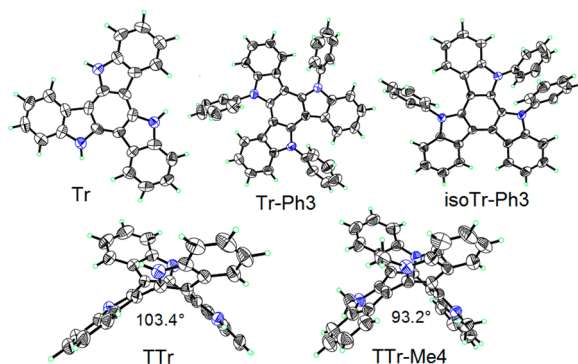


Figure 1. ORTEP plot of the title molecules.

We further synthesized the phenyl-substituted triindole (Tr-Ph3) by trimerizing *N*-phenylindolin-2-one with a yield of 19.1%. The X-ray structure (see Figure 1 and Table 1) indicates

the noncentrosymmetry of the Tr-Ph3 molecule (point group C_3) and its crystal (space group $P1$). In the course of synthesizing Tr-Ph3, the supposed tetramerized TTr-Ph4 was not found. Instead, an asymmetric trimerized isomer, named isoTr-Ph3, has been isolated (yield 3.0%), and its X-ray structure been determined (see Figure 1 and Table 1). To our knowledge, it is the first asymmetric triindole compound by cycling indolin-2-one derivatives. DFT geometry optimizations at the b3lyp/6-311g(d) level (see the SI) indicates that the energy (sum of electronic and zero-point energies) of Tr-Ph3 is slightly lower (0.131 eV) than that of isoTr-Ph3, which can rationalize the higher yield of Tr-Ph3 relative to isoTr-Ph3.

TTr was treated with a large excess of NaH (>8 equiv) and methylated with MeI, and TTr-Me4 was successfully synthesized. When the ratio of NaH:TTr was less than 5:1, monomethylated tetramer (TTr-Me1) was also isolated.

As shown in Figures 1 and 2, there are two very similar molecules in the asymmetric unit of the Tr-Ph3 crystal, which

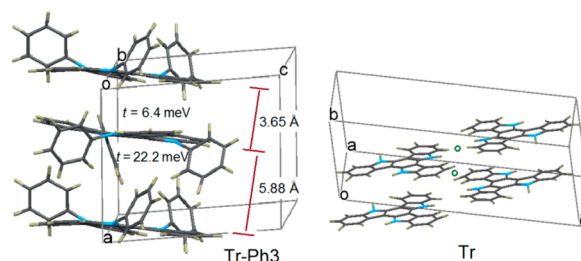


Figure 2. X-ray structures of Tr-Ph3 and Tr.

take a gearlike structure with the three peripheral phenyl rings sitting in the same side of the Tr core. The two molecules bear the same chirality and embed to each other in a face-to-face manner, forming a noncentrosymmetric dimeric piedfort unit. The piedfort unit is then translated along the *a*-axis to form a columnar structure. In a column, the intermolecular interactions, scaled by the electronic transfer integral *t* (see the SI), of the face-to-face pair in the piedfort (*t* = 22.2 meV) is larger than that of the back-to-back pair between piedforts (*t* = 6.4 meV), though the spacing (see Figure 2) between the two planar Tr cores in the piedfort (5.88 Å) is larger than that between piedforts (3.65 Å). The interactions between the two

Table 1. Structure Data, Linear and Nonlinear Optical Properties

	Tr	Tr-Ph3	isoTr-Ph3	TTr	TTr-Me4	TTr-Me1
<i>T</i> (K)	296	290	293	295	297	
space group	$P2_1/c$	$P1$	$P\bar{1}$	$I\bar{4}$	$P2_1/c$	
<i>a</i> (Å)	5.8395 (2)	9.5974 (14)	12.7810 (6)	15.3276 (10)	23.991 (6)	
<i>b</i> (Å)	12.1606 (4)	13.3267 (8)	16.0961 (8)	15.3276 (10)	10.921 (3)	
<i>c</i> (Å)	23.1234 (9)	13.4404 (8)	17.7266 (8)	4.8028 (3)	23.329 (6)	
α, β, γ (deg)	90, 94.89, 90	118.42, 93.30, 97.50	76.77, 89.91, 68.90	90, 90, 90	90, 118.39, 90	
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.075	0.051	0.087	0.037	0.088	
$\lambda_{\max, \text{abs}}$ ^a (nm)	308s, 322m, 340w	314s, 331m, 349w	306m, 353m, 401w	311m	311m	312m
$\lambda_{\max, \text{em}}$ ^a (nm)	378	390	414s, 434s	379	381	378
Φ (%) ^b	24	24	66	10.7	5.1	3.4
point group	C_{3h}	C_3	C_1	S_4	S_4	C_1
μ (D) ^c	0	1.924	3.073	0	0	
$\ \beta\ , \ \beta_{\parallel}\ $ (10 ⁻³⁰ esu)	15.52, 11.99	35.40, 29.54	11.28, 9.46	25.97, 21.17	25.04, 21.21	
SHG intensity ^d		5		11		1.3

^aIn 10⁻⁵ M THF solution. ^bIn 10⁻⁶ M THF solution (samples) and 10⁻⁶ M quinine sulfate solution in 0.1 M sulfuric (reference). ^cDipole moment calculated by DFT/b3lyp/6-311g(d) algorithm. ^dSHG intensity is the ratio of the average intensity of the sample to that of KDP.

“gears” of the piedfort are chiral-matchable, which is believed to play a critical role in the noncentrosymmetric structure of the piedfort and the crystal.

The X-ray structure of TTr (see Figures 1 and 3) indicates that the 8-membered cyclooctatetraene core of TTr takes a

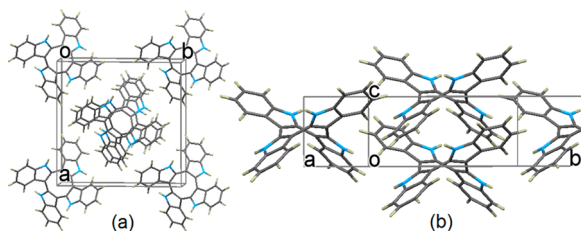


Figure 3. X-ray structure of TTr (a, top view; b, side view).

nonplanar boatlike conformation. The TTr molecule strictly belongs to S_4 point group and the TTr crystal also has a strict S_4 symmetry (space group $I4$), exemplifying a perfect inheritance of the molecular symmetry to the crystal. In the c -axis direction, the neighboring saddle-shaped TTr molecules are totally eclipsed and closely nestled in a concave–convex fashion to form a $\bar{4}$ symmetric column in which the centroid-to-centroid spacing between two TTr molecules is 4.80 Å and the intermolecular plane-to-plane distance between two indole subunits is 3.77 Å (see the SI).

The two TTr-Me4 molecules (A and B) in the asymmetric unit are similar and take a quasi- S_4 conformation. However, the space group ($P2_1/c$) of TTr-Me4 crystal is centrosymmetric, which is very different from the noncentrosymmetric TTr crystal ($I4$). What kind of molecular factor makes the difference between these two crystals? We believe that the molecular dihedral angle between the indole planes is the critical factor. In TTr crystal, the dihedral angle of the two indole planes in the same side of the saddle TTr molecule is 103.4° (see Figure 1). In TTr-Me4 crystal, the molecular dihedral angles are 93.2 and 93.1° (molecule A) or 90.6 and 94.2° (molecule B). The close-orthorhombic dihedral angle prevents the TTr-Me4 molecules from parallel superposing one by one like the way in TTr crystal. On the other hand, the large dihedral angle of TTr lowers the centroid of the saddle molecule, bringing about the elegant TTr-saddle way of packing, i.e., the way of concave–convex–nestled saddles.

The lower lying UV–vis absorption peaks (see Figure 4 and Table 1) of these compounds are located in the region of $\lambda =$

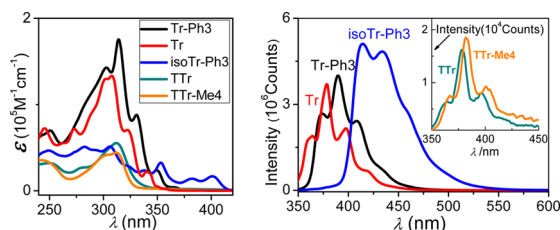


Figure 4. Absorption spectra (left) and fluorescent spectra (right) of the title compounds (10^{-5} mol/L in THF).

310–350 nm, except the isoTr-Ph3 with the absorption edge being red-shifted about 50 nm relative to that of Tr-Ph3. This indicates that the UV-transparency of the octupolar Tr-Ph3 is better than that of the dipolar isoTr-Ph3 (see the SI for discussion) and can be explained in the viewpoint of molecular

symmetry.^{2d} All these compounds are transparent for the frequently used 1064 nm of fundamental light and the 532 nm light of SHG.

The fluorescent spectra of these compounds (Figure 4) show a fine vibronic structure. Similarly to the absorption, the emission of isoTr-Ph3 again exhibits a significant red-shift (24 nm compared to Tr-Ph3). In addition, isoTr-Ph3 has a high fluorescence quantum efficiency ($\Phi = 0.66$), which is about 3 times that of Tr-Ph3 (Table 1). This can be attributed to its relatively rigid structure. For Tr-Ph3, all three phenyl groups keep the freedom of intramolecular rolling in solution to inactivate the excited state. For isoTr-Ph3, two phenyl groups are π – π locked and one phenyl remains relatively free. On the basis of its intense fluorescence, isoTr-Ph3 may find some applications.

The sum-over-states approach was adopted to calculate the β_{ijk} values³¹ at the level of CIS/6-311g(d) by using G09 programs (see the SI for details). The molecular second-NLO coefficient can be assessed by the modulus of the β tensor, defined by^{2b}

$$\|\beta\| = \sqrt{\|\beta\|^2} = \left(\sum_{i,j,k} \beta_{ijk}^2\right)^{1/2} \quad (1)$$

The $\|\beta\|$ data in Table 1 are the values at 1064 nm, and the $\|\beta_0\|$ data are the values at 20000 nm, which prove to be virtually equivalent to the zero-frequency limit ($\lambda \rightarrow \infty$). The S_4 -symmetric TTr and TTr-Me4 are pure octupoles (dipole moment $\mu = 0$). As a comparison, the $\|\beta\|$ and $\|\beta_0\|$ values of the dipolar molecule *p*-nitroaniline (*p*NA) were calculated to be 16.29×10^{-30} and 13.12×10^{-30} esu, respectively, by the same method.

Tr-Ph3 is not a strict octupole disclosed by its small dipole moment ($\mu = 1.9$ D). By decomposing its β tensor into the vector ($\beta_{j=1}$) and octupolar ($\beta_{j=3}$) components

$$\beta = \beta_{j=1} + \beta_{j=3}, \quad \|\beta\|^2 = \|\beta_{j=1}\|^2 + \|\beta_{j=3}\|^2 \quad (2)$$

by Zyss's method,^{2b} the ratio of $\|\beta_{j=3}\|/\|\beta_{j=1}\|$ of Tr-Ph3 turns out to be 6.5. This indicates that the octupolar component is the dominant and Tr-Ph3 is essentially an octupolar molecule.

The macroscopic powder SHG intensities were measured according to the Kurtz method³² at 1053 nm of pulses from a Nd:YLF laser. TTr (powder sample) exhibits a remarkable SHG ($\lambda_{\text{SHG}} = 526.5$ nm) intensity which is 11 times that of the KDP reference (Table 1). Tr-Ph3 and TTr-Me1 solids are also SHG active, with a intensity being 5 and 1.3 times that of KDP, respectively (Table 1). For Tr and isoTr-Ph3, no SHG signals were detected because of the centrosymmetry of the crystals. The molecular second-NLO property of Tr-Ph3 is better than that of isoTr-Ph3 (larger $\|\beta\|$ value and better transparency of Tr-Ph3), due to the C_3 octupolar symmetry. Though the molecular $\|\beta\|$ value of TTr is not as large as that of Tr-Ph3, TTr exhibits the best macroscopic second-NLO property. This can be attributed to its saddle-like S_4 octupolar symmetry, which results in the excellent concave–convex–nestled way of packing in crystal.

In summary, we have synthesized a series of cyclized indole derivatives and well determined their X-ray structures. Among them, the C_3 -symmetric Tr-Ph3 molecules and the S_4 -symmetric TTr molecules crystallized into noncentrosymmetric crystals, which exhibit remarkable second-NLO (SHG) intensities. If *p*NA and TATB are the prototypical molecules in the well-developed 1-D dipolar and 2-D C_3 -symmetric

octupolar molecular NLO, there are no suitable prototype candidate molecules in the infant 3-D S_4 -symmetric octupolar organic NLO. To the best of our knowledge, the saddle-like TTr is the first well-characterized pure octupolar organic compound which holds strict S_4 -symmetry (at both molecular and crystalline levels) and exhibits remarkable macroscopic second-NLO effect. On the basis of this work, further study to improve the synthetic yield and the second-NLO properties of TTr derivatives is ongoing in our laboratory.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.5b01912](https://doi.org/10.1021/acs.orglett.5b01912).

Crystallographic data for Tr-Ph3 (CIF)

Crystallographic data for TTr (CIF)

Crystallographic data for Tr (CIF)

Crystallographic data for isoTr-Ph3 (CIF)

Crystallographic data for TTr-Me4 (CIF)

Experimental details; NMR, MS, computational details (PDF)

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Notes

The authors declare no competing financial interest.

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