DFT Investigation of Triarylamine-α-cyanoacrylic Acid Compounds: Structural, Electronic, and Nonlinear Optical Properties

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Abstract
Using the density functional theory and finite field method, nonlinear optical properties of nine triarylamine-α-cyanocinnamic acid derivatives were investigated at the M06-2X/6–311++G(d,p) and ωB97X-D/6–311++G(d,p) levels of theory. Except for (E)-2-cyano-3-(4-(di([1,1′-biphenyl]-4-yl)amino)phenyl)acrylic acid (a), which had a D–π–A electronic structure, all the other eight derivatives had an A–π–D–π–A structure. The results suggest that the lowest energy transition of the nine triarylamine derivatives was the π–π* transition from the HOMO to LUMO. The absorption maxima of the derivatives in their ethanol solution were redshifted with respect to those in the gas phase. The introduction of conjugated C=C or C≡C bonds between the biphenyl unit of molecule a had a minor effect on the second-order nonlinear optical properties of the molecule. However, the introduction of C=C bond into the parent molecule improved the third-order nonlinear optical properties. The introduction of a heterocyclic ring (furan ring or thiophene ring) between the triarylamine moiety and the branched chain containing the cyanocinnamic acid group enhanced the second- and third-order nonlinear optical properties; especially, the second- and third-order polarisabilities of molecules b3 and c3, which were obtained by introducing a thiophene ring, were the highest. The second- and third-order polarisabilities of b3 were 0.13 × 10^5 and 27.13 × 10^5 a.u., respectively, while those of c3 were 0.14 × 10^5 and 28.10 × 10^5 a.u., respectively. This suggests that b3 and c3 have desirable second- and third-order nonlinear optical properties and can be used for designing efficient second- and third-order nonlinear optical materials.

Keywords Triarylamine-α-cyanoacrylic acid · Density functional theory · Finite field method · Nonlinear optical properties · Molecular modelling

Introduction
Compared to traditional inorganic nonlinear optical materials, organic nonlinear optical materials have excellent characteristics such as high electro-optic coefficients, fast response speeds, and high chemical and thermal stability [1, 2]. These materials are easy to process, and their molecular structures can be readily modified. Furthermore, they have a broad range of potential applications in high-speed optical communication, optical information processing, optical storage, and fabrication of high-frequency (terahertz) electro-optic devices, among others. Consequently, the design of organic nonlinear optical molecules with high nonlinear optical coefficients is of great interest to theoretical and experimental researchers [3–7]. Although a large number of nonlinear optical chromophores have been developed in the past two decades, only a few of them have shown good performance in optoelectronic devices [8, 9] Further improvement of their nonlinear optical properties requires rational designing of the molecular structure based on an in-depth understanding of the structure–property relationships. The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) are widely used in the
computational studies of organic nonlinear optical properties [3–5, 10–16].

High-performance nonlinear optical materials can be designed by ordering the connectivity among novel electron acceptors (A) and electron donors (D) and π-conjugated systems (π); for example, connectivities such as D-π-A, A-π-D-π-A, or D-π-A-π-D can be established or the substituents on A, π, and D can be varied [6, 17]. In the previously reported triarylamino-α-cyanocinnamic acid-based optical materials, triphenylamine (TPA) was typically used as an electron donor and cyanocinnamic acid was used as an electron acceptor, and the donor and acceptor were bridged by a π-conjugated system to afford organic dyes [18–21]. TPA lowered the LUMO+1 energy level of the organic system, thus lowering the energy gap between LUMO and LUMO+1 and resulting in a broader absorption spectrum [18]. Because the acceptor and donor are connected by a π-conjugated system, intramolecular charge transfer from the donor to acceptor pre-polarises the electronic ground state [22, 23]. For example, Janjua et al. [24] used the TDDFT to predict the second-order nonlinear optical properties of triphenylamine-α-cyanocinnamic acid derivatives conjugated with acetylenyl benzene. The static second-order polarisability (β0) showed that the intramolecular charge transfer along the triphenylamine group to α-cyanocinnamic acid played a key role in influencing the nonlinear optical response, and the addition of electron accepting fluorine atoms in the phenyl-conjugated system increased the β value.

In this study, the Gaussian 16 A.03 programme was used to optimise the molecular structures of nine triarylamino-α-cyanocinnamic acid molecules (Fig. 1). Theoretical electronic spectra and nonlinear optical properties were also computed. The influence of changes in the electron donor structure and the effect of introducing π-conjugated heterocyclic rings on the nonlinear optical properties of these molecules were systematically investigated. Specifically, based on the structure of parent molecule a, (E)-2-cyano-3-(4-(di[(1,1’-biphenyl)-4-y1]amino) phenyl)acrylic acid, unsaturated bonds (C=C or C≡C bonds) were added to expand the conjugated system. Furthermore, π-conjugated heterocycles (furan and thiophene rings) were introduced into the D-A triarylamino-α-cyanocinnamic acid system to form a D-π-A structure. The results provided a theoretical framework for the further design and synthesis of triarylamino-α-cyanocinnamic acid compounds with excellent nonlinear optical properties.

### Computational details

Usually, the electric field-induced second harmonic generation method is used to measure the second-order nonlinear optical property β′μ, which is the projection of the direction of β the dipole moment. In this article, to obtain reference data for the experiment, the following formulas were used [4, 5, 13, 14]:

\[
\beta'_{\mu} = \frac{(\mu, \beta_x + \mu, \beta_y + \mu, \beta_z)}{(\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}} \tag{1}
\]

\[
\beta_i = \frac{1}{3} \sum_k (\beta_{ikk} + \beta_{ik} + \beta_{kik})_{i,k=x,y,z} \tag{2}
\]

\[
\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \tag{3}
\]

where μx, μy, and μz are the components of the dipole moment in the x, y, and z directions, respectively. βi is the component of the second-order nonlinear optical property along direction i, and βikk is the third-order tensor component. The finite field method is an effective method for calculating the nonlinear optical properties of organic molecules [4, 26]. In this study, we used the finite field method, the hybrid functional M06-2X, and the Hartree–Fock (HF) long-range correction hybrid functional ωB97X-D [27–30] mixed with 100% HF in the progressive region to calculate the third-order tensor components of its second-order nonlinear optical properties. The hybrid functional M06-2X was used to calculate the fourth-order tensor components of its third-order nonlinear optical properties, and the values of β′μ, β0, and γ were obtained using formulas (1), (3), and (4).

\[
\gamma = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yzzz})/5, \tag{4}
\]

where γxxxx, γyyyy, γzzzz, γxxyy, γxxzz, γyzzz, and γyzzz are the fourth-order tensor components. The centre of the N atom of triarylamine was chosen as the coordinate origin when calculating the nonlinear optical properties. The X axis was located on the benzene ring containing the cyanocinnamic acid branch, the Z axis was perpendicular to the conjugate plane formed by the N atom and benzene ring, and the dipole moment of the molecule was roughly the same as that of the X axis.

### Results and discussion

#### Geometric structures

Calculations were optimised at the M06-2X /6-311++G(d,p) level to obtain stable configurations of the triarylamine derivative molecules, without imaginary frequencies, as shown in Figure S1. The dihedral angles between the two benzene rings in the molecule obtained by structural optimisation are shown in Table S1. It is evident that the two benzene rings in the a- and c-series molecular...
structures were not coplanar, while those in the b-series molecular structures were almost coplanar.

The bond order is a numerical value indicating the strength of the bond between two atoms in a molecule. A bond order close to 1 indicates the formation of a single covalent bond between two atoms. Similarly, a bond order close to 2 indicates the formation of two covalent bonds. When the bond order is between 1 and 1.5, a conjugate bond intermediate between a single and double bond is formed. The Wiberg bond order values calculated by the M06-2X method are shown in Figure S2. For the nine molecular structures studied, the bond order of all the C–C, C–O, and C–S single bonds lay between 1 and 1.3, indicating significant molecular conjugation, which is beneficial to charge flow within a molecule.

Electronic structures

The TD-M06-2X method and the same basis set were used to calculate the excited-state properties of the molecules in the gas phase and ethanol. Based on this, the frontier molecular orbitals and electronic absorption spectra were obtained (Fig. 2 and Table 1, respectively). The energy gaps between the frontier molecular orbitals, HOMO and LUMO of molecules a, b and c owing to the electron cloud distributions, were close to 3.06, 2.83, and 2.90 eV, respectively [10]. Analysis of the data in Fig. 1 suggests that the energy gap of the molecules decreased in the order a > b > c; b > b1 > b2 > b3 and c > c1 > c2 > c3, indicating that the introduction of conjugated C=C or C≡C bonds into parent molecule a and the introduction of a benzene, furan, or thiophene ring between the branched chain containing cyanocinnamic acid and triarylamines facilitated electronic transitions within the molecule. The HOMO electron clouds (which are the π orbitals involved in bond formation) of each molecule were uniformly distributed over the entire molecule, while the LUMO electron clouds (which are the anti-bonding π* orbitals) were distributed on the branched chain bearing the cyanocinnamic acid group.

The UV absorption maxima of molecules a, b, and c (Table 1) were close to 410, 410, and 424 nm, respectively [10]. The electronic transitions in the nine molecules in the low-energy excited states corresponded mainly to the S0 → S1 transition between HOMO and LUMO. The absorption maxima of these molecules were in the range of 388–434 nm, which corresponds to the visible range. Table 2
shows that the absorption spectra of the molecules in ethanol were redshifted by 6–31 nm relative to those in the gas phase (Figure S3).

**Natural population analysis**

To explore the correlation between the charge transfer properties and nonlinear optical properties of organic nonlinear optical materials, the charge distribution of the molecules was calculated by the natural bond orbital method. The natural population analysis of each part of a molecule is listed in Table 2. I corresponds to the two benzene rings at the ends of the two biphenyl-containing branched chains in the triarylamine derivatives; II is an ethynyl-conjugated bridge or vinyl-conjugated bridge between the two biphenyls in the triarylamine derivatives; III corresponds to the benzene rings, furan rings, and thiophene rings introduced from triarylamine or triarylamine and cyanoacrylic acid-containing branched chains; and IV is the cyanoacrylic acid group.

Table 2 shows that structural units II and III of the nine molecules were positively charged and behaved as donors in the molecular system. Except for parent molecule a, structural units I and IV were negatively charged and behaved as the acceptor in the molecular system. Therefore, molecule a

| Comp. | λ/ nm | $E_g$/ev | $F$ | Major contribution |
|-------|-------|---------|-----|-------------------|
| Gas phase | | | | |
| a | 378 | 3.28 | 1.0203 | HOMO→LUMO (91%) |
| b | 387 | 3.20 | 1.1014 | HOMO→LUMO (87%) |
| c | 393 | 3.15 | 1.0158 | HOMO→LUMO (87%) |
| b1 | 382 | 3.25 | 1.0697 | HOMO→LUMO (77%) |
| b2 | 407 | 3.04 | 1.4551 | HOMO→LUMO (76%) |
| b3 | 404 | 3.07 | 1.3352 | HOMO→LUMO (75%) |
| c1 | 392 | 3.16 | 0.9814 | HOMO→LUMO (78%) |
| c2 | 415 | 2.98 | 1.3447 | HOMO→LUMO (76%) |
| c3 | 414 | 3.00 | 1.2350 | HOMO→LUMO (76%) |
| Ethanol solvent system | | | | |
| a | 409 (410$^*$) | 3.03 | 1.1836 | HOMO→LUMO (91%) |
| b | 405 (410$^*$) | 3.05 | 1.2234 | HOMO→LUMO (87%) |
| c | 416 (424$^*$) | 2.98 | 1.1194 | HOMO→LUMO (87%) |
| b1 | 388 | 3.19 | 1.1331 | HOMO→LUMO (77%) |
| b2 | 427 | 2.90 | 1.5425 | HOMO→LUMO (76%) |
| b3 | 420 | 2.95 | 1.4491 | HOMO→LUMO (75%) |
| c1 | 403 | 3.08 | 1.0914 | HOMO→LUMO (78%) |
| c2 | 415 | 2.98 | 1.3447 | HOMO→LUMO (76%) |
| c3 | 434 | 2.86 | 1.3164 | HOMO→LUMO (76%) |

Electronic transition: $S_0 \rightarrow S_1$. The data in brackets are experimental values in ethanol solution [31]
can be considered having a D-π-A structure, while the other eight molecules can be considered having an A-π-D-π-A structure. Therefore, the introduction of C=C or C≡C bonds between biphenyls in molecule a and the introduction of a benzene ring, furan ring, or thiophene ring in the branched chain-containing cyanoacrylic acid group changed the charge distribution of the molecules. With the introduction of a heterocyclic ring into the b-series and c-series derivatives, with b and c as the parent molecule, the charge of structural unit II remained almost unchanged, while the charge of the other structural units increased significantly, indicating enhanced delocalisation of electrons.

**Nonlinear optical response of the molecules**

### Second-order nonlinear optical properties

For the nine optimised, stable triarylamine structures, the hybrid functional M06-2X, and the long-range-corrected hybrid functional ωB97X-D were used to calculate the third-order tensor components of the second-order nonlinear optical properties (Table 3); β_y is the first hyperpolarisability in the direction of the dipole moment, and β_z is the total effective value of the first hyperpolarisability (or static first hyperpolarisability).

Table 3 shows that the calculated results obtained using the hybrid functional M06-2X and the long-range-corrected hybrid functional ωB97X-D. However, the value calculated by the hybrid functional M06-2X was very high. The exchange potential of the HF-type exchange functional is asymptotically correct and can eliminate autocorrelation errors in the asymptotic region. Therefore, mixing a larger proportion of the HF-type exchange functionals in the asymptotic region can effectively improve the overestimation of the second-order polarizability by the DFT exchange functional [27–30]. The proportion of HF-type exchange functionals mixed in the asymptotic region of the hybrid functional M06-2X is less than that of the long-range-corrected hybrid functional ωB97X-D, which may result in overestimation of the second-order polarizability. However, the ωB97X-D can effectively prevent the overestimation of the second-order polarisability using the DFT.
exchange functionals, owing to the mixing of 100% HF in the asymptotic region. Therefore, calculation of the second-order polarizability using the oB97X-D functional can provide more reliable variation trends.

Further, Table 3 shows that the $\beta_\alpha$ value in the second-order nonlinear optical coefficient component was relatively large, which indicated that $\beta_\alpha$ contributed significantly to $\beta_\mu$ (or $\beta_\rho$) and that the charge transfer within the XY plane was the main reason for the origin of the second-order nonlinear optical properties. The second-order polarisability of molecules a, b, and c did not change significantly, indicating that the introduction of conjugated C=C or C≡C bonds between the biphenyls in the molecular structure of molecule a had little effect on the second-order nonlinear optical properties of the molecules. When a benzene ring, furan ring, or thiophene ring was introduced between the benzene ring and cyanocinnamic acid group in the b- and c-series molecules, the second-order polarisability increased and was the highest for molecules b3 and c3, which were obtained by introducing a thiophene ring. The second-order polarisabilities of molecules b3 and c3 were 0.13 × 10^3 and 0.14 × 10^3 a.u., respectively. These were similar to the second-order (0.14 × 10^3 a.u.) and third-order (0.12 × 10^3 a.u.) polarisabilities of chalcone derivatives, which were ~6 and ~20 times larger than those of p-nitroaniline [32]. These results indicate good nonlinear response from molecules b3 and c3 for second- and third-order nonlinear optical applications.

We used the two-level model [33, 34] to qualitatively describe the contribution of molecular charge transfer to the second-order nonlinear optical properties:

$$\beta \propto \Delta\mu_{eg} f / E_{eg}^3,$$

where $\Delta\mu_{eg}$ is the difference between the dipole moments of the excited state and ground state, $f$ is the oscillator strength, and $E_{eg}$ is the transition energy. Formula (5) suggests that for molecules with a larger dipole moment difference between the excited state and ground state, a smaller transition energy and larger oscillator strength will result in a larger second-order nonlinear optical coefficient $\beta$.

Table S2 shows the difference between the excited state and ground state dipole moments of the b- and c-series molecules calculated using the M06-2X/6–311+++G(d,p) functional. It is evident that the difference increased when heterocyclic rings were introduced into the triarylamine system.

Table 1 shows that the transition energy $E_{eg}$ of molecules a, b, c, b1, and c1 is close to the calculated oscillator strength $f$. However, compared with the values of parent molecules b and c, the transition energy $E_{eg}$ of molecules b2, b3, c2, and c3 decreased, while oscillator strength $f$ increased significantly. Therefore, the introduction of heterocyclic rings into the triarylamine system enhanced the second-order nonlinear optical properties.

### Third-order nonlinear-optical properties

To consider more electron transfer processes, it is necessary to use more complex polarisation and diffusion functions. Therefore, we used the triple-split basis set 6–311++G(d,p). Using the 6–311++G(d,p) basis set and the finite field and M06-2X methods, an electric field in the range of 0.0010–0.004 a.u was applied in the X, Y, and Z directions, and the charge amplitude was set to 0.00025–0.0005 a.u (Table 4). The first hyperpolarizability, $\beta_0$, of each molecule under different applied electric fields was calculated, and the results were compared with the calculated total effective $\beta_0$ value of the first hyperpolarisability (or the static first hyperpolarisability $\beta_0$) in the absence of applied electric fields. The closest electric field value between the two groups was the optimal value of the applied electric field. The non-zero components and average values of the third-order polarisability of each triarylamine molecule calculated under applied electric fields are shown in Table 4. It is evident that the third-order polarisability of the non-zero component $\gamma_{xxxx}$ is the largest, followed by $\gamma_{yyyy}$ and $\gamma_{zzzz}$ (smallest). This indicates that the third-order nonlinear optical properties of the triarylamine derivative molecules were mainly derived from the charge transfer along the X axis, in addition to

| Comp. | $\gamma_{xxxx}$ | $\gamma_{xxy}$ | $\gamma_{xxz}$ | $\gamma_{yyy}$ | $\gamma_{yyz}$ | $\gamma_{zzz}$ | $\gamma$ |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|--------|
| a     | 19.75          | 3.37           | 0.37           | 7.25           | 0.25           | 1.01           | 6.90   |
| b     | 25.68          | 7.91           | 0.00           | 25.68          | -0.59          | 1.97           | 13.59  |
| c     | 37.53          | 13.83          | 5.93           | 33.58          | 5.93           | 5.93           | 25.67  |
| b1    | 72.49          | 10.27          | 0.00           | 31.21          | 0.00           | 0.59           | 24.97  |
| b2    | 78.13          | 11.88          | 0.63           | 29.38          | -1.25          | -0.63          | 25.88  |
| b3    | 86.88          | 11.25          | -0.63          | 28.75          | -1.25          | 1.25           | 27.13  |
| c1    | 80.00          | 20.00          | 0.00           | 30.00          | 0.00           | -19.99         | 26.00  |
| c2    | 69.12          | 16.62          | 0.49           | 35.19          | 0.13           | 0.49           | 27.94  |
| c3    | 49.99          | 10.00          | -10.00         | 59.99          | 9.99           | 10.00          | 28.00  |
the contribution from the charge transfer along the Y axis. Table 4 shows that the third-order polarisability of non-zero components \( \gamma_{xxx} \) and \( \gamma_{zzz} \) and the third-order polarizability \( \gamma \) of molecules \( a \), \( b \), and \( c \) increase in the order \( a < b < c \), indicating that the introduction of C=C bonds between biphensyl in molecule \( a \) significantly increased the third-order nonlinear optical properties of the molecules compared to the case when C=C bonds were introduced. For \( b \)- and \( c \)-series molecules, the third-order polarisability increased after the introduction of a benzene ring, furan ring, or thiophene ring between the triarylamine and cyanocinnamic acid group. The third-order polarisabilities of molecules \( b_2, b_3, c_2 \), and \( c_3 \) obtained by introducing a furan ring or thiophene ring were relatively large; especially, the third-order polarisabilities of molecules \( b_3 \) and \( c_3 \) obtained by introducing a thiophene ring were the largest (27.13 \( \times \) 10\(^3\) and 28.10 \( \times \) 10\(^5\) a.u., respectively). This shows that molecules with an A-\( \pi \)-D-\( \pi \)-A basic structural unit formed by introducing heteroatomic rings into triarylamine molecules can be used for designing efficient third-order nonlinear optical materials.

Conclusions

Nonlinear optical properties of nine triarylamine derivatives were computed using the hybrid M06-2X functional, long-range-corrected hybrid functional oB97X-D, and finite field method. The introduction of conjugated C=C or C≡C bonds on the parent molecule, \((E)\)-2-cyano-3-(4-(di[(1,1’-biphenyl)-4-yl]amino)phenyl)acrylic acid (a), has little effect on the second-order nonlinear optical properties of the molecules. However, the introduction of C=C bonds improves the third-order nonlinear-optical properties, while the introduction of a heterocyclic ring into the triarylamine system enhances the second-order and third-order nonlinear optical properties; particularly, the second-order and third-order polarisabilities of molecules \( b_3 \) and \( c_3 \) obtained by introducing a thiophene ring were the largest. Thus, molecules \( b_3 \) and \( c_3 \) have beneficial second- and third-order nonlinear optical properties and can be used as the basis for designing efficient second- and third-order nonlinear optical materials.

Conflict of interest

The authors declare no competing interests.

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Author contribution

Ziran Chen: methods, writing, and data analysis.
Yuhong Zhang: result analysis, manuscript first draft.
Yuan Li: simulations, analysis, manuscript editing.
Wenhao Yu: project management, manuscript editing.

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Data availability

Not applicable.

Code availability

Not applicable.

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