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Optical and electrical properties of thiarubrine A simulated via the Hückel method and the nonequilibrium Green's function

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Introduction: Thiarubrine A, a fascinating class of linear carbon chains, can be extracted from certain plants and are known for their photolabile pigment properties.

Methods: In this study, a modified Hückel method to investigate the optical properties of thiarubrine A has been employed, determining its absorption spectrum and wavelength-dependent complex refractive index. Additionally, using the nonequilibrium Green's function formalism, the conductance of a single thiarubrine A molecule has been derived.

Results and discussion: Light absorption, complex refractive index dispersion, and conductance of thiarubrine A have been simulated. Exploiting its photolability, a light-induced switch in single-molecule conductance has been demonstrated through ultraviolet-visible irradiation, which produces a photoproduct containing a thiophene group. These findings enhance our understanding of the optical properties of naturally occurring polyynes and highlight their potential applications in single-molecule junctions for nanoelectronics.

KEYWORDS

polyynes, single-molecule conductance, nonequilibrium Green's function, modified Huckel method, linear carbon chain

Introduction

Linear chains of carbon atoms can exist in two idealized isomeric forms: cumulenes, characterized by consecutive double bonds ($C=C=C$) (Fujiwara et al., 1991), and polyynes, which feature alternating single and triple bonds ($C-C\equiv C$) (Matsutani et al., 2009; Chalifoux and Tykwinski, 2010; Chalifoux et al., 2009). Polyynes are particularly intriguing due to their unique optical and electrical properties (Milani et al., 2009; Fazzi et al., 2013; Milani et al., 2017; Gao and Tykwinski, 2022; Marabotti et al., 2021). Many organisms can synthesize polyynes (Minto and Blacklock, 2008). Among these, thiarubrines stand out as a significant class, garnering attention for their distinctive reactivity, unique biological activity, and potential medicinal applications (Block et al., 1996; Wang et al., 1998). Thiarubrines are red, phototoxic polyynes found in the Asteraceae family (Balza and Towers, 1993), notable for their high instability in light (Page and Towers, 2002). The optical properties of these polyynes can be theoretically studied using various methods, such as the Hückel method. In Hückel theory, molecular orbitals are expressed as linear combinations of atomic orbitals (LCAOs). The key approximations in this theory include the following: i) the Born–Oppenheimer approximation, which assumes fixed

nuclei positions; and ii) the representation of molecular orbitals as linear combinations of p_z orbitals, neglecting electron–electron interactions (Guy and Troy, 2022). With the Hamiltonian built within the framework of the Hückel theory, it is possible to find the conductance of the single molecule *via* the use of nonequilibrium Green's function formalism.

In this study, a modified Hückel method, as detailed by Solomon et al. (2011), has been utilized to investigate the optical properties of thiarubrine A. Its absorption spectrum and wavelength-dependent complex refractive index have been determined. Additionally, using nonequilibrium Green's function formalism, the conductance of a single thiarubrine A molecule has been derived. Finally, by leveraging the photolability of thiarubrine A, which produces a thiophene-containing photoproduct upon ultraviolet-visible irradiation, a light-induced switch in the single molecule's conductance has been demonstrated.

Methods

Herein, a modified Hückel method, following has been Solomon et al. (2011), followed. Within this framework, the time-independent Schrödinger equation is given by the following Equation 1:

$$H|\psi\rangle = E|\psi\rangle. \quad (1)$$

Here, H represents the Hamiltonian, ψ represents the eigenfunction, and E represents the eigenvalue. Subsequently, eigenvalues and eigenfunctions have been determined. In order to find the transition probabilities, the Fermi golden rule has been used (Equation 2):

$$\Gamma_{i \rightarrow j} = \frac{2\pi}{\hbar} |\langle \psi^j | H | \psi^i \rangle|^2. \quad (2)$$

The transition probabilities have been estimated between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbitals. Gaussian peaks have been used for the simulation of the absorption spectra. Studying the transitions from the ground state i to the different j th excited states, the absorption coefficient can be written as in Equation 3:

$$\alpha(E) = \sum_j \Gamma_{i \rightarrow j} \exp\left(\frac{(E - (E_j - E_i))^2}{2c^2}\right), \quad (3)$$

with a linewidth c of the peaks of 0.2 eV. In order to extract from the absorption spectrum the imaginary part of the complex refractive index, the following expression (Equation 4) has been used, modifying the one reported in Kohandani and Saini (2022):

$$k(E) = \frac{A\alpha(E)}{4\pi}, \quad (4)$$

with the parameter A set to 1×10^{15} . The real part of the complex refractive index can be obtained *via* the Kramers–Kronig relations (Pankove, 1975) (Equation 5):

$$n(\bar{\nu}) - 1 = \frac{2}{\pi} \mathcal{P} \int_0^\infty \frac{\omega k(\omega)}{\omega^2 - \bar{\nu}^2} d\omega. \quad (5)$$

It is noteworthy that the Kramers–Kronig relations are Hilbert transforms (Ogilvie and Fee, 2013). In the case of the real part of the

refractive index, a constant offset of 1.5 has been applied, as in Scotognella (2020); Wiebeler et al. (2014).

The complex refractive index can be thus written as in Equation 6:

$$n(E) = n_{real}(E) + k(E). \quad (6)$$

For the calculation of the elastic transmission, nonequilibrium Green's function formalism has been employed, following Solomon et al. (2011). Assuming that only a single site of the molecule couples to each electrode, for thiarubrine A, the vector for the left electrode is (Equation 7):

$$V_L = [\gamma \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0]. \quad (7)$$

However, the vector for the right electrode is (Equation 8):

$$V_R = [0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ \gamma \ 0 \ 0]. \quad (8)$$

The value of γ is -1 eV, following Solomon et al. (2011). The broadening function is (Equation 9)

$$\Gamma^{L(R)} = 2\pi\rho V_{L(R)} V_{L(R)}^\dagger, \quad (9)$$

where ρ is the density of state of the electrode, set to $1/2\pi$ (eV)⁻¹ [following Solomon et al. (2011)]. With the broadening function, it is possible to determine the tunneling self-energy, which is purely imaginary (Equation 10):

$$\Sigma_T^{L(R)} = -\frac{i}{2}\Gamma^{L(R)}. \quad (10)$$

The energy-dependent retarded Green's function can thus be determined as in Equation 11:

$$G^r(E) = (E - H_{mol} - \Sigma_T^L - \Sigma_T^R)^{-1}. \quad (11)$$

The advanced Green's function $G^a(E)$ is the conjugated transpose of the retarded Green's function. With the broadening functions and Green's functions, it is possible to determine the energy-dependent elastic transmission (Equation 12):

$$T(E) = Tr[\Gamma^L G^r(E) \Gamma^R G^a(E)]. \quad (12)$$

The transmission is related to the conductance through the (Chang et al., 2014) (Equation 13):

$$G = G_0 T(E_F). \quad (13)$$

G_0 is the quantum of conductance (with value 7.748×10^{-5} S).

For density functional theory (DFT) calculations, the geometries of molecules have been optimized with the Avogadro package (Hanwell et al., 2012). The electronic transitions have been calculated by means of the density functional theory, with the ORCA package, developed by Frank Neese and coworkers (Neese, 2012). In these calculations, the B3LYP functional has been employed (Lee et al., 1988). Moreover, the Ahlrichs split valence basis set (Schäfer et al., 1992), together with the all-electron nonrelativistic basis set SVPalls1 (Eichkorn et al., 1997; Schäfer et al., 1994), the Libint library (E.-F.-Valeev, 2014), and the Libxc library (Lehtola et al., 2018; Marques et al., 2012), has been employed. For the modified neglect of diatomic overlap method (MNDO) calculations (Dewar and Thiel, 1977), the ORCA package has been employed.

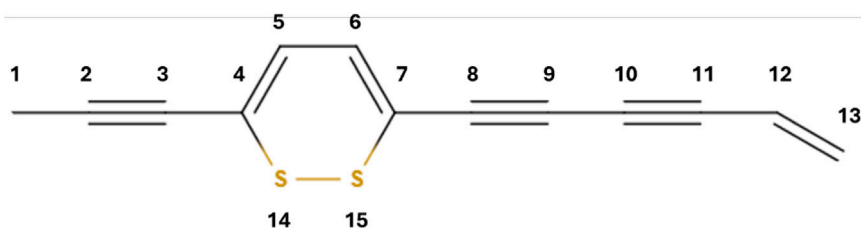


FIGURE 1
Chemical structure of thiarubrine A. The numbering of the atomic site corresponds to the index in the Hamiltonian.

TABLE 1 Parameters used in the Hamiltonian used in the time-independent Schrödinger equation (Equation 1) for thiarubrine A.

Parameter	Value (eV)
A	0
B	-3
bD	-4.2
bT	-5.8
aS	-3.33
bB	-1.89
bS	-2.07

Results and discussion

In Figure 1, the chemical formula of thiarubrine A has been drawn. In order to construct the Hamiltonian in the framework of the Hückel method, numbering of the molecule atomic site has been adopted, as depicted in Figure 1.

Thus, the Hamiltonian for thiarubrine A has been built in the following way (Equation 14):

$$H = \begin{bmatrix} a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ b & a & bT & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & bT & a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & b & a & bD & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bS & 0 \\ 0 & 0 & 0 & bD & a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & b & a & bD & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & bD & a & b & 0 & 0 & 0 & 0 & 0 & 0 & bS \\ 0 & 0 & 0 & 0 & 0 & 0 & b & a & bT & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & bT & a & b & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & a & bT & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bT & a & b & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & a & bD & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bD & a & 0 & 0 \\ 0 & 0 & 0 & bS & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & aS & bB \\ 0 & 0 & 0 & 0 & 0 & 0 & bS & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bB & aS \end{bmatrix} \quad (14)$$

In the Hamiltonian, a is the on-site energy for carbon atoms, b is the carbon-carbon single-bond coupling element, bD is the carbon-carbon double-bond coupling element, bT is the carbon-carbon single-bond coupling element, aS is the on-site energy for sulfur atoms, bB is the sulfur-sulfur single-bond coupling element, and bS is the carbon-sulfur single-bond coupling element. Taking into account the experimental absorption

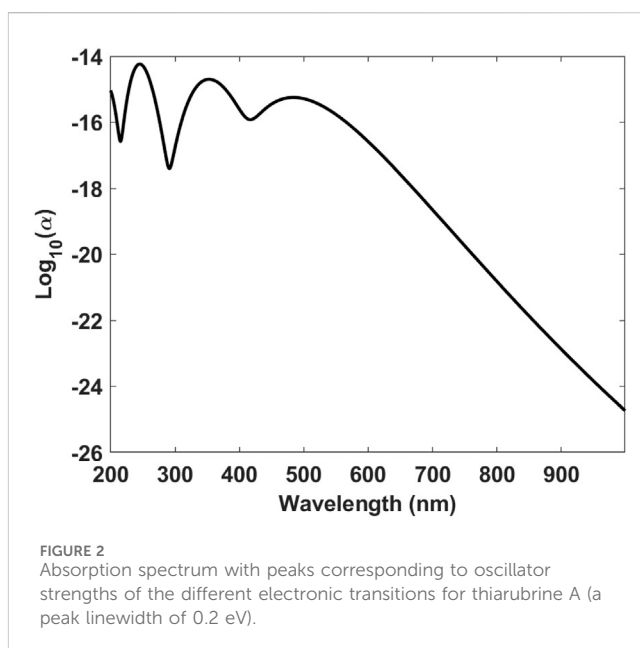
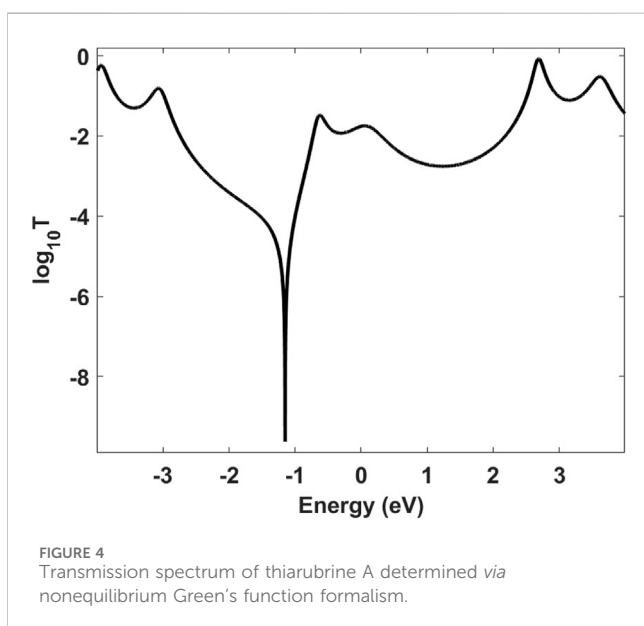
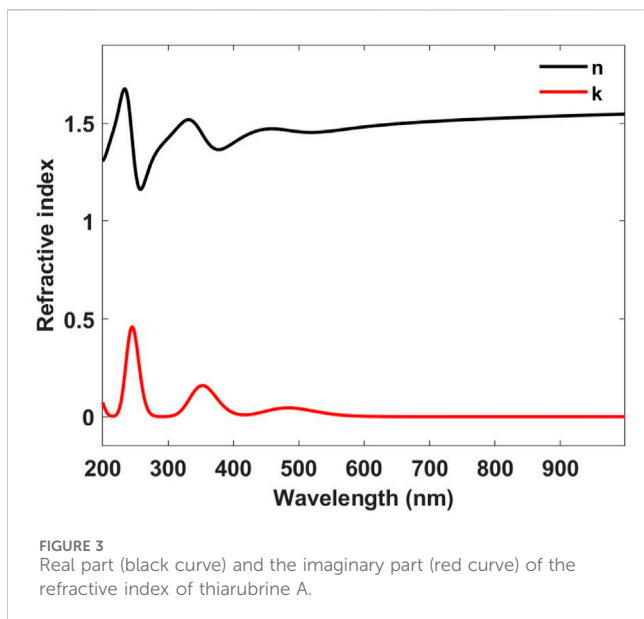


FIGURE 2
Absorption spectrum with peaks corresponding to oscillator strengths of the different electronic transitions for thiarubrine A (a peak linewidth of 0.2 eV).

spectrum of thiarubrine A (Page and Towers, 2002; Reyes et al., 2001), with characteristic peaks at 345 nm and 490 nm, a fair agreement is found with the parameters reported in Table 1.

The simulated absorption spectrum is depicted in Figure 2. The peaks correspond to oscillator strengths of the different electronic transitions, as described in Equation 3. In Supplementary Appendix Figure A1 in the Appendix, the absorption spectrum of thiarubrine A, calculated with the modified Hückel method, with DFT, and the MNDO method, is reported. A fair agreement between the modified Hückel method and DFT is found, with the lowest transition at 484 nm using the modified Hückel method and at 517 nm using the DFT, respectively. The lowest transition using the MNDO method is at longer wavelengths, i.e., 627 nm, but shows a small oscillator strength, while the second lowest transition, with a higher oscillator strength, is at 433 nm. The first 12 transitions used for the absorption spectrum are reported in Supplementary Appendix Table SA1, while the employed optimized geometry of thiarubrine A is reported in Supplementary Appendix Table SA3.

By using Equations 4, 5, it is possible to determine the wavelength-dependent complex refractive index of thiarubrine A, starting from the calculated absorption spectrum. The real part (black curve) and the imaginary part (red curve) of the refractive index are depicted in Figure 3.



By employing the nonequilibrium Green's function formalism, it is possible to determine the elastic transmission of thiarubrine A (Equation 12), depicted in Figure 4.

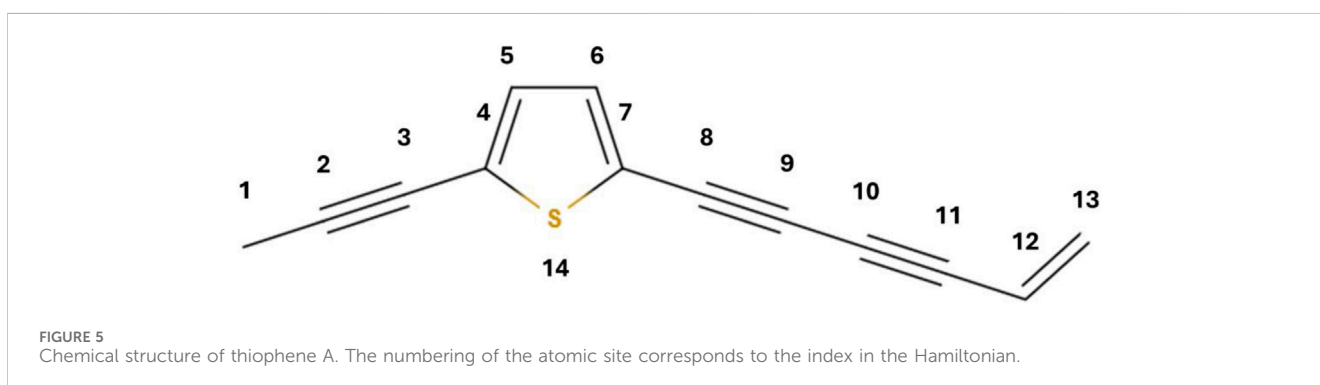
Setting the Fermi energy at 0 eV, the conductance of the molecule is 1.35 μS (Equation 13). Upon light irradiation, thiarubrine A is converted to a photoproduct thiophene A, depicted in Figure 5 (Page and Towers, 2002).

The Hamiltonian H' related to the photoproduct thiophene A can be written in the following way (Equation 15):

$$H' = \begin{bmatrix} a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ b & a & bT & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & bT & a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & b & a & bD & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bS \\ 0 & 0 & 0 & bD & a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & b & a & bD & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & bD & a & b & 0 & 0 & 0 & 0 & 0 & bS \\ 0 & 0 & 0 & 0 & 0 & 0 & b & a & bT & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & bT & a & b & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & a & bT & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bT & a & b & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & a & bD & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & bD & a & 0 \\ 0 & 0 & 0 & bS & 0 & 0 & bS & 0 & 0 & 0 & 0 & 0 & 0 & aS \end{bmatrix}. \quad (15)$$

The values of the parameters used in the Hamiltonian H' for thiophene A are the same ones of the Hamiltonian H for thiarubrine A. In Supplementary Appendix Figure A2 in the Appendix, the calculated absorption spectrum, calculated with the modified Hückel method, DFT, and the MNDO method, of thiophene A, is reported. The DFT lowest transition is at 319 nm, significantly higher with respect to that calculated with the MNDO method (i.e., 394 nm) and modified Hückel method (i.e., 437 nm). There are reports of incorrect results with DFT for thiophene (Prlj et al., 2015). For this, a comparison of absorption spectra calculated by different methods has proved necessary. The first 12 transitions used for the absorption spectrum are reported in Supplementary Appendix Table SA2, while the employed optimized geometry of thiophene A is reported in Supplementary Appendix Table SA4.

For thiophene A, the conductance, calculated using Equation 13, is 0.56 μS . Thus, a light-induced variation in the electrical behavior can be achieved in the presented molecular system. The advantage of using the thiarubrine A molecule is twofold: (i) on one hand, polynes are considered good candidates for molecular wires as electronic



transport along the sp-carbon chain should be independent of rotation about the single bonds (Gao et al., 2025); (ii) thiarubrine A under the effect of light can be precisely converted to thiophene A with the resulting change in conductance. It is noteworthy that the conductance of thiarubrine A is more than double with respect to that of the thiophene-based molecule T1 reported in Chang et al. (2014). The conductance can also be studied by carefully analyzing orbitals for the different molecules. There are relevant reports of the prediction of charge transport parameters in organic semiconductors (Fazzi et al., 2011). In this work, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of thiarubrine A and thiophene A are reported. However, a careful study on the relationship between the orbitals of the two molecules and the properties related to charge transport in them is beyond the scope of this paper and could be the subject of future studies.

Conclusion

In this work, the optical and electric properties of the molecule thiarubrine A have been simulated by using a modified Hückel method [exhaustively described in Solomon et al. (2011)] and the nonequilibrium Green's function formalism. The strength of this simple model lies in the fact that by constructing a Hamiltonian, it is possible to simulate the optical and electronic properties of the investigated molecules. The simulated absorption spectrum has been determined, and by choosing the proper parameters in the Hamiltonian, good matching with the experimental data can be found. From the simulated absorption spectrum, it is possible to derive the wavelength-dependent complex refractive index. Moreover, with the employment of nonequilibrium Green's function formalism, the conductance of the single molecule has been found. Taking into account the photolability of thiarubrine A, *via* light irradiation, a change in conductance can be achieved. Such findings can be interesting for the understanding of the optical properties of polyynes occurring in nature and for their exploitation in nanoelectronics.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

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FS: conceptualization, methodology, writing—original draft, and writing—review and editing.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fphot.2025.1535015/full#supplementary-material>

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