Substituent effects on the UV–visible spectrum and excited electronic states of dithiocarboxylates

Abraham K. Newman¹ · Ava M. Henry¹ · Jose P. Madriaga^{1,2} · J. Michael Sieffert^{1,3} · Shannon E. Heinrich^{1,4} · Juliana T. Jarboe¹ · Vincent M. Swift¹ · Alicia Y. Y. Cheong¹ · M. Taylor Haynes¹ · David F. Zigler¹

Received: 2 September 2021 / Accepted: 17 November 2021 / Published online: 23 February 2022

© The Author(s), under exclusive licence to European Photochemistry Association, European Society for Photobiology 2022

Abstract

The absorption spectra of a series of dithiocarboxylates were investigated in the ultraviolet–visible region. Two questions that this study aimed to address were as follows: (1) What transitions give rise to the features in the electronic spectra? And (2) what are the long- and short-range substituent effects on the absorption spectra? A series of 11 dithiocarboxylates were prepared as organic soluble salts. Time-dependent density functional theory (TDDFT) was used to calculate excited state energies and oscillator strengths of electronic transitions. TDDFT at the CAM-B3LYP/def2-TZVPD level of theory predicts two low-energy $n \rightarrow \pi^*$ transitions and two $\pi \rightarrow \pi^*$ transitions at higher energy, consistent with the experimental spectra. This state ordering and density is in contrast to the better studied thiocarbonyls for which only two transitions within the singlet manifold appear in the UV–visible region. For derivatives of dithiobenzoate, the energy of the three lowest energy states are insensitive to changes to substituents *para* to the dithiocarboxylate group. In contrast, the energy of the highest $\pi\pi^*$ state varies by 0.78 eV. This work shows that the results of TDDFT calculations can be used to predict the electronic absorption spectra of dithiocarboxylates, providing a useful tool for designing dithiocarboxylate light absorbers.

Graphical abstract

Keywords UV–visible · Dithiocarboxylates · Sulfur · TDDFT · Substituent Effects

✉ M. Taylor Haynes
mthaynes@calpoly.edu

✉ David F. Zigler
dzigler@calpoly.edu

¹ Department of Chemistry and Biochemistry, California Polytechnic State University, 1 Grand Ave., San Luis Obispo, CA 93405, USA

² Present Address: Department of Chemistry, Virginia Tech, Blacksburg, VA 24060, USA

³ Present Address: Department of Chemistry, McGill University, Montreal, QC H3A0G4, Canada

⁴ Present Address: Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

1 Introduction

Sulfur-containing chromophores tend to absorb light at lower energies than oxygen-containing analogs. Among these, thiocarbonyls such as thiones ($R_2C=S$), thioaldehydes ($RCHS$), and dithiocarboxy esters ($RCSSR'$) are studied for their ability to fluoresce from the second singlet excited electronic state (S_2 , a $^1\pi\pi^*$ state) in violation of Kasha's rule [1–7]. This unusual behavior for thiocarbonyl dyes is attributed to a 2 to 3 eV energy gap between S_2 and the lower energy $^1n\pi^*$ state, S_1 , that slows internal conversion [8–10]. The $S_0 \rightarrow S_2$ transition is symmetry allowed, thus results in an intense absorption band in the UV-region of the spectrum. Excitation into the weaker $S_0 \rightarrow S_1$ transition in the visible region is quickly followed by intersystem crossing to populate the lowest triplet state, $^3n\pi^*$ or T_1 . While thiones are photostable in inert media, both the S_2 and T_1 states are reactive with each giving a unique set of photoproducts [6, 11].

Dithiocarboxylates are chromophores often included as a subset of the better-known thiocarbonyls, but for which exist few dedicated examinations. Previous investigations of dithiocarboxylates have focused on metal coordination, electrochemistry, structure, and nucleophilicity [12–20]. Like thiocarbonyls, the dithiocarboxylates absorb strongly in the UV region and have weaker absorptions in the visible region of the spectrum. And as with thiocarbonyls, the UV bands are assigned to $\pi \rightarrow \pi^*$ transitions, while the visible region contains bands linked to $n \rightarrow \pi^*$ transitions [14, 21]. Although there are many reports on dithiocarboxylate esters [22], transition metal complexes [13, 23, 24], *N*-heterocyclic carbene adducts with carbon disulfide [25–27], and the conjugate thiocarboxylic acids [12, 21], few have examined the electronic absorption spectra of the base in isolation.

Modeling electronic spectra employs computations of the excited electronic states. As a class of compound, dithiocarboxylates have a single report attempting to model the spectra using the Pariser–Pople–Parr method with a *p*-orbital basis, which matched reasonably with the UV region of the spectrum [14]. More modern methods may better model the entire spectrum and illuminate low-lying states that are otherwise obscured by overlapping absorptions. Time-dependent density functional theory (TDDFT) strikes a good balance of accuracy and computational cost for developing a model of electronic absorption. For thiocarbonyls in particular, a simple correction applied to the TDDFT results allows for the prediction of the $\lambda_{\max}$ for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions for a range of dyes [5, 28–30]. Methods using range-separated functionals such as the well-known CAM-B3LYP [28, 29, 31] have a large absolute error (0.2–0.5 eV), but the errors are systematic

Fig. 1 The singlet manifold of dithiocarboxylates (right) has a higher density of states than the corresponding thiocarbonyl analogs. The term symbols are derived from C_{2v} point group symmetry

and once accounted for using an empirical correction factor allow for the accurate description of observed electronic transitions of thiocarbonyls.

In this work we aim to describe the electronic absorption spectra of dithiocarboxylates and the transitions that give rise to these spectra. A series of aryl- and α -carbonyl-dithiocarboxylates was synthesized and absorption spectra measured in the UV–Vis region. We show that TDDFT can be used to both assign the spectrum to specific transitions and predict the spectroscopic features for both series of dithiocarboxylates. We confirm a higher density of singlet states for dithiocarboxylates compared to analogous thiones. Additional low energy $n\pi^*$ and $\pi\pi^*$ states are a direct result of the change in symmetry and additional high energy electrons introduced by the anionic sulfur on the dithiocarboxylate group, Fig. 1. Transitions to these states are directly observed in the experimental electronic absorption spectra. These results provide the framework for a strategy to tune the UV–visible spectrum of dithiocarboxylate-containing compounds.

2 Materials and methods

2.1 Materials

All reagent grade materials and solvents were purchased from Sigma-Aldrich, Acros Organics, or Oakwood Chemical and used as received. Solvents used for UV–Vis spectroscopy were HPLC-grade or spectrophotometric grade and used without further purification.

2.2 Synthetic methodology

General synthetic procedures are presented in this section, Scheme 1. Detailed procedures and characterization data for each compound can be found in Section S1 in the Supporting

A) Synthesis of α -carbonyldithiocarboxylates

B) Synthesis of aryl-dithiocarboxylates

Scheme 1 Synthesis of the dithiocarboxylates used in this study

Information. Individual IR, ^1H -NMR, and UV–visible spectra for each are available in an Appendices A1–A3 at the end of the Supporting Information.

2.3 General synthetic procedure A—preparation of α -functionalized dithiocarboxylates

The synthesis of α -functionalized dithiocarboxylates was adapted from the method of Strauch et al. [32] with modifications by Zigler et al. [33]. Briefly, sulfur (60.0 mmol) and triethylamine (12.5 mL, 90.0 mmol) were stirred in 30 mL of deaerated DMF. The primary alkyl-halide (RCH_2Cl , 30 mmol) was added dropwise slowly and let stir for 2 h while maintaining the temperature below 30°C with a water bath. Solid triethylammonium chloride was removed by vacuum filtration and benzyltriphenylphosphonium chloride (30 mmol in methanol) was added to the filtrate. Deionized water (80 mL) added dropwise to the mixture caused the phosphonium salt to precipitate. After vacuum filtration, the crude solid was triturated with diethyl ether, and then the crude salt was recrystallized from dichloromethane/isopropanol. The isolated crystals were dried in a desiccator under vacuum (45–85% yield). Compounds synthesized by this method were benzyltriphenylphosphonium salts of 1,1-dithiopyruvate (**dtpyr**), *O*-methyl-1,1-dithiooxalate (**dtmo**), *O*-*tert*-butyl-1,1-dithiooxalate (**dtbto**), and cyanodithioformate (**dtcf**).

2.4 General procedure B—preparation of aryl-dithiocarboxylates

Aryl-dithiocarboxylates were synthesized using methods adapted from Houben and Pohl [34–36] with modifications employed by Bonnans-Plaisance [20]. Magnesium ribbon (30 mmol) activated by trace iodine vapor and/or 1,2-dibromoethane (0.1 mL), was suspended in 20 mL of deaerated, dry THF. The aryl halide (30 mmol) was slowly added dropwise maintaining the temperature of the reaction near 60 – 70°C . The reaction was heated to reflux for 35 min,

cooled to 0°C , and carbon disulfide (60 mmol) was added dropwise with careful monitoring of the reaction temperature. The reaction was quenched after 1–2 h with 5 mL of deionized water, filtered if necessary to removed insoluble magnesium salts, and then acidified with 40 mL of 1.0 M hydrochloric acid. The aqueous layer was washed twice with 20 mL of ether and the combined organic layers containing the dithioacid were neutralized with 0.75 M potassium hydroxide. The aqueous layer containing the potassium aryl-dithiocarboxylate salt was washed with diethyl ether and added to an aqueous solution of NBu_4Br (30 mmol, 0.6 M) to precipitate the tetra-*n*-butylammonium dithiocarboxylate salt. The solid was collected by vacuum filtration, rinsed, and dried under vacuum (13–90% yield). Compounds synthesized by this method were tetrabutylammonium salts of *para*-methoxydithiobenzoate (**dtbOMe**), *para*-methylthiobenzoate (**dtbMe**), *para*-fluorodithiobenzoate (**dtbF**), *para*-(trifluoromethyl)dithiobenzoate (**dtbCF₃**), dithiobenzoate (**dtb**), naphtho-1-ate (**dt1n**), and naphtho-2-ate (**dt2n**).

2.5 NMR spectroscopy

Nuclear magnetic resonance spectra were acquired on Bruker instruments (300 or 400 MHz for ^1H -NMR and 75 or 100 MHz for ^{13}C -NMR). All samples prepared by dissolving the solid salt in CDCl_3 or $\text{DMSO-}d_6$. The chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane and referenced to the residual ^1H resonance of the deuterated solvent.

2.6 IR spectroscopy

Infrared spectra of neat compounds were collected using attenuated total reflectance-Fourier transform infrared spectrometry (ATR-FTIR) using a Perkin-Elmer Spectrum 100 spectrometer.

2.7 UV–Vis spectroscopy

UV–Vis spectra were collected using an Agilent Technologies Cary 60 spectrophotometer. Samples were prepared using standard volumetric solution methods. Tetra-*n*-butylammonium salts were measured in absolute ethanol. Benzyltriphenylphosphonium salts were measured in methanol. Complete sets of spectra are available in the supporting information (Figs. S1–S3, SI Appendix).

2.8 Computational methodology

The electronic structure for the series of dithiocarboxylates and reference compounds was modeled using density functional theory (DFT) for ground state calculations and using time-dependent DFT (TDDFT) for calculating excited

states. All calculations were performed without symmetry restrictions using the GAMESS 2016 computational package [37, 38]. Fine Lebedev grids were used (radial points/angular points) for DFT (99/590) and TDDFT (93/302). Basis sets were those published on the Basis Set Exchange [39]. Ground state structures were optimized using spin-restricted PBE0 [40] including Grimme's D3BJ dispersion correction [41], the Karlsruhe split valence polarization basis sets with added diffuse functions, def2-SVPD [42], and an implicit solvent model (SMD) to account for solvent effects [43] (PBE0/def2-SVPD/SMD(solvent)). The solvent models used for this study were methanol, ethanol, and water. All optimized structures were confirmed as minima by the absence of imaginary frequencies in vibrational analysis (coordinates are in Appendix A4 in the SI). Excited states were calculated by starting with the optimized geometries and using TDDFT under the Tamm-Dancoff approximation at the CAM-B3LYP/def2-TZVPD/PCM(solvent) level of theory [30, 31]. The conductor-like polarizable continuum model (PCM) was used to account for solvent effects on the energies of vertical transitions [44]. Natural transition orbitals (NTOs) construction and electron-hole population analysis were from the TDDFT eigenvectors using TheoDORE [45–47]. NTOs and tabulated results from TDDFT are in the Supporting Information (Figs. S4–S17, Tables S1–S14). Structures with canonical Kohn–Sham orbitals were plotted in wxMacMolPlt [48] and natural transition orbitals were plotted with Jmol [49]. Orbitals are plotted with an isosurface value of 0.05 unless otherwise stated.

2.9 Simulating spectra

Spectra were simulated from computed transition energies and oscillator strengths using a previously reported method [50] that relies on a classical oscillator model and Gaussian broadening to approximate the experimental spectra. Briefly, the Gaussian function was centered at the calculated transition energy for each state, $\tilde{\nu}_{0,i}$ and scaled by the calculated oscillator strength, f_i (Eq. 1):

$$\epsilon(\tilde{\nu}) = \sum_i \sqrt{\frac{\ln 16}{\pi}} \cdot \frac{f_i \cdot B}{\text{FWHM}} \cdot 2^{-4 \left(\frac{\tilde{\nu} - \tilde{\nu}_{0,i}}{\text{FWHM}} \right)^2} \quad (1)$$

The coefficient B is derived from the relationship between oscillator strength and molar absorptivity [1, 51]:

$$B = \frac{N_A e^2}{\epsilon_0 m_e c^2}, \quad (2)$$

where ϵ_0 is the permittivity of free space, m_e is the rest mass of an electron, c is the speed of light, N_A is Avogadro's constant, and e is the elementary charge, such that B equals $2.318 \times 10^8 \text{ M}^{-1} \text{ cm}^{-2}$. A broadening was applied to the

simulated spectrum based on the full-width half-maximum (FWHM) of bands in the experimental spectra. For **dtpyr**, **dtmo**, **dtbbo**, **dtcf**, and **dt1n** a FWHM of 3800 cm^{-1} was used and a FWHM of 6000 cm^{-1} was chosen for the spectra of the aryl series, **dtbR** and **dt2n**. Plots comparing all of the experimental and simulated spectra are available in the Supporting Information (Figs. S1–S3). The simulated spectra were calculated without applying a correction. A complete list of states energies and oscillator strengths used to simulate the spectra is presented in the Supporting Information (Tables S1–S14).

3 Results and discussion

The work presented in this section uses a combination of experimental methods and computational chemistry to model the electronic absorption spectra of dithiocarboxylates. After introducing the organic soluble dithiocarboxylates made and used in this study (Sect. 3.1), we present a comparison between the results of density functional theory (DFT) calculations and experimental structures in support of our theoretical approach (Sect. 3.2). Next we show how substituent effects manifest in the electronic absorption spectra (Sect. 3.3) and use time-dependent density functional theory (TDDFT) to predict which electronic states are involved in the UV–visible region (Sect. 3.4). The TDDFT results are used to simulate the UV–visible spectra for the series of dithiocarboxylates (Sect. 3.5), which allows us to assign the bands in the experimental spectra to specific electronic transitions (Sect. 3.6). In the final section we address the limitations of the approach and model (Sect. 3.7).

3.1 Making a series of dithiocarboxylates

A series of dithiocarboxylate salts was synthesized and isolated as organic soluble salts with tetra-*n*-butylammonium or benzyltriphenylphosphonium, Fig. 2. A detailed synthetic method for each is presented in the Supporting Information alongside the spectra for all the compounds synthesized. The compounds were stable at room temperature for at least 1 year, with exception of [PBnPh₃][**dtpyr**], which was stored over anhydrous calcium sulfate in an air tight jar at 5 °C to slow decomposition. The solid salts range in color from yellow, brown, green, and red. Benzyltriphenylphosphonium salts of α -carbonyldithiocarboxylates, [PBnPh₃][**dtXX**], are moderately soluble in methanol and soluble in dichloromethane. The dithiocarboxylate salts forming a stable solution in dichloromethane is surprising as dichloromethane is known to react with NMe₄⁺ salts of dithiocarboxylates [52], forming the methylene-bis(dithioester). We have observed this reaction at elevated temperatures for [PBnPh₃][**dtbOMe**]. We suspect that cation-anion association in DCM solution

contributes to this effect and the aryl pocket around PBNPh_3^+ protects the nucleophilic dithiocarboxylate functional group from the solvent. Tetra-*n*-butylammonium salts of *para*-substituted aryl-dithiocarboxylates, $[\text{NBu}_4][\text{dtbR}]$, are soluble in most polar organic solvents (e.g. ethanol, acetonitrile, THF) and insoluble in nonpolar solvents (toluene, hexanes, diethyl ether).

3.2 Ground state DFT calculations

An electronic model for the dithiocarboxylates was constructed using Density Functional Theory (DFT). Geometries were calculated at the PBE0/def2-SVPD/SMD(solvent) level of theory (where the solvent was methanol or ethanol) and were compared to reported crystal structures, Table 1. Only small errors are observed for the carbon–sulfur bond distance ($\leq 0.021 \text{ \AA}$) and the sulfur–carbon–sulfur bond angle ($\leq 2.2^\circ$). The C–C distance for **dtb** is calculated to be much longer than the experimental value, but it should be noted the experimental value has relatively large associate error ($\pm 0.05 \text{ \AA}$) [53]. As others have noted the sulfur–carbon–sulfur bond angles ($\angle\text{SCS}$) are wider than the expected 120° for an sp^2 carbon, which suggests deviation of the carbon toward sp -hybridization. The torsion angle about the carbon–carbon bond connecting the substituent and dithiocarboxylate ($\angle\text{S}_2\text{C–R}$) has larger error for the aryl-dithiocarboxylates. The reported dihedral angles from crystal structures of dithiobenzoates are known to depend on the identity of the cation and crystallizing conditions [19]. The calculated dihedral angles for the **dtbR** series were consistently ca. 35° , while the dithiocarboxylates with α -COR

Table 1 Selected experimental and calculated^a structural properties^b for a subset of dithiocarboxylate anions

Compound		C–S (Å)	C–C (Å)	$\angle\text{SCS}$	$\angle\text{S}_2\text{C–R}^c$
dtb	exp. ^d	1.67	1.40	123°	–
	calc.	1.69	1.51	125°	–
dtcf	exp. ^e	1.68	1.45	129°	–
	calc.	1.67	1.44	131°	–
dtbbo	exp. ^f	1.66	1.53	129°	89.4°
	calc.	1.67	1.51	130°	88.0°
dtbOMe	exp. ^g	1.67	1.50	125°	71.6°
	calc.	1.69	1.49	125°	34.9°
dtbMe	exp. ^g	1.68	1.49	125°	43.3°
	calc.	1.69	1.50	125°	36.8°
dtb	exp. ^h	1.69	1.50	125°	39.4°
	calc.	1.69	1.49	125°	39.5°

^aAll calculated geometries were optimized at the PBE0/def2-SVPD/SMD(solvent) level of theory

^bAveraged bond distance and angles

^cTorsion angle formed between the dithiocarboxylate and planar substituent

^d $[\text{K}(\text{dtb})]$, Borel and Ledesert [53]

^e $[\text{NEt}_4][\text{dtcf}]$, Engler et al. [54]

^f $[\text{PBNPh}_3][\text{dtbbo}]$, Zigler et al. [31]

^g $[\text{NMe}_4][\text{dtbOMe}]$ and $[\text{NMe}_4][\text{dtbMe}]$, Kato et al. reported alkali salts with torsion angles varying from 33° to 50° [19]

^h $[\text{NBnMe}_3][\text{dtb}]$, Mahjoub [55]

group were perpendicular to the substituent. These dihedral angles may reflect the electron density distribution and whether electron density is delocalized between the dithiocarboxylate group and substituent.

Keeping with the focus of this investigation, the canonical frontier Kohn–Sham (KS) orbitals resulting from single-point energy calculations at the CAM-B3LYP/def2-TZVPD/PCM level were examined in the context of the molecular symmetry. Both the dithiocarboxylate functional group and thiocarbonyl group are well described using C_{2v} local symmetry, Fig. 3. Thus the symmetry of the frontier KS orbitals can be approximated using the C_{2v} irreducible representations (familiar orbital designations are in parentheses). A

Fig. 2 The dithiocarboxylate compounds used in this study fall into two principal categories: the α -functionalized dithiocarboxylates (**dtXX**, top row), and the aryl-dithiocarboxylates (**dtbR**, middle row)

Fig. 3 Simple thione (left) and dithiocarboxylate (right) compounds displaying the principal rotation axis with local C_{2v} symmetry

key difference between the often reported thiocarbonyl dyes and dithiocarboxylates is the location of the principal rotation axis relative to the C–S bond(s). To illustrate the effect of symmetry on the frontier KS orbitals, we compared two simple systems, thioacetone (**Me₂CS**) and dithioacetate (**dta**), Fig. 4. The ground state electron configuration of thioacetone is $a_1(n)^2b_1(\pi)^2b_2(n)^2b_1(\pi^*)^0$ for the frontier set of orbitals with most of the density localized to the thiocarbonyl functional group. Similarly, the highest energy orbitals of **dta** have electron density localized to the dithiocarboxylate functional group. The anion of **dta** contributes to higher energy orbitals than for **Me₂CS**. The additional sulfur 3*p*-orbitals mixing in **dta** causes the frontier occupied orbitals to split. Near the HOMO–LUMO gap the frontier electron

configuration is $a_1(n)^2b_2(n)^2b_1(\pi)^2a_1(n)^2a_2(\pi)^2b_2(n)^2b_1(\pi^*)^0$, Fig. 4. The higher density of energy levels leads to a higher density of electronic states for **dta** compared to **Me₂CS**. In particular, the energy range for the highest three occupied orbitals of **dta** is especially small (0.8 eV) relative to **Me₂CS** (3.6 eV).

Applied to more complicated dithiocarboxylates, the frontier orbitals mirror those of **dta** with energetic shifts associated with the substituents. All the dithiocarboxylates have closely spaced HOMO, H–1, and H–2 orbitals and are, respectively, $b_2(n)$, $a_2(\pi)$, and $a_1(n)$, Fig. 5. The energy range varies from less than 0.1 eV for **dtpyr** to 0.9 eV for the series of dithiobenzoates, **dtbR**. For all the compounds, the LUMO is a π^* orbital with b_1 symmetry and the calculated HOMO–LUMO gap is ca. 7 eV. The LUMO, HOMO, H–1, and H–2 are localized to the dithiocarboxylate functional group; thus, the orbital energies are sensitive to changes adjacent to the dithiocarboxylate carbon. For example, the LUMO of **dtcf** (R = CN) is stabilized by 1.2 eV compared to **dta** (R = CH₃).

Distal functional groups like the *para*-substituents in the **dtbR** series barely impact the frontier orbital energies. For **dtbR** series the HOMO, H–1, and H–2 are localized to the dithiocarboxylate. The LUMO is more delocalized, but most of the density is localized to the dithiocarboxylate and the identity of the substituent minimally influences the LUMO energy level. The next occupied orbital (H–3) has $b_1(\pi)$ symmetry and there is a large, but consistent difference in energy between the highest occupied $b_1(\pi)$ and $a_1(n)$ orbitals for **dta**, **dtpyr**, **dtmo**, **dtmo**, and **dtcf** (ca. 2 eV). This picture changes for the **dtbR** series, in that more of the $b_1(\pi)$ density is delocalized onto the aryl ring. Electrons in this $b_1(\pi)$ -orbital are sensitive to the distal substituent, such that with an electron rich methoxy group (i.e. **dtbOMe**) this orbital is higher energy than the electron-deficient substituted **dtbCF₃** by 1.1 eV. The varying sensitivity of the frontier electrons suggests that different regions of the electronic spectra might

Fig. 4 Frontier Kohn–Sham orbitals for thioacetone (left) and dithioacetate (right) calculated at the CAM-B3LYP/def2-TZVPD/PCM(water) level of theory. The irreducible representation assignments are based on C_{2v} point group symmetry

Fig. 5 The Kohn–Sham orbitals of each of the dithiocarboxylate compounds were calculated at the CAM-B3LYP/def2-TZVPD/PCM level of theory using a conductor-like polarizable continuum model

for solvent (water, methanol, or ethanol). Irreducible representations describe the orbitals based on the local symmetry of the dithiocarboxylate functional group (C_{2v})

Fig. 6 The density is plotted for the LUMO of dithionaphthoate with the dithiocarboxylate group at the 1- or 2-position. The Kohn–Sham orbitals are from DFT at the CAM-B3LYP/def2-TZVPD/PCM(ethanol) level and plotted with 0.04 isosurfaces

be independently tuned by choice of substituent identity and position.

The arene coupled to the dithiocarboxylate in the **dtbR** series leads to a high density of energy levels near the HOMO–LUMO gap. The dithionaphthoate derivatives **dt1n** and **dt2n** also have a high density of states, owing to the larger ring structure capable of better delocalizing electron density. The calculated geometry of **dt2n** reflects the stabilizing effect of conjugation between the ring and dithiocarboxylate group as was seen for the **dtbR** series (e.g. the dithiocarboxylate–ring dihedral angle is 48°). For **dt1n** a wide $\angle$ SCS-angle (127.6°) and proximity of the 8-hydrogen contributes to a perpendicular dihedral angle between the ring and dithiocarboxylate group (84.7°). From our DFT calculations, this steric constraint is correlated with the LUMO of **dt1n** being highly localized to the dithiocarboxylate, Fig. 6. The localized LUMO of **dt1n** is similar to the non-aryl dithiocarboxylates like **dtbbo**, which also have a severe dihedral angle.

3.3 Electronic spectra

A key aim of this work was to address how substitution, both proximal (α -position) and distal (*para*-R-phenyl), influences the spectra of dithiocarboxylates and how clues to these changes could inform us of the electronic transitions. Dithiocarboxylates generally have an intense feature (or features) in the ultraviolet region of the spectrum and a weaker absorption in the visible. The visible absorptions give the compounds their characteristic colors, ranging from yellow to red in solution. The absorption spectra for a number of the series have been reported, usually as alkali metal salts in aqueous or ethanolic solutions [12, 17, 21]. These prior reports serve as an important point of reference for confirming our spectroscopic observations. In this section we present the spectra for related sets of dithiocarboxylates and describe variations in the electronic spectra that result from differences in their molecular structure.

The spectra of non-aryl dithiocarboxylates are generally simpler than for those conjugated to an arene. A

Fig. 7 The electronic absorption spectra of benzyltriphenylphosphonium salts of **dtbbo** (dotted line), **dtpyr** (dashed line), and **dtcf** (solid line) in methanol with a 50-fold expansion of the low energy region of the spectra

representative set of spectra from dithiocarboxylates substituted with an α -carbonyl: 1,1-dithiopyruvate (**dtpyr**) and *O*-*tert*-butyl-1,1-dithiooxalate (**dtbbo**), or an α -cyano, cyano-dithioformate (**dtcf**) is shown in Fig. 7. We also examined the spectrum of *O*-methyl-1,1-dithiooxalate (**dtmo**) which is nearly identical to that of **dtbbo** (Fig. S1 in the supporting information). All the benzyltriphenylphosphonium salts have a structured band near 275 nm due to cation localized transitions. Weak absorptions near 450 nm and 400 nm ($\epsilon \approx 200 \text{ M}^{-1} \text{ cm}^{-1}$) are consistent with $n \rightarrow \pi^*$ transitions and appear as shoulders to a much stronger absorption in the UV region. Spectra for all the C=O containing compounds have a single strong absorption near 345 nm (FWHM $\approx 3000 \text{ cm}^{-1}$, $\epsilon \approx 13,000 \text{ M}^{-1} \text{ cm}^{-1}$). The $\pi \rightarrow \pi^*$ band is red-shifted to 380 nm for **dtcf**, likely due to the more electron-deficient cyano substituent. These stronger bands are assigned to $\pi \rightarrow \pi^*$ transitions. An absorbance at 299 nm in the spectrum of **dtpyr** is not observed for **dtmo** and **dtbbo** and may be due to a CO localized $\pi \rightarrow \pi^*$ transition that is blue shifted for the oxy-esters. Although red-shifted, the spectral features for **dtbbo**, **dtmo**, **dtpyr**, and **dtcf** are similar to the reported spectrum of dithioacetate (**dtta**) and consistent with transitions that are localized to the dithiocarboxy group [12, 17, 21].

The electronic absorption spectra for the series of *para*-substituted dithiobenzoates share spectral features with non-aryl compounds, Fig. 8. Compounds vary at the substitution of the *para* position of the aromatic substituent: dithiobenzoate (**dtb**); *para*-methylthiobenzoate (**dtbMe**); *para*-methoxydithiobenzoate (**dtbOMe**); *para*-fluorodithiobenzoate (**dtbF**); and *para*-(trifluoromethyl)dithiobenzoate (**dtbCF₃**). Spectra for the alkali salts of several dithiocarboxylates in water and ethanol were reported by Kato and co-workers and Furlani et al. [17, 21]. For members of our series that overlap with prior reports, the spectra we measured are essentially identical. All spectra from the

Fig. 8 The electronic absorption spectra of tetrabutylammonium salts of **dtbOMe** (dotted line), **dtb** (dashed line), and **dtbCF₃** (solid line) in ethanol with a 50-fold expansion of the low energy region of the spectra

dtbR series have a well-resolved, albeit weak, absorption near 500 nm ($\epsilon \approx 200 \text{ M}^{-1} \text{ cm}^{-1}$), and a strong signal ca. 360 nm ($\epsilon \approx 7000 \text{ M}^{-1} \text{ cm}^{-1}$), each of which is remarkably insensitive to the identity of the substituent. Contrary to the dithiooxalates, only a single absorption is seen in the visible region. A third UV absorption that is distinct to the spectra of the benzoate series is between 250 and 330 nm and is variable with substitution at the 4-position of the phenyl ring. There is a 0.78-eV red-shift in this band between the extremes of **dtbCF₃** (260 nm) and **dtbOMe** (321 nm). This shift is likely the result of the charge transfer nature of the transition, as originally proposed by Bossa and Furlani [13, 14]. All of the spectral bands have similar bandwidth (FWHM $\approx 5000 \text{ cm}^{-1}$), which is wider than the non-aryl compounds.

When the aryl-system is extended to naphthyl rings for dithionaphtho-1-ate (**dt1n**) and dithionaphtho-2-ate (**dt2n**), the position of the dithiocarboxyl group on the naphthyl ring has a profound impact on the absorption spectrum, Fig. 9. As with the dithiobenzoates, the spectrum of **dt2n** has a

Fig. 9 The electronic absorption spectra of tetrabutylammonium salts of **dt1n** (dashed line) and **dt2n** (solid line) in ethanol with a 50-fold expansion of the low energy region of the spectra

weak band at 511 nm ($\epsilon = 250 \text{ M}^{-1} \text{ cm}^{-1}$). The analogous band for **dt1n** is well-resolved, blue-shifted to 484 nm, and has half of the intensity of other aryl-dithiocarboxylates ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$). The spectrum of **dt2n** extends well into the UV-region, with a progression of bands at 356 nm ($\epsilon \approx 8,700 \text{ M}^{-1} \text{ cm}^{-1}$), 314 nm ($\epsilon \approx 14,300 \text{ M}^{-1} \text{ cm}^{-1}$), and 272 nm ($\epsilon \approx 28,700 \text{ M}^{-1} \text{ cm}^{-1}$). In contrast, the spectrum of **dt1n** has a narrow band at 349 nm ($\epsilon \approx 11,200 \text{ M}^{-1} \text{ cm}^{-1}$) and a high energy shoulder ca. 310 nm. The spectra of these isomers may differ due to structural constraints on **dt1n**. The optimized geometry by DFT shows that **dt1n** has a larger dihedral angle between the naphthyl and dithiocarboxylate groups, leading to more localized frontier orbitals. This localization in **dt1n** leads it to behave like the non-aryl dithiocarboxylates, Fig. 10. The $\pi \rightarrow \pi^*$ absorption bands of **dt1n** and **dt2n** overlap and have similar broadening, which suggests that the oscillator strength, vibronic coupling, and solvent stabilization between the ground state and resonant excited state are similar to each other. The spectrum of **dt2n** is more comparable to a typical aryl-dithiocarboxylate like **dtb**, showing broader absorption bands than spectra from the non-aryl set. A dihedral angle approaching 90° may result in the decoupling of the CS_2 -localized π -system from the naphthyl ring, leading the dithiocarboxylate and naphthyl chromophores to present independent spectroscopic signatures. A similar decoupling of conjugated naphthyl systems due to substitution at the internal position was shown in a series of anthracene-based chromophores [56].

Fig. 10 Spectra in ethanol of **A dt2n** (dashed line) overlaid with **dt1n** (solid line) and **B dtb** (dashed line) with **dt2n** (solid line)

3.4 TDDFT—excited state calculations

Time-dependent density functional theory calculations provide additional detail about the origin of the electron absorption spectrum. The calculations were performed at the CAM-B3LYP/def2-TZVPD level of theory using the Tamm-Dancoff approximation. The choice of functional and basis set was based on prior reports of this method delivering reasonable balance between accuracy and computational cost for a range of heteroatom-containing dyes [5, 28, 29].

For dithiocarboxylates the lowest energy states calculated by TDDFT are readily described using a simple hole–electron representation (e.g. $\pi\pi^*$) with term symbols derived from C_{2v} point group symmetry. Natural transition orbitals (NTO) illustrate the electron–hole density calculated for the excited state, Figs. 11 and 12. Additional NTOs, state energies, and assignments are available in the supporting information (Figs. S4–S17). After the ground state, the lowest singlet state results from the $b_2(n) \rightarrow b_1(\pi)$ excitation ($^1A_2(n\pi^*)$), followed the $^1B_1(n\pi^*)$ and $^1B_2(\pi\pi^*)$ states at higher energy. All three states have 80–95% of the excited electron–hole density localized to the dithiocarboxylate group in **dtb**, **dtpyr**, **dtmo**, and **dtbtho**. For the **dtbR** series, the $^1A_2(n\pi^*)$, $^1B_1(n\pi^*)$, and $^1B_2(\pi\pi^*)$ states all have the excited hole localized to the dithiocarboxylate group (80–95%), but the excited electron has density on the ring as well (20–50%), consistent with participation of the more delocalized LUMO. Among members of the **dtbR** series the next low-lying $\pi\pi^*$ state, $^1A_1(\pi\pi^*)$, has 60–70% of the hole density on the ring, consistent with the aryl-to-dithiocarboxylate charge transfer nature of this state.

As with the electronic spectra, the energies of the excited electronic states depend on the substituents. The $^1A_2(n\pi^*)$ state corresponds to the HOMO $\rightarrow$ LUMO transition from the ground state, and is shifted to lower energy with a proximal electron-deficient substituent or more delocalized

Fig. 11 The natural transition orbitals for the three lowest singlet excited states of **dtmo** showing (left to right) hole- and electron density localized to the dithiocarboxylate functional group. Terms are from C_{2v} symmetry. NTOs are plotted with a 0.035 isosurface

Fig. 12 The natural transition orbitals for the four lowest singlet excited states of **dtb** showing electron- and hole-density localized to the dithiocarboxylate functional group for S_1 – S_3 and the charge transfer state (S_4). Terms are from C_{2v} symmetry. NTOs are plotted with a 0.035 isosurface

LUMO (e.g. **dtbR** series), Fig. 13. A $^1A_2(n\pi^*)$ state is also the lowest state for thiocarbonyls like **Me₂CS**, Table 2 [6, 11]. In contrast to thiocarbonyl compounds, the next two states by TDDFT are $^1B_1(n\pi^*)$ and $^1B_2(\pi\pi^*)$, and they are close in energy. The relative energy of the first three states depends on the proximal substituent, consistent with these states involving orbitals that were sensitive to proximal substitution at the *para*-position is reflected in the relative energy for $^1A_2(n\pi^*)$, $^1B_1(n\pi^*)$, and $^1B_2(\pi\pi^*)$ states between members of the **dtbR** series. Similar behavior is reported for the $^1A_1(\text{GS}) \rightarrow ^1B_2(n\pi^*)$ transition of aryl-thiones and attributed to a C = S localized state [8–10]. A fourth allowed state common to the **dtbR** series, $^1A_1(\pi\pi^*)$, increases in energy

Fig. 13 The Jablonski diagram compares the lowest singlet states from TDDFT calculations (lines) to the energies of vertical transitions estimated from the electronic absorption spectra (open points). TDDFT calculations were at the CAM-B3LYP/def2-TZVPD/PCM level of theory. The state labels correspond to irreducible representations from the C_{2v} point group. The circles ($\circ$, $n\pi^*$) and squares ($\square$, $\pi\pi^*$) are the experimental values from this work or the literature (**Me₂CS** Fabian and Mehlhorn [57], Paone et al. [58]; **dtb** Furlani et al. [21])

Table 2 Energies and oscillator strengths (*f*) of selected electronic states of dithiocarboxylates calculated using TDDFT^a

Compound ^b	Solvent ^c	¹ A ₂ (<i>n</i> π*)		¹ B ₁ (<i>n</i> π*)		¹ B ₂ (ππ*)		¹ A ₁ (ππ*)	
		<i>E</i> (eV)	<i>f</i>	<i>E</i> (eV)	<i>f</i>	<i>E</i> (eV)	<i>f</i>	<i>E</i> (eV)	<i>f</i>
Me₂CS	water	2.75	0.000	–	–	–	–	5.79	0.444
dta	water	2.73	6.00 × 10 ^{−6}	3.45	5.33 × 10 ^{−4}	4.07	0.391	–	–
dtpyr	MeOH	2.97	1.30 × 10 ^{−4}	3.13	4.98 × 10 ^{−4}	3.99	0.142	–	–
dtmo	MeOH	2.85	2.70 × 10 ^{−5}	3.16	8.13 × 10 ^{−4}	4.10	0.365	–	–
dtbbo	MeOH	2.83	4.00 × 10 ^{−6}	3.16	7.52 × 10 ^{−4}	4.05	0.373	–	–
dtcf	MeOH	2.31	0.000	2.84	1.50 × 10 ^{−3}	3.78	0.381	5.62	3.40 × 10 ^{−3}
dtbOMe	EtOH	2.47	6.83 × 10 ^{−3}	3.29	1.43 × 10 ^{−3}	3.82	0.297	4.34	0.477
dtbMe	EtOH	2.46	5.52 × 10 ^{−3}	3.26	1.10 × 10 ^{−3}	3.81	0.299	4.56	0.432
dtb	EtOH	2.46	4.81 × 10 ^{−3}	3.25	1.05 × 10 ^{−3}	3.82	0.304	4.76	0.351
dtbF	EtOH	2.45	4.30 × 10 ^{−3}	3.26	1.27 × 10 ^{−3}	3.82	0.301	4.71	0.349
dtbCF₃	EtOH	2.49	6.57 × 10 ^{−3}	3.22	9.03 × 10 ^{−4}	3.82	0.304	4.76	0.351
dt1n	EtOH	2.66	4.26 × 10 ^{−4}	3.30	1.53 × 10 ^{−3}	4.00	0.300	–	–
dt2n	EtOH	2.51	1.11 × 10 ^{−2}	3.25	5.95 × 10 ^{−4}	3.86	0.291	–	–

^aA complete list of calculated states used to simulate spectra is available in the Tables S1–S14 in the Supporting Information

^bThe abbreviations refer to compounds calculated as the free ion (or neutral) and are as follows: **Me₂CS**=thioacetone; **dta**=dithioacetate; **dtpyr**=1,1-dithiopyruvate; **dtmo**=*O*-methyl-1,1-dithiooxalate; **dtbbo**=*O*-*tert*-butyl-1,1-dithiooxalate; **dtcf**=cyanodithioformate; **dtbOMe**=*para*-methoxydithiobenzoate; **dtbMe**=*para*-methylthiobenzoate; **dtb**=dithiobenzoate; **dtbF**=*para*-fluorodithiobenzoate; **dtbCF₃**=*para*-(trifluoromethyl)dithiobenzoate; **dt1n**=dithionaphtho-1-ate; **dt2n**=dithionaphtho-2-ate

^cImplicit polarizable continuum model (PCM) was used to approximate solvent effects

with an electron-deficient *para*-substituent. This is because the donor orbital for this state, *b*₁(π), has higher density on the aryl ring, Fig. 12. The strong aryl-to-dithiocarboxylate charge-transfer character for the ¹A₁(GS) → ¹A₁(ππ*) transition causes a blue-shift as more electron-deficient substituents stabilize electrons on the aryl-group. Finally, both **dtcf** and the benchmark compound **Me₂CS** have closely spaced Rydberg and ¹A₁(ππ*) states calculated within the first 6 eV. The 3.1 eV energy difference between the calculated ¹A₂(*n*π*) and ¹A₁(ππ*) states of **Me₂CS** matches the experimental *S*₁/*S*₂ energy gap (3.3 eV) [57, 58]. This large energy gap is well known for thiocarbonyls and dithioesters, and is responsible for the Kasha's rule-breaking fluorescence that make them especially interesting (*S*₂(ππ*) → *S*₀(GS)) [6]. All of the dithiocarboxylate compounds have a higher density of states and have no recorded photoluminescence.

The theoretical energies are strongly correlated to the transitions in the experimental spectra throughout the series. The *n*π*-states are within 0.2 eV of the experimental values, in agreement with Jacquemin et al. [5] from their examination of thiocarbonyls. Close examination of the values calculated here shows that although the absolute error is high for the calculated versus experimental ππ*-states (0.43 eV), there is a tight correlation linking the experimental spectra to the applied level of theory (*r*=0.99), Fig. 14. In a separate study Jacquemin et al. [29] showed that for a range of commercial dyes with predominantly ππ* absorptions,

Fig. 14 The energies from bands in the electronic absorption spectroscopy of dithiocarboxylates are compared to the vertical energies calculated from TDDFT at the CAM-B3LYP/def2-TZVPD/PCM level of theory. The circles are *n*π*-states (○=¹B₁ or ¹A₂) and the ππ*-states are plotted as squares (□=¹B₂) and triangles (Δ=¹A₁). The heavy dashed line represents a perfect 1:1 correlation and the light dashes represent a 1:1 correlation offset by ±0.5 eV

CAM-B3LYP satisfactorily predicts auxochromic effects like those seen here, but with a systemic over-estimation of energy of the transition (e.g. substituted anthraquinones

ca. +0.3 eV). From our analysis, the relationship between the experimental and theoretical $\pi\pi^*$ states is given in Eq. 3 as follows:

$$E_{\text{TDDFT}} = E_{\text{exp}} + 0.43 \text{ eV}, \quad (3)$$

where E_{TDDFT} is the energy of the vertical transition output from the TDDFT calculation and E_{exp} is the experimental λ_{max} converted to eV. This relationship holds for all of the dithiocarboxylates studied here, and is not dependent on the nature of the $\pi\pi^*$ -state, i.e. $^1A_1(\pi\pi^*)$ or $^1B_2(\pi\pi^*)$. Although this empirical relationship is useful for predicting band energies in the experimental spectra, from this analysis there is no clear criteria of when this correction should be applied. Selective application to $\pi\pi^*$ states prior to simulating spectra could improve their fits to the experimental spectra, but may miss other important states and give misleading state orders. Because of this uncertainty, we chose to not use a correction factor before simulating the electronic spectra from TDDFT results.

3.5 Comparing experimental and simulated spectra

Simulating the electronic absorption spectra derived from quantum chemical calculations helps to evaluate the success of the TDDFT method. We simulated the spectra as a sum of Gaussian functions weighted by the oscillator strengths, Eq. 1. Transitions are centered at the calculated vertical transition energies. All of the spectra and comparisons can be found in the Supporting Information (Section S2). Figure 15 shows spectra for the representative compounds **dtbbo** and **dtb**. In the UV region, the number of bands in the simulated spectra match the experimental spectra. Consistent with the state comparisons, the simulated bands are ca. 0.5 eV higher in energy relative to the experimental spectra. The calculated molar absorptivity also is 30–50% higher for these systems. To improve the agreement in the UV region of the spectrum the correlation between experiment and theory (Eq. 3) can be used as a scaling factor for the energies before inputting into the simulation. Although scaling the energies improves the agreement of transitions to $\pi\pi^*$ -states, the fit in the visible region of the spectrum is negatively impacted. For the **dtbR** series, the spectra correctly predict the molar absorptivity and wavelength in the visible region without modification, Fig. 15. A mismatch between bandwidth of the lowest energy absorption is likely due to the simple function used to simulate the spectrum serving as a poor proxy for a more rigorous statistical mechanical model of inhomogeneous broadening [59]. The calculated spectra of the **dtpyr**, **dtmo**, **dtbbo**, and **dtcf** in the visible region are more poorly matched to the experimental spectra. Based on the comparison of state energies and the λ_{max} , the transition to the second $n\pi^*$ state, $^1B_1(n\pi^*)$ likely contributes to the shape of the absorption spectrum. The close lying $\text{GS} \rightarrow ^1B_1(\pi\pi^*)$

Fig. 15 A comparison of experimental (dashed line) and simulated (solid line) electronic absorption spectra of a representative set of dithiocarboxylates: $[\text{PBnPh}_3][\text{dtbbo}]$ in methanol and $[\text{NBu}_4][\text{dtb}]$ in ethanol. The structured absorption between 250 and 275 nm in the **dtbbo** spectrum is from the cation. The spectra were simulated using energies and oscillator strengths (gray circles with vertical lines) from TDDFT at the CAM-B3LYP/def2-TZVPD/PCM level of theory. Gaussian functions were used to simulate broadening and applied with a FWHM of 3800 cm^{-1} (**dtbbo**) or FWHM of 6000 cm^{-1} (**dtb**)

transition also obscures the weak absorptions in the visible region. Finally, the relaxation of symmetry selection rules in solution is unaccounted for by TDDFT, likely leading to a higher molar absorptivity than expected for transitions in the visible region.

3.6 Assigning the electronic transitions

The simulated spectra and comparison of calculated state energies to the experimental spectra allow us to assign bands in the absorption spectra to specific transitions. The lowest energy band for all dithiocarboxylates is from the transition to the $^1A_2(n\pi^*)$ state, with **dtcf** as an exception (Table 3). The visible shoulder in the spectrum of **dtcf** is assigned here to the higher energy $^1A_1(\text{GS}) \rightarrow ^1B_1(n\pi^*)$ transition based on the trend between calculated and observed states, Fig. 13. The higher symmetry of **dtcf** also means that the transition

Table 3 Experimental electronic absorption spectral data for α -carbonyl-dithiocarboxylates in methanol

Compound ^b	$B_2(\pi\pi^*)^a$		$B_1(n\pi^*)^a$		$A_2(n\pi^*)^a$	
	$\lambda_{\max}^c$	ϵ^c	$\lambda_{\max}^c$	ϵ^c	$\lambda_{\max}^c$	ϵ^c
dtta ^d	333	15.5	—	—	438	0.04
dtpyr	347	10.9	—	—	462 ^e	0.16
dtbbo	349	13.3	418 ^e	0.12	473 ^e	0.03
dtmo	346	13.5	420 ^e	0.16	480 ^e	0.07
dtcf	380	13.0	460 ^e	0.22	—	—

— a transition that was not observed

^aAssignments reference C_{2v} irreducible representations to describe the primary character of the excited state A

^bAll have benzyltriphenylphosphonium, PBNPh_3^+ , as the counter ion unless otherwise indicated

^cMaximal wavelength $\lambda_{\max}$ in nm and molar absorptivity ϵ is in units of $10^3 \text{ M}^{-1} \text{ cm}^{-1}$

^dSodium salt in water, Furlani et al. [21]

^eShoulder

to the $^1A_2(n\pi^*)$ state is symmetry forbidden, thus expected to be much weaker than for the other dithiocarboxylates. Both **dtbbo** and **dtmo** have a second weak shoulder in the visible region that aligns with a $^1A_1(\text{GS}) \rightarrow ^1B_1(n\pi^*)$ transition.

The spectra for the compounds in the **dtbR** series follow a similar assignment with two exceptions. First, absorption from the $^1A_1(\text{GS}) \rightarrow ^1A_2(n\pi^*)$ transition is well resolved and with higher molar absorptivity than the non-aryl compounds, Table 4. The high molar absorptivity may be due to symmetry relaxation caused by rotation of the dithiocarboxylate group relative to the phenyl ring. When co-planar or perfectly perpendicular, all the benzoate compounds in this study fall into the C_{2v} point group. There is an energetic barrier to co-planarity introduced by the repulsive interaction between the dithiocarboxylate sulfurs and hydrogens on the phenyl ring *ortho* to the dithiocarboxylate [19]. A dihedral angle between 0° and 90° lowers the compound

to C_2 symmetry. We do not observe a feature corresponding to the $^1A_1(\text{GS}) \rightarrow ^1B_1(n\pi^*)$ transition predicted to appear at approximately 380 nm, likely due to overlap from the strong $^1B_2(\pi\pi^*)$ band in the same region of the spectrum, Fig. 15. The UV band for **dtta**, **dtpyr**, **dtmo**, **dtbbo**, and **dtcf** is assigned to the transition to the $^1B_2(\pi\pi^*)$. The prominent bands in the UV region of the spectrum for the **dtbR** series are assigned to the $^1B_2(\pi\pi^*)$ and $^1A_1(\pi\pi^*)$ transitions. Consistent with the TDDFT prediction, the transition to the $^1B_2(\pi\pi^*)$ state is insensitive to the substituent for the compounds in the **dtbR** series. The band corresponding to the $^1A_1(\text{GS}) \rightarrow ^1A_1(\pi\pi^*)$ is very sensitive to substituents. Significant electron density of the $b_1(\pi)$ molecular orbital resides on the aryl ring and imparts charge transfer character to the lowest $^1A_1(\pi\pi^*)$ state. This same auxochromic trend is observed in aryl-dithiocarboxylates between 250 and 350 nm as the para substituent is varied from $-\text{OMe}$

Table 4 Experimental electronic absorption spectral data for aryl-dithiocarboxylates

Compound ^b	$A_1(\pi\pi^*) (\text{CT})^a$		$B_2(\pi\pi^*)^a$		$A_2(n\pi^*)^a$	
	$\lambda_{\max}^c$	ϵ^c	$\lambda_{\max}^c$	ϵ^c	$\lambda_{\max}^c$	ϵ^c
dtbOMe	321	14.3	363	8.37	507	0.21
dtbMe	296	9.51	363	6.99	500	0.21
dtb	286	10.3	361	9.07	504	0.18
dtbF	291	9.29	365	8.20	502	0.17
dtbCF₃	267	8.99	363	5.94	520 ^d	0.15
dt1n	— ^e	— ^e	349	11.2	484	0.10
dt2n	— ^e	— ^e	356	8.70	511	0.25

^aAssignments reference C_{2v} irreducible representations to describe the primary character of the excited state. CT is aryl-to dithiocarboxylate charge transfer

^bDerivatives of the dithiobenzoate anion, **dtb**, with the indicated *para*-substituent and all have tetra-*n*-butyl-ammonium, NBu_4^+ , as the counter ion

^cMaximal wavelength $\lambda_{\max}$ in nm and molar absorptivity ϵ is in units of $10^3 \text{ M}^{-1} \text{ cm}^{-1}$

^dShoulder

^eAlthough more bands are present in the UV, these are difficult to assign from the TDDFT results

to $-\text{CF}_3$. Changes in position of the CT band show a positive correlation with the *para*-Hammett parameters, σ_p [60], supporting a stabilization of the component orbitals by electron-deficient aryl substituents. For the range of compounds studied, the experimental electronic absorption spectra of aryl-dithiocarboxylates in the UV–visible region of the spectrum are entirely consistent with the model derived from our TDDFT calculations.

The higher energy electronic transitions for dithionaphthoates are more challenging to assign using TDDFT. The lowest energy bands in the visible region of the spectrum match well with the **dtbR** series and are assigned to the $^1A_1(\text{GS}) \rightarrow ^1A_2(n\pi^*)$ transition. The first $\pi \rightarrow \pi^*$ band also matches well with an assignment to the transition to the $^1B_2(\pi\pi^*)$ state. Higher energy bands, particularly in the spectrum of **dt2n** are difficult to assign because each state has multiple contributors by TDDFT. This additional band structure at 316 nm and 270 nm is consistent with a naphthyl chromophore substituted at the 2-position [61]. These potential naphthyl bands have a high ϵ , potentially due to strong mixing between the $b_1(\pi)$ molecular orbital on the dithiocarboxylate with the π -system of the naphthalene. The other isomer, **dt1n**, has comparatively fewer bands in the UV region. For both **dt2n** and **dt1n**, the transition to the $^1B_2(\pi\pi^*)$ state is well described as HOMO-1 $\rightarrow$ LUMO. The excited electron in the $^1B_2(\pi\pi^*)$ state is localized to the dithiocarboxylate for **dt1n** (85% versus 53% for **dt1n**, Fig. 16), consistent with weak vibronic coupling between the naphthyl and dithiocarboxylate subunits causing the narrow bandwidth in the UV–Vis spectrum.

3.7 Limitations of the model

A number of important discrepancies between our experimental systems and the computational model underlie the model's utility for predicting the UV–visible spectra of dithiocarboxylates. Although we use the C_{2v} point group and irreducible representations for comparing states, only **dtcf** is truly a member of C_{2v} . For **dtcf**, the $^1A_1(\text{GS}) \rightarrow ^1A_2(n\pi^*)$ transition has zero oscillator strength as this transition is symmetry forbidden. Thus, we have assigned the shoulder in the visible spectrum of **dtcf** to the allowed

$^1A_1(\text{GS}) \rightarrow ^1B_1(n\pi^*)$ transition, Table 3. The others in the series, **dtpyr**, **dtmo**, and **dtbbo**, are members of C_s for which transitions to both $n\pi^*$ states are allowed. It is reasonable to assume that these compounds are similar to glyoxal or oxalate in solution and have a low barrier to rotation around the central C–C bond, and even their assignment to the C_s point group is tenuous. Improvements in using TDDFT to simulate spectra are made when coupled with molecular dynamics to build a statistical ensemble of solution structures and Franck–Condon calculations to account for vibronic factors [59, 62]. This may also improve the fit for the UV region of the spectrum where several spectra show clear evidence of vibronic structure. The compounds in the **dtbR** series are members of the C_2 point group, which also has two allowed $n \rightarrow \pi^*$ transitions to which they have been assigned (analogous to $^1A_1(\text{GS}) \rightarrow ^1B_1(n\pi^*)$ and $^1A_1(\text{GS}) \rightarrow ^1A_2(n\pi^*)$). For members with C_2 symmetry, the lowest energy $n \rightarrow \pi^*$ transition is the most intense. This helps to explain why the absorption in the visible region appears as a clearly resolved band for the **dtbR** series, but is a shoulder for the others. A particularly striking example is the difference between spectra of **dt1n** and **dt2n**, Fig. 5. The sterically constrained torsion angle for **dt1n** means that it is a member of C_s , and the calculated and experimental bands assigned to the lowest energy $n \rightarrow \pi^*$ transition is weak compared to **dt2n** isomer.

3.8 Conclusions

The absorption spectra for a series of 11 dithiocarboxylates are presented and interpreted with the aid of time-dependent density functional theory (TDDFT). The spectra in the visible and ultraviolet regions align well with prior reports, but TDDFT shows that the manifold of singlet states is more complicated than the thiocarbonyl compounds to which dithiocarboxylates often are compared. States predicted by TDDFT are directly observed in the experimental spectra. Spectra simulated from TDDFT results predict the experimental spectra when accounting for a scaling factor. We show that substituent groups tune the energy of transitions in the UV and visible region with independent tuning possible for the region of the spectrum between 200 and 300 nm. Steric constraints can disrupt conjugation between the dithiocarboxylate group and an attached aryl group, giving an additional handle to modify the electronic absorption spectra of a dithiocarboxylate chromophore. In combination, these results provide a framework for developing and making dithiocarboxylate chromophores with specific absorption spectra.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00144-5>.

Fig. 16 Natural transition orbitals for the third singlet excited electronic state of dithionaphthoate isomers. The plots are 0.035 isosurfaces

Acknowledgements We thank The Frost Fund (<https://cosam.calpoly.edu/frost-fund>) for supporting this research with the purchase of a UV-visible Spectrophotometer, and for funding summer research supplies and stipends. Start-up funds from the Cal Poly College of Science and Mathematics were also used to support this research. We also thank undergraduate students whose contributions to other projects supported the group success: Mark Mattison (B.S. 2018), Terrace Wong (B.S. 2019), Jonathan Richarte, Micah McClure (B.S. 2021), Kiely Payne (Templeton H.S. 2019), Henry Mull (B.S. 2019), Nicholas Baird, Erik McCutchen, An Pham, and Monica Aichouri. DFZ thanks Dr. Megan Grabenauer of RTI, International for editorial discussions during preparation of the manuscript.

Author contributions The manuscript was written through contributions of all authors. All authors have given approval to the manuscript.

Funding The work herein was financially supported by The Frost Fund (<https://cosam.calpoly.edu/frost-fund>) and with start-up funds from the Cal Poly College of Science and Mathematics

Availability of data and materials The data used for this study are presented in the manuscript and supporting information.

Code availability All software used in herein is publicly available from the cited publishers.

Declarations

Conflict of interest The authors have no conflicts or competing interests to declare.

References

- Turro, N. J., Ramamurthy, V., & Scaiano, J. C. (2010). *Molecular Photochemistry of Organic Molecules* (2nd ed.) University Science Books: Sausalito, CA.
- Coyle, J. D. (1985). The photochemistry of thiocarbonyl compounds. *Tetrahedron*, 41, 5393–5425. [https://doi.org/10.1016/S0040-4020\(01\)91341-9](https://doi.org/10.1016/S0040-4020(01)91341-9)
- Steer, R. P., & Ramamurthy, V. (1988). Photophysics and intramolecular photochemistry of thiones in solution. *Accounts of Chemical Research*, 21, 380–386. <https://doi.org/10.1021/ar00154a005>
- Clouthier, D. J., & Moule, D. C. (1989). Periodic group relationships in the spectroscopy of the carbonyls, ketenes and nitriles: the effect of substitution by sulfur, selenium, and phosphorus. *Topics in Current Chemistry*, 150, 167–247. <https://doi.org/10.1007/BFb0111261>
- Jacquemin, D., Wathelet, V., & Perpète, E. A. (2006). Ab initio investigation of the $n \rightarrow \pi^*$ transitions in thiocarbonyl dyes. *Journal of Physical Chemistry A*, 110, 9145–9152. <https://doi.org/10.1021/jp062580d>
- Maciejewski, A., & Steer, R. P. (1993). The photophysics, physical photochemistry, and related spectroscopy of thiocarbonyls. *Chemical Reviews*, 93, 67–98. <https://doi.org/10.1021/cr00017a005>
- Kasha, M. (1950). Characterization of electronic transitions in complex molecules. *Discussions of the Faraday Society*, 9, 14–19. <https://doi.org/10.1039/DF9500900014>
- Hui, M. H., De Mayo, P., Suau, R., & Ware, W. R. (1975). Thione photochemistry: fluorescence from higher excited states. *Chemical Physics Letters*, 31, 257–263. [https://doi.org/10.1016/0009-2614\(75\)85016-0](https://doi.org/10.1016/0009-2614(75)85016-0)
- Korver, O., Veenland, J. U., & De Boer, T. J. (1965). Spectroscopic investigations of thiobenzophenones: I. Electronic spectra. *Recueil des Travaux Chimiques des Pays-Bas*, 84, 289–303. <https://doi.org/10.1002/recl.19650840304>
- Korver, O., Veenland, J. U., & De Boer, T. J. (1965). Spectroscopic investigations of thiobenzophenones: II. Electronic spectra. Correlation of substituent effects on the arylthiocarbonyl absorption maximum with substituent parameters. *Recueil des Travaux Chimiques des Pays-Bas*, 84, 304–309. <https://doi.org/10.1002/recl.19650840305>
- de Mayo, P. (1976). Thione photochemistry, and the chemistry of the S_2 state. *Accounts of Chemical Research*, 9, 52–59. <https://doi.org/10.1021/ar50098a002>
- Hantzsch, A., & Bucerius, W. (1926). Über die Konstitution der Dithiocarbonsäuren und ihrer Salze. *Berichte der deutschen chemischen Gesellschaft A/B*, 59, 793–814. <https://doi.org/10.1002/cber.19260590438>
- Furlani, C., & Luciani, M. L. (1968). Complexes of dithiocarboxylic acids. *Inorganic Chemistry*, 7, 1586–1592. <https://doi.org/10.1021/ic50066a021>
- Bossa, M. (1969). MOLCAO calculations on some sulphur-containing π -electron systems. *Journal of the Chemical Society B*. <https://doi.org/10.1039/J29690001182>
- Grote, J., Friedrich, F., Berthold, K., Hericks, L., Neumann, B., Stämmler, H. G., & Mitzel, N. W. (2018). Dithiocarboxylic acids: an old theme revisited and augmented by new preparative, spectroscopic and structural facts. *Chemistry*, 24, 2626–2633. <https://doi.org/10.1002/chem.201704235>
- Deronzier, A. (1979). Les Propriétés Electrochimiques de Quelques Acides Dithiobenzoïques, de Leurs Sels de Sodium et des Disulfures Correspondants. *Electrochimica Acta*, 24, 1257–1266. [https://doi.org/10.1016/0013-4686\(79\)87082-6](https://doi.org/10.1016/0013-4686(79)87082-6)
- Kato, S., Ito, I., Hattori, R., Mizuta, M., & Katada, T. (1978). Eine einfache Methode zur Darstellung von wasserfreien Natriumdithiocarboxylaten. *Zeitschrift für Naturforschung*, 33b, 976–977. https://zfn.mpg.de/data/Reihe_B/33/ZNB-1978-33b-0976.pdf
- Kato, S., Yamada, S., Goto, H., Terashima, K., Mizuta, M., & Katada, T. (1980). A convenient Preparation Method of Anhydrous Lithium, Potassium, Rubidium and Cesium Dithiocarboxylates. *Zeitschrift für Naturforschung*, 35b, 458–462. https://zfn.mpg.de/data/Reihe_B/35/ZNB-1980-35b-0458.pdf
- Kato, S., Kitaoka, N., Niyomura, O., Kitoh, Y., Kanda, T., & Ebihara, M. (1999). Heavy alkali metal arenedithiocarboxylates: a facile synthesis, dimeric structure, and nonbonding interaction between the metals and aromatic ring carbons. *Inorganic Chemistry*, 38, 496–506. <https://doi.org/10.1021/ic9808089>
- Bonnans-Plaisance, C., Gressier, J.-C., Levesque, G., & Mahjoub, A. (1985). Synthesis of dithiocarboxylates by reaction of dithiocarboxylic acids and their salts (magnesium halides or quarternary ammonium-salts) on halogen compounds, aldehydes and epoxides. *Bulletin de la Société Chimique de France*, 5, 891–899.
- Furlani, C., Flamini, A., Sgamellotti, A., Bellitto, C., & Piovesana, O. (1973). Electronic spectral studies of dithio- and perthiocarboxylato-nickel(II) complexes. *Journal of the Chemical Society, Dalton Transactions*. <https://doi.org/10.1039/DT9730002404>
- Kitchin, A. D., Velate, S., Chen, M., Ghiggino, K. P., Smith, T. A., & Steer, R. P. (2007). Photophysics of a dithioester RAFT polymerization agent and the acenaphthenyl model light-harvesting chromophore. *Photochemical & Photobiological Sciences*, 6, 853–856. <https://doi.org/10.1039/b702811c>
- Cauquis, G., & Deronzier, A. (1980). Electrochemical behaviour of Fe(III), Cr(III) and Co(III) dithiobenzoate complexes. *Journal of Inorganic and Nuclear Chemistry*, 42, 1447–1452. [https://doi.org/10.1016/0022-1902\(80\)80111-4](https://doi.org/10.1016/0022-1902(80)80111-4)

24. Kano, N., & Kawashima, T. (2005). Dithiocarboxylic Acid Salts of Group 1–17 Elements (Except for Carbon). *Topics of Current Chemistry*, 251, 141–180. <https://doi.org/10.1007/b101008>
25. Borer, L. L., & Kong, J. V. (1989). Structure of 1,3-dimethylimidazolium-2-dithiocarboxylate. *Acta Crystallographica*, C45, 1169–1170. <https://doi.org/10.1107/S0108270189000739>
26. Delaude, L., Demonceau, A., & Wouters, J. (2009). Assessing the potential of Zwitterionic NHC·CS₂ adducts for probing the stereoelectronic parameters of N-heterocyclic carbenes. *European Journal of Inorganic Chemistry*. <https://doi.org/10.1002/ejic.200801110>
27. Petz, W. (2015). Addition compounds between carbones, CL₂, and main group Lewis acids: a new glance at old and new compounds. *Coordination Chemistry Reviews*, 291, 1–27. <https://doi.org/10.1016/j.ccr.2015.01.007>
28. Jacquemin, D., Perpète, E. A., Vydrov, O. A., Scuseria, G. E., & Adamo, C. (2007). Assessment of long-range corrected functional performance for n→π* transitions in organic dyes. *Journal of Chemical Physics*, 127, 094102. <https://doi.org/10.1063/1.2770700>
29. Jacquemin, D., Perpète, E. A., Scuseria, G. E., Cofini, I., & Adamo, C. (2008). TD-DFT performance for the visible absorption spectra of organic dyes: conventional versus long-range hybrids. *Journal of Chemical Theory and Computation*, 4, 123–135. <https://doi.org/10.1021/ct700187z>
30. Jacquemin, D., Wathelet, V., Perpète, E. A., & Adamo, C. (2009). Extensive TD-DFT benchmark: singlet-excited states of organic molecules. *Journal of Chemical Theory and Computation*, 5, 2420–2435. <https://doi.org/10.1063/1.2770700>
31. Yanai, T., Tew, D. P., & Handy, N. C. (2004). A new hybrid exchange-correlation functional using the coulomb-attenuating method (CAM-B3LYP). *Chemical Physics Letters*, 393, 51–57. <https://doi.org/10.1016/j.cplett.2004.06.011>
32. Strauch, P., Dempe, B., Kempe, R., Dietzsch, W., Sieler, J., & Hoyer, E. (1994). 1,1-Dithiooxalsäurederivate als Liganden in Übergangmetallkomplexen: Struktur von O-Methyl-1,1-dithiooxalato-bis(triphenylphosphin)kupfer(I) und -silber(I) *Zeitschrift für anorganische und allgemeine Chemie*, 620, 498–504. <https://doi.org/10.1002/zaac.19946200317>
33. Zigler, D. F., Tordin, E., Wu, G., Iretskii, A., Cariati, E., & Ford, P. C. (2011). Mononuclear copper(I) complexes of O-*t*-butyl-1,1-dithiooxalate and of O-*t*-butyl-1-perthio-1-thiooxalate. *Inorganica Chimica Acta*, 374, 261–268. <https://doi.org/10.1016/j.ica.2011.02.037>
34. Houben, J. (1906). Ueber Carbitiosäuren. I. Arylcarbitiosäuren. *Berichte der deutschen chemischen Gesellschaft*, 39, 3219–3233. <https://doi.org/10.1002/cber.190603903140>
35. Houben, J., & Pohl, H. (1907). Über Carbitiosäuren. II. Die geschwefelte Essigsäure, CH₃OS.SH. *Berichte der deutschen chemischen Gesellschaft*, 40, 1303–1307. <https://doi.org/10.1002/cber.19070400212>
36. Houben, J., & Pohl, H. (1907). Über Carbitiosäuren. III. Die geschwefelte Propion-, Butter-, Isobaldrian- und Isocapronsäure. *Berichte der deutschen chemischen Gesellschaft*, 40, 1725–1730.
37. Schmidt, M. W., Baldrige, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M., & Montgomery, J. A., Jr. (1993). General atomic and molecular electronic structure system. *Journal of Computational Chemistry*, 14, 1347–1363. <https://doi.org/10.1002/cber.19070400269>
38. Gordon, M. S., & Schmidt, M. W. (2005). Advances in Electronic Structure Theory: GAMESS a Decade Later. In C. E. Dykstra, G. Frenking, K. S. Kim, & G. E. Scuseria (Eds.), *Theory and Applications of Computational Chemistry, the first forty years*. (Elsevier, Amsterdam, pp 1167–1189). <https://doi.org/10.1016/B978-044451719-7/50084-6>
39. Pritchard, B. P., Altarawy, D., Didier, B., Gibson, T. D., & Windus, T. L. (2019). A new basis set exchange: an open, up-to-date resource for the molecular sciences community. *Journal of Chemical Information Modeling*, 59, 4814–4820. <https://doi.org/10.1021/acs.jcim.9b00725>
40. Adamo, C., & Barone, V. (1999). Toward reliable density functional methods without adjustable parameters: the PBE0 model. *Journal of Chemical Physics*, 110, 6158–6170. <https://doi.org/10.1063/1.478522>
41. Grimme, S., Antony, J., Ehrlich, S., & Krieg, H. A. (2010). Consistent and accurate Ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *Journal of Chemical Physics*, 132, 154104. <https://doi.org/10.1063/1.3382344>
42. Weigend, F., & Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. *Physical Chemistry Chemical Physics*, 7, 3297–3305. <https://doi.org/10.1039/B508541A>
43. Marenich, A. V., Cramer, C. J., & Truhlar, D. G. (2009). Universal solution model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *Journal of Physical Chemistry B*, 113, 6378–6396. <https://doi.org/10.1021/jp810292n>
44. Wang, Y., & Li, H. (2009). Smooth potential energy surface for cavitation, dispersion, and repulsion free energies in polarizable continuum model. *Journal of Chemical Physics*. <https://doi.org/10.1063/1.3268921>
45. Plasser, F., & Lischka, H. (2012). Analysis of excitonic and charge transfer interactions from quantum chemical calculations. *Journal of Chemical Theory and Computation*, 8, 2777–2789. <https://doi.org/10.1021/ct300307c>
46. Plasser, F. (2016). Entanglement entropy of electronic excitations. *Journal of Chemical Physics*, 144, 194107. <https://doi.org/10.1063/1.4949535>
47. Mai, S., Plasser, F., Dorn, J., Fumanal, M., Daniel, C., & González, L. (2018). Quantitative wave function analysis for excited states of transition metal complexes. *Coordination Chemistry Reviews*, 361, 74–97. <https://doi.org/10.1016/j.ccr.2018.01.019>
48. Bode, B. M., & Gordon, M. S. (1998). Macmolplt: a graphical user interface for GAMESS. *Journal of Molecular Graphics and Modelling*, 16, 133–138. [https://doi.org/10.1016/S1093-3263\(99\)00002-9](https://doi.org/10.1016/S1093-3263(99)00002-9)
49. Jmol: an open-source Java viewer for chemical structures in 3D. <http://www.jmol.org>
50. O’Boyle, N. M., Tenderholt, A. L., & Langner, K. M. (2008). A library for package-independent computational chemistry algorithms. *Journal of Computational Chemistry*, 29, 839–845. <https://doi.org/10.1002/jcc.20823>
51. Lewis, G. N., & Calvin, M. (1939). The color of organic substances. *Chemical Reviews*, 25, 273–328. <https://doi.org/10.1021/cr60081a004>
52. Bonnans-Plaisance, C., & Gressier, J.-C. (1988). Nucleophilic substitution by benzodithioate anions. *Journal of Chemical Education*, 65, 93–94. <https://doi.org/10.1021/ed065p93>
53. Borel, M. M., & Ledesert, M. (1975). The crystal structure of potassium dithioacetate. *Zeitschrift für anorganische und allgemeine Chemie*, 415, 285–288. <https://doi.org/10.1002/zaac.19754150313>
54. Engler, V. R., Dräger, M., & Gattow, G. (1974). Über Chalkogenolate. LXIV Untersuchungen über Thioameisensäuren 7. Kristallstruktur von Tetraäthylammoniumcyanodithioformiat. *Zeitschrift für anorganische und allgemeine Chemie*, 403, 81–86. <https://doi.org/10.1002/zaac.19744030110>

55. Mahjoub, A. (2005). Crystal structure of benzyltrimethylammonium dithiobenzoate, $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3][\text{C}_6\text{H}_5\text{CS}_2]$. *Zeitschrift für Kristallographie*, 220, 473–474. <https://doi.org/10.1524/ncrs.2005.220.3.473>
56. Sartor, S. M., Lattke, Y. M., McCarthy, B. G., Miyake, G. M., & Damrauer, N. H. (2019). Effects of naphthyl connectivity on the photophysics of compact organic charge-transfer photoredox catalysts. *Journal of Physical Chemistry A*, 123, 4727–4736. <https://doi.org/10.1021/acs.jpca.9b03286>
57. Fabian, J., & Mehlhorn, A. (1967). Beschreibung der Thiocarbonylvorbande mit Hilfe der einfachen HMO-Methode. *Zeitschrift für Chemie*, 5, 192–194. <https://doi.org/10.1002/zfch.19670070517>
58. Paone, S., Moule, D. C., Bruno, A. E., & Steer, R. P. (1984). Vibronic Analyses of the Rydberg and lower intervalence electronic transitions in thioacetone. *Journal of Molecular Spectroscopy*, 107, 1–11. [https://doi.org/10.1016/0022-2852\(84\)90260-1](https://doi.org/10.1016/0022-2852(84)90260-1)
59. Zuehlsdorff, T. J., & Isborn, C. M. (2018). Combining the ensemble and Franck-Condon approaches for calculating spectral shapes of molecules in solution. *Journal of Chemical Physics*, 148, 024110. <https://doi.org/10.1063/1.5006043>
60. Hansch, C., Leo, A., & Taft, R. W. (1991). A survey of Hammett substituent constants and resonance and field parameters. *Chemical Reviews*, 91, 165–195. <https://doi.org/10.1021/cr00002a004>
61. Adams, N. G., & Richardson, D. M. (1951). Aromatic hydrocarbons in some diesel fuel fractions. *Analytical Chemistry*, 23, 129–133. <https://doi.org/10.1021/ac60049a026>
62. Marenich, A. V., Cramer, C. J., & Truhlar, D. G. (2015). Electronic absorption spectra and solvatochromic shifts by the vertical excitation model: Solvated clusters and molecular dynamics sampling. *Journal of Physical Chemistry B*, 119, 958–967. <https://doi.org/10.1021/jp506293w>