Two small 1,1,4,4-tetracyanobutadiene-functionalized chromophores were obtained by careful leverage of the regioselectivity of the cycloaddition reaction of tetracyanoethylene with anthracene-ynamide derivatives, inducing either a [2+2] or a [4+2] Diels–Alder process. DFT calculations unraveled the mechanism of the [2+2] cycloaddition-retroelectrocyclization reaction sequence with ynamides and elucidated the differing mechanisms in the two substrates. The synthesized dyes presented panchromatic absorption extending into the near-IR, and far-red/near-IR photoluminescence in the solid-state up to 1550 nm.
1,1,4,4-tetracyanobutadiene-functionalized anthracenes: regioselectivity of cycloadditions in the synthesis of small near-IR dyes

Clotilde Philippe, Anh Thy Bui, Sabrinah Batsongo-Boulingui, Ziemowit Pokladek, Katarzyna Matczyszyn, Olivier Mongin, Loïc Lemiègre, Frédéric Paul, Trevor A. Hamlin, Yann Trolez

A Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France
B Faculty of Chemistry, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland
C Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS), and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

ABSTRACT: Two small 1,1,4,4-tetracyanobutadiene-functionalized chromophores were obtained by careful leverage of the regioselectivity of the cycloaddition reaction of tetracyanoethylene with anthracene-ynamide derivatives, inducing either a [2+2] or a [4+2] Diels–Alder process. DFT calculations unraveled the mechanism of the [2+2] cycloaddition-retroelectrocyclization reaction sequence with ynamides and elucidated the differing mechanisms in the two substrates. The synthesized dyes presented panchromatic absorption extending into the near-IR, and far-red/near-IR photoluminescence in the solid-state up to 1550 nm.

Push-pull chromophores, consisting of electron donor and acceptor groups bridged together by a π-conjugated backbone, are a class of molecules that play a prominent role in organic molecular materials.1 Thanks to their particular arrangement that facilitates intramolecular charge transfer (ICT) interactions, they feature in scores of applications including nonlinear optics (NLO)2 and organic photovoltaics (OPVs).3 This persistently intriguing topic has stimulated the exploration of 1,1,4,4-tetracyanobutadiene (TCBD) derivatives and their chemistry by several groups in the past decade.4–10 The elegance of their approach stems from the simplicity of its synthetic route: the TCBD motif can indeed be installed via a facile, high-yield, catalyst-free [2+2] cycloaddition-retroelectrocyclization (CARE) sequence, using tetracyanoethylene (TCNE) and an electron-rich alkyne,5 thus allowing for practical synthetic strategies such as post-polymerization functionalizations.11 TCBD is now established as a valuable strong electron acceptor group, with a rapidly expanding family of dyes including this motif. Beyond its straightforward incorporation in push-pull chromophores, other advantages of TCBD were put forward: its twisted conformation was shown to increase chromophore solubility and reduce aggregation, thereby improving the poling process efficiency in NLO materials.12 Despite a number of studies that have promisedly demonstrated photoinduced charge separation in TCBD-appended chromophores, fast nonradiative deactivation of the excited state in these molecules constitutes a major drawback to their implementation in optoelectronic applications. As suggested by Armaroli et al., in anilino-TCBDs, torsional motions following photoexcitation give rise to a low-energy twisted intramolecular charge transfer (TICT) state that can deactivate to the ground state...
through accessible conical intersections.\textsuperscript{13} As a direct consequence, these molecules are generally nonluminescent and fluorescence that involves a TCBD moiety has seldom been reported.\textsuperscript{14}

In an effort to modify the prototypical anilino-TCBD fragment, our group discovered that ynamides can engage in the [2+2]-CARE reaction with TCNE to form a sulfonamido-TCBD motif, producing dyes with markedly altered optoelectronic properties.\textsuperscript{15,17} We recently revealed that such chromophores could exhibit near-infrared (NIR) luminescence in the solid-state, extending to 1350 nm.\textsuperscript{18} This surprising result prompted us to further investigate compounds based on a similar design, i.e. sulfonamido-TCBD-PAH (polycyclic aromatic hydrocarbon). Interestingly, others have also described solid-state fluorescence involving an ICT to TCBD in push-pull chromophores bearing a PAH.\textsuperscript{19}

Whilst examining the structures of photoactive multi-component systems that integrate TCBD units, one can remark that anthracene is a strikingly rare building block, with only two examples (to the best of our knowledge) bearing a TCBD motif attached to strong electron-donating groups and remote from the anthracene moiety.\textsuperscript{20,21} A possible explanation is the presence of a competing Diels–Alder (DA) reaction which makes this PAH seemingly incompatible with the [2+2]-CARE sequence — a pitfall that was also encountered with other acenes.\textsuperscript{22} Herein we report a synthetic strategy to overcome this limitation, a complete mechanistic picture by density functional theory (DFT) calculations, and the optical properties of the synthesized molecules A-TCBD and DPA-TCBD (Scheme 1).

**Scheme 1. Reaction pathways for the synthesis of A-TCBD and DPA-TCBD**

We have previously identified the lack of reactivity of the triple bond when the ynamide is grafted to the 9-position of anthracene,\textsuperscript{23} which prompted us to investigate anthracenes functionalized in a different position. Brominated derivatives 1a and 1b were therefore selected as starting molecules to access 2-substituted anthracenes. Sonogashira cross-coupling with trimethylsilylacetylene and subsequent deprotection gave the precursor compounds 3a\textsuperscript{25} and 3b. The terminal alkynes were brominated to afford compounds 4a and 4b in 78% and 70% yield respectively. The latter underwent copper-catalyzed amidation using Hsung’s conditions,\textsuperscript{24} leading to ynamides 5a in moderate yield (36%) and 5b in very good yield (89%). Compounds 5a and 5b were then reacted with one equivalent of TCNE. While 9,10-diphenylanthracene derivative 5b yielded DPA-TCBD (62%), compound A-TCBD was not isolated and the DA product 6 was obtained instead (80% yield).

The [4+2] cycloaddition of anthracene with TCNE has already been well documented by several groups.\textsuperscript{25,26,27} The modulation of the equilibrium for addition of TCNE to anthracene by the solvent was discussed by Brown and Cookson and the dissociation was found to be favored in dioxane.\textsuperscript{28} Furthermore, Sauer et al. demonstrated the recovery of the anthracene addend using a different anthracene derivative to trap TCNE.\textsuperscript{29} In the light of these studies, we sought to harness the reversibility of the DA reaction by testing various methods for the recovery of the anthracene structure and formation of the TCBD group. When 5a was heated at 80°C in dioxane in the presence of 1 equivalent of TCNE, even though the retro-DA reaction is expected to be feasible under these condi-
tions, the anilide degraded without significant conversion into A-TCBD. At room temperature, the same reaction led only to cycloadduct 6 in 62% yield. Under UV irradiation (365 nm) in toluene, compound 5a did not provide the [4+4] photodimerization product and its degradation was exclusively observed, invalidating the preliminary protection of the 9,10-positions of the anthracene core by formation of a dimer as an alternate strategy. We endeavored to construct the TCBD motif from cycloadduct 6 instead. In the presence of a second equivalent of TCNE, compound 6 was successfully converted into bisadduct 7 in 50% isolated yield. Using 5 equivalents of TCNE, 5a could be directly transformed into 7 in a much higher yield (73%) than through the combined two-step procedure (40%). Both cycloaddition products 6 and 7 were moderately stable and decomposed in solution within a few hours. Different conditions for the extrusion of TCNE from the anthracene core were then assessed. When a 0.01 M solution of 7 in dioxane was heated at 80°C, A-TCBD could be isolated in only 3% yield after 3 hours. To inhibit the forward [4+2] cycloaddition, rather than another anthracene derivative and DA reaction, 1.5 equivalents of commercially available 4-ethyl-N,N-dimethylanilene 8 were used to scavenge extruded TCNE, considering the known efficiency and irreversibility of the 2+2-CARE reaction. Thus, when stirred for 3 hours at 80°C in the presence of 7, a solution of 8 in dioxane provided compound A-TCBD in a satisfactory yield of 76%. The newly synthesized dyes A-TCBD and DPA-TCBD were characterized by 1H and 13C NMR spectroscopy, HRMS, and cyclic voltammetry (Supporting Information).

Density functional theory (DFT) calculations at COSMO(DCM)-BLYP-D3(BJ)/TZ2P using ADF (see SI for computational details) were carried out to pinpoint the origin of disparate regioselectivity of 5a and 5b. For the calculations, the tosyl group (Ts) of 5a and 5b was replaced with mesyl group (Ms) and the substrates are denoted as 5'a and 5'b. The energy profiles associated with the [2+2]-CARE and [4+2] DA sequences of 5'a and 5'b are provided in Figure 1 and are in line with others in the literature.22 It can be seen that 5'a preferentially reacts via the DA sequence, whereas 5'b reacts via the [2+2]-CARE sequence. The origin of this observed regioselectivity is traced back to the steric bulk at the 9- and 10-position of the anthracene: the unsubstituted 5'a can facilitate the DA reaction of TCNE at anthracene to afford 6', whereas the 9,10-diphenylanthracene 5b is too sterically demanding for the DA reaction and the [2+2]-CARE pathway becomes more energetically viable.

![Figure 1](image-url)  
Figure 1. a) Energy profiles (ΔE_{DCM} in kcal mol⁻¹) for the competing catalyst-free [2+2] cycloaddition-retroelectrocyclization (CARE, in black) and [4+2] Diels–Alder (DA) reactions (in blue) of 5'a and 5'b with TCNE; b) key transition state geometries (in Å) and activation strain analysis (ΔE_{DCM} = ΔE_{DCM, strain} + ΔE_{DCM, int} in kcal mol⁻¹). All data computed at COSMO(DCM)-BLYP-D3(BJ)/TZ2P.
First, we focus on the reactivity of the unsubstituted anthracene 5a'. The DA sequence of 5a' (Figure 1a, go left) begins with the formation of a reactant complex 5a'-INT1* that is more stable (from enhanced π-π stacking) than the corresponding complex 5a'-INT1 of the [2+2]-CARE pathway. From 5a'-INT1*, the DA reaction proceeds through a concerted asynchronous transition state 5a'-TS1* (ΔE‡ = 0.4 kcal mol⁻¹) to afford the experimentally isolated 6'. The first step of the [2+2]-CARE sequence involves the nucleophilic attack of 5a' at TCNE, which goes via an unfavorably high energy transition state 5a'-TS1 (ΔE‡ = 2.6 kcal mol⁻¹) and formation of an unstable zwitterionic intermediate.

Now, we analyze the reactivity of the 9,10-diphenylanthracene derivative 5b' (Figure 1a, go right). The reactant complex 5b'-INT1* is a resting state on the energy surface and cannot proceed further due to an unsurmountable DA barrier via 5b'-TS1* (ΔE‡ = 10.0 kcal mol⁻¹) that goes with a highly destabilizing strain (ΔEstrain = 100.3 kcal mol⁻¹) due to steric clash between TCNE and the phenyl groups at the 9- and 10- positions of the anthracene (Figure 1b). Instead, 5b'-INT1* reversibly dissociates to the reactants and then to the slightly less stable 5b'-INT1, which can undergo nucleophilic attack via 5b'-TS1* to generate a metastable zwitterionic intermediate 5b'-INT2. Rotation and subsequent cyclization via 5b'-TS2 (ΔE‡ = 0.7 kcal mol⁻¹) accomplishes the stepwise [2+2] cycloaddition and generates the cycloadduct 5b'-INT3. Retrocyclization via 5b'-TS3 (ΔE‡ = -19.7 kcal mol⁻¹) provides the s-cis DPA-TCBD' which can then rotate to complete the CARE sequence and furnish s-trans DPA-TCBD'.

The UV-vis absorption spectra of A-TCBD and DPA-TCBD were recorded in dichloromethane (Figure A). Compared to their ynamide precursors, the clear and characteristic finger-like structured absorption bands of anthracene that were observed between 335 nm and 400 nm in 5a and 5b are now absent. New features arose in both TCBD derivatives, causing their absorption spectra to span the whole visible range. Most remarkably, a very broad and structureless low-energy absorption band, attributed to an ICT transition resulting from interactions between the PAH moiety and TCBD, covers the visible region between 450 nm and 800 nm, with a maximum located at 527 nm (ε = 3.5 × 10³ M⁻¹ cm⁻¹) for A-TCBD and at 557 nm (ε = 4.3 × 10³ M⁻¹ cm⁻¹) for DPA-TCBD. Comparison with published data on pyrene and perylene derivatives decorated with a TCBD unit⁶⁸ reveals a pronounced bathochromic effect as well as a slight hyperchromic effect associated with the increase in the PAH π-conjugation (Table S2).

Finally, the photoluminescence (PL) properties of A-TCBD and DPA-TCBD were examined. As reported with analogous dyes,⁸⁸ no emission was detected in dichloromethane, but in rigid media, both compounds displayed a very comparable and broad PL band (Figure B). In diluted rigid matrices (2-methyltetrahydrofuran at 77 K and PMMA at room temperature, Table S3), where the intermolecular interactions are minimized, this band lied between the red and the first near-infrared window (NIR-I, 700–950 nm). Powders of the products exhibited PL in the NIR-I region with a maximum centered at 865 nm and 875 nm for A-TCBD and DPA-TCBD respectively, and a remarkably long tail extending to 1550 nm in the second near-infrared window (NIR-II, 1000–1700 nm), even farther than the upper limit in pyrene and perylene derivatives (ca. 1350 nm). This PL enhancement in the solid-state can be ascribed to the restriction of molecular motions following light absorption, which helps reduce the nonradiative losses in these environments.⁷⁹

![Figure 3](image-url) (A) UV-vis absorption spectra of ynamide precursors 5a and 5b, and compounds A-TCBD and DPA-TCBD in dichloromethane. Inset: zoom on the low-energy band of A-TCBD and DPA-TCBD. (B) Normalized photoluminescence spectra of A-TCBD and DPA-TCBD in PMMA (λexc = 500 nm and 515 nm resp.), organic glass (MeTHF at 77 K, λexc = 480 nm and 520 nm resp.), and powders (λexc = 585 nm and 600 nm resp.). The different detectors used are represented as follows. Continuous line: R928; filled symbols: R2658; open symbols: InGaAs.

Besides the successful synthesis of two TCBD-appended anthracene derivatives A-TCBD and DPA-TCBD, our joined experimental and theoretical investigations showed that the regioselectivity of the cycloaddition reaction of TCNE with 5a and 5b, favoring either a [4+2] Diels–Alder process with the anthracene core in 5a or a [2+2]-CARE reaction with the triple bond in 5b, is dictat-
ed by steric effects at the 9,10-positions. DFT calculations uncovered the mechanism of the \([2+2]\)-CARE sequence with ynamides for the first time, demonstrating that the reaction proceeds through stepwise \([2+2]\) cyclization to produce a cyclobutene intermediate which then opens to give the TCBD moiety. When the DA reaction was preferential, it could advantageously be used to deactivate the 9,10-positions prior to the \([2+2]\)-CARE, then its reversibility exploited to unmask the anthracene core thanks to a scavenger. In addition to insight into the reactivity of some \(\pi\)-systems with TCNE, we expect the synthetic method developed to obtain A-TCBD to be applicable to other acene-TCBD targets. Both A-TCBD and DPA-TCBD displayed optical properties that were remarkable for such small dyes. They presented panchromatic absorption in DCM that extends into the NIR-I region, and solid-state PL signals lying between the far-red and the NIR-II range. This latter feature, rare in TCBD-functionalized molecules, thus further substantiate that new molecular designs comprising this fragment can offer room for unusual photophysical properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

General and synthetic procedures, characterization data, cyclic voltammograms, complementary UV-vis and photoluminescence data, excitation spectra, full computational details (PDF).

AUTHOR INFORMATION

Corresponding Author

Yann Trolez – Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France; orcid.org/0000-0002-5421-9556; E-mail: yann.trolez@ensc-rennes.fr

Trevor A. Hamlin – Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS), and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boeoolaan 1083, 1081 HV Amsterdam, The Netherlands; orcid.org/0000-0002-5128-1004; E-mail: t.a.hamlin@vu.nl

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This study is part of the project ANR JCJC Flutoet 17-CE07-0038-01 from the Agence Nationale pour la Recherche. A. T. B. and C. P. thank the Région Bretagne for funding postdoctoral and doctoral grants, respectively. PHC Polonium 37629XG (2017-2018) is acknowledged for funding. The authors would like to acknowledge Dr Olivier Maury and the Laboratoire de Chimie at ENS de Lyon for access to the Horiba Jobin-Yvon fluorimeters. Dr François Riobé is also thanked for assistance with the corresponding measurements and fruitful discussions. T. A. H. thanks the Netherlands Organization for Scientific Research (NWO) for support.

REFERENCES

(1) Kivala, M.; Diederich, F. Acetylene-Derived Strong Organic Acceptors for Planar and Nonplanar Push–Pull Chromophores. Acc. Chem. Res. 2009, 42 (2), 235–248. https://doi.org/10.1021/ar800128x.

(2) Barlow, S.; Marder, S. R. Nonlinear Optical Properties of Organic Materials. In Functional Organic Materials; Miller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006; pp 393–437. https://doi.org/10.1002/9783527610266.chu.

(3) Su, Y.-W.; Lan, S.-C.; Wei, K.-H. Organic Photovoltaics. Mater. Today 2012, 15 (12), 554–562. https://doi.org/10.1016/S1369-7021(12)70013-0.

(4) Mochida, T.; Yamazaki, S. Mono- and Diferrocenyl Complexes with Electron-Accepting Molecules Formed by the Reaction of Ferrocenylalkynes with Tetracyanoethylene. J. Chem. Soc. Dalton Trans. 2002, 48 (8), 5359–5364. https://doi.org/10.1039/B204166E.

(5) Leliègne, A.; Blanchard, P.; Rousseau, T.; Roncali, J. Triphenylamine/Tetracyanobutadiene-Based D-A-D \(\pi\)-Conjugated Systems as Molecular Donors for Organic Solar Cells. Org. Lett. 2011, 13 (20), 3098–3101. https://doi.org/10.1021/ol201002j.

(6) Koszelewski, D.; Nowak-Król, A.; Gryko, D. T. Selective Cycloaddition of Tetracyanoethene (TCNE) and 7,7,8,8-Tetracyano-p-Quinodimethane (TCNQ) to Afford Meso-Substituted Phenylethynyl Phosphyrins. Chem. – Asian J. 2012, 7 (8), 1887–1894. https://doi.org/10.1002/asia.201200179.

(7) Kato, S.; Noguchi, H.; Jin, S.; Nakamura, Y. Synthesis and Electronic, Optical, and Electrochemical Properties of a Series of Tetracyanobutadiene-Substituted Carbazoles. Asian J. Org. Chem. 2016, 5 (2), 246–250. https://doi.org/10.1002/ajoc.201500431.

(8) Michinobu, T.; Diederich, F. The \([2+2]\) Cycloaddition-Retroelectrocyclization (CA-RE) Click Reaction: Facile Access to Molecular and Polymeric Push-Pull Chromophores. Angew. Chem. Int. Ed. 2018, 57 (14), 3552–3577. https://doi.org/10.1002/anie.201711605.

(9) Patil, Y.; Misra, R. Rational Molecular Design towards NIR Absorption: Efficient Diketopyrrolopyrrole Derivatives for Organic Solar Cells and Photothermal Therapy. J. Mater. Chem. C 2019, 7 (42), 13920–13931. https://doi.org/10.1039/C9TC03640G.

(10) Shoji, T.; Okujima, T.; Ito, S. Development of Heterocycle-Substituted and Fused Azulenes in the Last Decade (2010–2020). Int. J. Mol. Sci. 2020, 21 (9), 7087. https://doi.org/10.3390/ijms21090787.

(11) Li, Y.; Ashizawa, M.; Uchida, S.; Michinobu, T. Colorimetric Sensing of Cations and Anions by Clicked Polystyrenes Bearing Side Chain Donor–Acceptor Chromophores. Polym. Chem. 2012, 3 (8), 1996–2005. https://doi.org/10.1039/C2PY02320A.

(12) Wu, X.; Wu, J.; Liu, Y.; Jen, A. K.-Y. Highly Efficient, Thermally and Chemically Stable Second Order Nonlinear Optical Chromophores Containing a 2-Phenyl-Tetracyanobutadienyl Acceptor. J. Am. Chem. Soc. 1999, 121, 472–473.

(13) Monti, F.; Venturini, A.; Menov, A.; Tancini, F.; Finke, A. D.; Diederich, F.; Armaroli, N. Anilino-Substituted Multicyanobuta-1,3-Diene Electron Acceptors: TICT Molecules with Accessible Conical Intersections. J. Phys. Chem. A 2015, 119 (43), 10677–10683. https://doi.org/10.1021/acs.jpca.5b09291.

(14) Perhaps the most notable description of this type of fluorescence concerns an intramolecular exciplex emission: Winterfeld, K. A.; Lavarda, G.; Guilleme, J.; Sekita, M.; Guldi, D. M.; Torres, T.; Bottari, G. Subphthalocyanines Axially Substitut-
ed with a Tetracyanobuta-1,3-Diene–Aniline Moiety: Synthesis, Structure, and Physicochemical Properties. J. Am. Chem. Soc. 2017, 139 (15), 5520–5529. https://doi.org/10.1021/jacs.7b01460

For other interesting reports, see for example: Xu, J.; Liu, X.; Lv, J.; Zhu, M.; Huang, C.; Zhou, W.; Yin, X.; Liu, H.; Li, Y.; Ye, J. Morphology Transition and Aggregation-Induced Emission of an Intramolecular Charge-Transfer Compound. Langmuir 2008, 24 (8), 4231–4237. https://doi.org/10.1021/la707662w; Dar, A. H.; Gowri, V.; Gopal, A.; Muthukrishnan, A.; Bajaj, A.; Sartaliya, S.; Selim, A.; Ali, M. D.; Jayamurugan, G. Designing of Push–Pull Chromophores with Tunable Electronic and Luminescent Properties Using Urea as the Electron Donor. J. Org. Chem. 2019, 84 (14), 8941–8947. https://doi.org/10.1021/acs.joc.9b00841.

(15) Betou, M.; Kerisi, N.; Meledeje, E.; Leroux, Y. R.; Katan, C.; Halet, J.-F.; Guillemin, J.-C.; Trolez, Y. High-Yield Formation of Substituted Tetracyanobutadienes from Reaction of Ynamides with Tetracyanoethylene. Chem. - Eur. J. 2014, 20 (31), 9553–9557. https://doi.org/10.1002/chem.201402653.

(16) Betou, M.; Durand, R. J.; Sallustrau, D. A.; Goussé, C.; Le Coz, E.; Leroux, Y. R.; Toupet, D. L.; Trzp, E.; Roisnel, T.; Trolez, Y. Reactivity of Functionalized Ynamides with Tetracyanoethylene: Scope, Limitations and Optoelectronic Properties of the Adducts. Chem. - Asian J. 2017, 12 (12), 1338–1346. https://doi.org/10.1002/asia.201700353.

(17) Bouvier, R.; Durand, R.; Faveureau, L.; Srebro-Hooper, M.; Dorcet, V.; Roisnel, T.; Vanthuyne, N.; Végas, Y.; Donnelly, J.; Hernandez, F.; Autschbach, J.; Trolez, Y.; Crassous, J. Helicenes Grafted with 1,1,4,4-Tetracyanobutadiene Moieties: π-Helical Push-Pull Systems with Strong Electronic Circular Dichroism and Two-Photon Absorption. Chem. - Eur. J. 2018, 24 (54), 14484–14494. https://doi.org/10.1002/chem.201802763.

(18) Bui, A. T.; Philippe, C.; Beau, M.; Richy, N.; Cordier, M.; Roisnel, T.; Lemière, L.; Mongin, O.; Paul, F.; Trolez, Y. Synthesis, Characterization and Unusual near-Infrared Luminescence of 1,1,4,4-Tetracyanobutadiene Derivatives. Chem. Commun. 2020, 56 (24), 3571–3574. https://doi.org/10.1039/C9CC09560H.

(19) Marqués, P. S.; Andrés Castán, J. M.; Raul, B. A. L.; Lendi, G.; Ramírez, I.; Pshenichnikov, M. S.; Beljonne, D.; Walzer, K.; Blais, M.; Allain, M.; Cabanetos, C.; Blanchard, P. Triphenylamine/Tetracyanobutadiene-based Π-Conjugated Push-Pull Molecules End-capped with Arene Platforms: Synthesis, Photophysics, and Photovoltaic Response. Chem. – Eur. J. 2020, chem.202002810. https://doi.org/10.1002/chem.202002810.

(20) Gautam, P.; Misra, R.; Siddiqui, S. A.; Sharma, G. D. Unsymmetrical Donor–Acceptor–Acceptor–π-Donor Type Benzothiadiazole-Based Small Molecule for a Solution Processed Bulk Heterojunction Organic Solar Cell. ACS Appl. Mater. Interfaces 2015, 7 (9), 10283–10292. https://doi.org/10.1021/acsami.5b02250.

(21) Rout, Y.; Mobin, S. M.; Misra, R. Tetracyanobutadiene (TCBD) Functionalized Benzo-thiadiazole Derivatives: Effect of Donor Strength on the [2+2] Cycloaddition–Retroelectrocyclization Reaction. New J. Chem. 2019, 43 (31), 12299–12307. https://doi.org/10.1039/C9NJ00887E.

(22) Lehnherr, D.; Adam, M.; Murray, A. H.; McDonald, R.; Hample, F.; Tykwinski, R. R. Synthesis, Physical Properties, and Chemistry of Donor–Acceptor-Substituted Pentacenes. Can. J. Chem. 2017, 95 (3), 303–314. https://doi.org/10.1139/cjc-2016-0450.

(23) Back, J. Y.; An, T. K.; Cheon, Y. R.; Cha, H.; Jang, J.; Kim, Y.; Baek, Y.; Chung, D. S.; Kwon, S.-K.; Park, C. E.; Kim, Y.-H. Alkyl Chain Length Dependence of the Field-Effect Mobility in Novel Anthracene Derivatives. ACS Appl. Mater. Interfaces 2015, 7 (1), 351–358. https://doi.org/10.1021/ami506303.

(24) Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. Copper Sulfate-Pentahydrate-1,10-Phenanthroline Catalyzed Amidations of Alkynyl Bromides. Synthesis of Heteroaromatic Amine Substituted Ynamides. Org. Lett. 2004, 6 (7), 1541–1544. https://doi.org/10.1021/ol049827e.

(25) Middleton, W. J.; Heckert, R. E.; Little, E. L.; Krespan, C. G. Cyanocarbon Chemistry. III. 1’ Addition Reactions of Tetracyanoethylene. J. Am. Chem. Soc. 1958, 80 (11), 2783–2788. https://doi.org/10.1021/ja0154405.

(26) Masci, B.; Pasquale, S.; Thüery, P. Supramolecular Control of a Fast and Reversible Diels–Alder Reaction. Org. Lett. 2008, 10 (21), 4835–4838. https://doi.org/10.1021/ol801909q.

(27) Ronson, T. K.; Pilgrim, B. S.; Nitschke, J. R. Pathway-Dependent Post-Assembly Modification of an Anthracene-Edged M11, L1 Tetrahedron. J. Am. Chem. Soc. 2016, 138 (33), 10417–10420. https://doi.org/10.1021/jacs.6b06710.

(28) Brown, P.; Cookson, R. C. Kinetics of Addition of Tetracyanoethylene to Anthracene and Bicyclo[2,2,1]Heptadiene. Tetrahedron 1965, 21 (8), 1977–1991. https://doi.org/10.1016/0040-4020(65)83737-1.

(29) Sauer, J.; Schröder, B.; Wiemer, R. Eine Studie der Diels-Alder-Reaktion, VI. Kinetischer Nachweis des Moleküls C6O6 (Dianhydryd der Äthylentetraenocarbonäure). Chem. Ber. 1967, 100 (1), 306–314. https://doi.org/10.1002/zbcr.19671000133.

(30) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. Donor-Substituted 1,1,4,4-Tetracyanobutadienes (TCBD): New Chromophores with Efficient Intramolecular Charge-Transfer Interactions by Atom-Economic Synthesis. Chem. – Eur. J. 2006, 12 (7), 1889–1905. https://doi.org/10.1002/chem.20050113.
1,1,4,4-tetracyanobutadiene-functionalized anthracenes: regioselectivity of cycloadditions in the synthesis of small near-IR dyes

Clotilde Philippe,∗a Anh Thy Bui,a Sabrinah Batsongo-Boulingui,a Ziemowit Pokladek,b Katarzyna Matczyszyn,b Olivier Mongin,a Loïc Lemiègre,a Frédéric Paul,a Trevor A. Hamlin,* c Yann Trolez*a

a Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France. Email: yann.trolez@ensc-rennes.fr
b Faculty of Chemistry, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland
c Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS), and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands) E-mail: t.a.hamlin@vu.nl

Supporting Information

Table of contents
1. General experimental procedures ........................................................................................................... 2
2. Syntheses.............................................................................................................................................. 2
3. 1H NMR and 13C NMR spectra................................................................................................................. 6
4. Electrochemical data .................................................................................................................................. 16
5. Photophysical data .................................................................................................................................. 16
6. Full computational details ..................................................................................................................... 18
1. General experimental procedures

Reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuterochloroform referenced to residual CHCl$_3$ ($^1$H, 7.26 ppm) or CDCl$_3$ ($^{13}$C, 77.2 ppm). Chemical shifts ($\delta$) are reported in ppm and coupling constants ($J$) are reported in Hz. The following abbreviations are used to describe multiplicity; s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. HRMS experiments were carried out on a Waters Q-Tof 2 (ESI-Electrospray Ionization, ASAP-Atmospheric Solids Analysis Probe) spectrometer. Analytical TLC was carried out on Merck 60 F$_{245}$ aluminium backed silica gel plates. Short wave UV radiation (245 nm) and KMnO$_4$ were used to visualize components. Compounds were purified by flash column chromatography using Geduran® silica gel 60 (0.040-0.063 mm).

The electrochemical measurements were performed with a conventional three-electrode system comprising a platinum electrode as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode.

UV-visible spectra were recorded on a Jasco V-750 spectrophotometer using 1 cm$^2$ quartz cuvettes. The photoluminescence spectra were measured using Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometers. Powders were placed in quartz tubes and the steady-state luminescence was excited with unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° with a Hamamatsu R928 photomultiplier tube (PMT), a Peltier cooled R2658 PMT, or a liquid nitrogen-cooled InGaAs detector as specified. Long-pass filters with a 515-nm, 550-nm, 610-nm, 665-nm, or 850-nm cut-on wavelength were used to reject scattered light. Spectra were reference-corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating).

2. Syntheses

Synthesis of 2-(bromoethynyl)anthracene 4a

To a solution of 3a (88 mg, 0.32 mmol) in acetone (10 mL), covered with an aluminum foil, was added AgNO$_3$ (7.6 mg, 0.04 mmol) and NBS (141.3 mg, 0.794 mmol). The resulting mixture was stirred at room temperature for 24 hours (monitored by TLC in pentane). The mixture was filtered through a short plug of SiO$_2$ and washed with pentane (30 mL). The yellow filtrate was evaporated under vacuum. The orange solid obtained was dissolved in dichloromethane (15 mL), washed with saturated solution of NaHCO$_3$ (3 x 15 mL), water (2 x 15 mL) and brine (2 x 20 mL). Organic layer was dried over Na$_2$SO$_4$ and evaporated under vacuum. The product was purified by silica gel column chromatography (pentane) to afford white-yellow powder (69.3 mg, 0.25 mmol, 78 %).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (d, 2H), 8.15 (m, J = 0.7 Hz, 1H), 8.03 – 7.96 (m, 2H), 7.92 (d, J = 8.7, 0.8 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.42 (d, J = 8.7, 1.6 Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 132.9, 132.4, 132.2, 130.9, 130.8, 128.5, 128.4, 128.3, 127.5, 126.5, 126.4, 126.1, 126.0, 119.5, 80.8, 50.7. HRMS (ASAP) calculated for C$_{16}$H$_9$Br [M$^+$] 279.988, found 279.989.

Synthesis of N,4-dimethyl-N-(anthracen-2-ylethynyl)benzenesulfonamide 5a

The bromoalkyne 4a (131.8 mg, 0.47 mmol), MeNHTs (79.2 mg, 0.43 mmol), CuSO$_4$·5H$_2$O (12.6 mg, 0.05 mmol) 1,10-phenanthroline (16.8 mg, 0.09 mmol) and K$_2$CO$_3$ (125.6 mg, 0.9 mmol) were placed under nitrogen. Dry degassed toluene (5 mL) was added and the mixture was stirred at 80°C for three
days. Dichloromethane (10 mL) was added to the mixture after cooling down, then filtered through celite, washed with dichloromethane (30 mL) and evaporated under vacuum. The product was purified by silica gel column chromatography (cyclohexane:dichloromethane 1:0 to 4:6) to afford a white yellow powder (60.4 mg, 0.16 mmol, 36%).

\[ \text{1}^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.37 \ (d, 2H), 8.04 \ (m, J = 1.5, 0.7 \text{ Hz, } 1H), 7.99 \ (m, 2H), 7.95 \ (J = 7.83 \text{ Hz, } 3H), 7.50 \ (J = 7.45 \text{ Hz, } 2H), 7.42 \ (J = 7.38 \text{ Hz, } 2H), 7.36 \ (dd, J = 8.8, 1.6 \text{ Hz, } 1H), 3.22 \ (s, 3H), 2.47 \ (s, 3H). \]

\[ \text{13C NMR} \ (101 \text{ MHz, Chloroform-d}) \delta 145.0, 133.4, 132.2, 132.2, 131.3, 131.2, 130.6, 130.0, 128.3, 128.3, 128.0, 127.7, 126.3, 126.2, 125.9, 119.6, 84.9, 70.0, 39.5, 21.8. \]

\[ \text{HRMS \ (ESI, CH}_3\text{OH/CH}_2\text{Cl}_2 \ 90/10) \text{ calculated for C}_{19}\text{H}_{19}\text{NO}_3\text{S [M+Na]^+} \ 408.103, \text{ found 408.103.} \]

**Synthesis of N,4-dimethyl-N-((11,11,12,12-tetracyano-9,10-dihydro-9,10-ethanoanthracen-2-yl)ethynyl)benzenesulfonamide 6**

To a solution of 5a (51.3 mg, 0.13 mmol) in dichloromethane (2 mL) was added TCNE (16.9 mg, 0.13 mmol). The resulting solution was stirred at room temperature for 24 hours. The solvent was removed under vacuum and the crude solid was purified by silica gel column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to afford a pink powder (53.2 mg, 0.10 mmol, 80%).

\[ \text{1}^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.86 \ (81 \text{ m, } 2H), 7.59 \ (J = 7.55 \text{ Hz, } 3H), 7.50 \ (J = 7.8 \text{ Hz, } 1H), 7.45 \ (dd, J = 5.5, 3.2 \text{ Hz, } 2H), 7.41 \ (J = 7.35 \text{ Hz, } 3H), 5.09 \ (s, 1H), 5.05 \ (s, 1H), 3.16 \ (s, 3H), 2.45 \ (s, 3H). \]

\[ \text{13C NMR} \ (101 \text{ MHz, Chloroform-d}) \delta 145.0, 134.2, 133.7, 133.7, 133.0, 132.8, 132.0, 129.9, 129.9, 129.8, 128.7, 127.6, 126.7, 126.7, 126.6, 124.9, 110.5, 110.5, 110.4, 110.4, 86.5, 68.0, 52.7, 52.6, 46.2, 46.1, 39.0, 21.5. \]

\[ \text{HRMS \ (ASAP) calculated for C}_{19}\text{H}_{19}\text{NO}_3\text{S [M+Na]^+} \ 514.133, \text{ found 514.133.} \]

**Synthesis of N,4-dimethyl-N-((11,11,12,12-tetracyano-9,10-dihydro-9,10-ethanoanthracen-2-yl)buta-1,3-dien-2-yl)benzenesulfonamide 7**

Method A: To a solution of 6 (49.9 mg, 0.097 mmol) in dichloromethane (2 mL) was added TCNE (13.1 mg, 0.1 mmol). The resulting solution was stirred at room temperature for 24 hours. The solvent was removed and the crude solid was purified by silica gel column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to afford a pale pink powder (31 mg, 0.048 mmol, 50%).

Method B: To a solution of 5a (83.6 mg, 0.22 mmol) in dichloromethane (5 mL) was added TCNE (142.3 mg, 1.10 mmol). The resulting solution was stirred at room temperature for 20 hours. The solvent was removed under vacuum and the crude solid was purified by silica gel column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to afford a pink powder (103.3 mg, 0.16 mmol, 73%).

\[ \text{1}^1\text{H NMR} \ (400 \text{ MHz, CD}_2\text{Cl}_2) \delta 7.91 \ (7.88 \text{ m, } 2H), 7.88 \ (J = 7.83 \text{ Hz, } 3H), 7.73 \ (tt, 2H), 7.71 \ (J = 7.66 \text{ Hz, } 2H), 7.59 \ (J = 7.53 \text{ Hz, } 2H), 7.49 \ (J = 7.43 \text{ Hz, } 2H), 5.31 \ (d, J = 2.0 Hz, 2H), 3.37 \ (s, 3H), 2.49 \ (s, 3H). \]

\[ \text{13C NMR} \ (101 \text{ MHz, Methylene Chloride-d2}) \delta 164.1, 162.6, 148.3, 140.5, 136.8, 133.5, 133.5, 133.1, 132.4, 132.2, 131.4, 130.9, 128.8, 128.5, 127.8, 127.7, 127.7, 111.7, 111.7, 111.5, 111.3, 111.2, 110.9, 110.8, 110.5, 92.8, 81.5, 53.0, 52.9, 46.8, 46.6, 41.4, 22.0. \]

\[ \text{HRMS \ (ESI, CH}_3\text{OH/CH}_2\text{Cl}_2 \ 90/10) \text{ calculated for C}_{19}\text{H}_{19}\text{NO}_3\text{S [M+Na]^+} \ 664.127, \text{ found 664.127.} \]

**Synthesis of N,4-dimethyl-N-((11,11,12,12-tetracyano-3-(anthracen-2-yl)buta-1,3-dien-2-yl)benzenesulfonamide A-TCBD**

A solution of compound 7 (102 mg, 0.158 mmol) and 4-ethynyl-N,N-dimethylaniline 8 (34 mg, 0.235 mmol) in 1,4-dioxane (17 mL) was stirred at 80°C for 3 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to give product A-TCBD (62 mg, 0.121 mmol, 76%) as a purple solid, and anilino-TCBD 9 (17 mg, 0.061 mmol, 26%) as a purple solid.
1H NMR (400 MHz CDCl₃) δ 8.63 (s, 1H), 8.50 (d, J = 1.4 Hz, 2H), 8.17 (dd, J = 9.0, 0.9 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.80 – 7.68 (m, 2H), 7.66 – 7.54 (m, 3H), 7.47 – 7.35 (m, 2H), 3.51 (s, 2H), 2.48 (s, 3H).

13C NMR (101 MHz, CDCl₃) δ 165.0, 163.8, 163.8, 148.0, 135.0, 134.6, 133.0, 132.6, 132.3, 131.2, 130.8, 130.4, 130.3, 129.1, 128.7, 128.7, 128.5, 128.3, 127.3, 127.2, 123.5, 112.7, 112.6, 111.4, 111.1, 89.2, 80.9, 41.4, 21.9. HRMS (ESI, CH₃OH/CH₂Cl₂ 90/10) calculated for C₃₀H₁₉N₅O₂Na [M+Na]+ 536.115, found 536.115.

Synthesis of (9,10-diphenylanthracen-2-yl)ethynyl)trimethylsilane 2b

A solution of 2-bromo-9,10-diphenylanthracene (505 mg, 1.234 mmol) in Et₃N (2 mL) and dry THF (8 mL) was treated with trimethylacetylene (0.35 mL, 2.526 mmol), CuI (27 mg, 0.142 mmol), PPh₃ (32 mg, 0.122 mmol) and [PdCl₂(PPh₃)₂] (43 mg, 0.061 mmol). The reaction mixture was stirred at reflux over 20 h. The reaction mixture was filtered through celite with cyclohexane, concentrated under reduced pressure and purified by column chromatography (cyclohexane) to give protected alkyne 2b (462 mg, 1.083 mmol, 88%) as a yellow solid.

1H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 1.6, 0.7 Hz, 1H), 7.71 – 7.54 (m, 9H), 7.47 (m, 4H), 7.38 – 7.28 (m, 3H), 0.24 (s, 9H).

13C NMR (101 MHz, CDCl₃) δ 138.8, 138.7, 137.5, 137.3, 131.5, 131.4, 131.2, 130.6, 130.5, 129.4, 129.1, 128.7, 128.6, 127.8, 127.6, 127.3, 127.1, 127.1, 125.6, 125.5, 119.7, 106.0, 95.4, 27.1, 0.1. HRMS (ASAP) calculated for C₃₁H₂₇Si [M+H]+ 427.188, found 427.188.

Synthesis of 2-ethynyl-9,10-diphenylanthracene 3b

A solution of alkyne 2b (238 mg, 0.558 mmol) in MeOH (5 mL) and THF (5 mL) was treated with K₂CO₃ (164 mg, 1.187 mmol). After 18 h at room temperature, the reaction was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane) to give alkyne 3b (165 mg, 0.465 mmol, 83%) as a yellow solid.

1H NMR (400 MHz, CDCl₃) δ 7.90 (dt, J = 1.5, 0.6 Hz, 1H), 7.72 – 7.53 (m, 9H), 7.52 – 7.43 (m, 4H), 7.40 – 7.29 (m, 3H), 3.09 (d, J = 0.5 Hz, 1H).

13C NMR (101 MHz, CDCl₃) δ 138.8, 138.5, 137.5, 137.4, 131.9, 131.4, 131.4, 130.7, 129.3, 129.2, 128.7, 128.6, 127.9, 127.8, 127.4, 127.3, 127.3, 127.2, 125.8, 125.6, 118.5, 84.6, 78.0. HRMS (ASAP) calculated for C₂₈H₁₉ [M+H]+ 355.148, found 355.149.

Synthesis of 2-(bromoethynyl)-9,10-diphenylanthracene 4b

A solution of alkyne 3b (164 mg, 0.463 mmol) in acetone (9 mL) was treated with NBS (101 mg, 0.555 mmol) and AgNO₃ (15 mg, 0.093 mmol). After 17 h at room temperature in the dark, the reaction mixture was filtered and concentrated under reduced pressure. The residue obtained was purified by column chromatography (cyclohexane) to give bromoalkyne 4b (140 mg, 0.323 mmol, 70%) as an orange solid.

1H NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 1.7, 0.7 Hz, 1H), 7.71 – 7.52 (m, 9H), 7.52 – 7.43 (m, 4H), 7.40 – 7.29 (m, 3H), 3.09 (d, J = 0.5 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 138.8, 138.5, 137.5, 137.4, 131.9, 131.4, 131.4, 130.7, 129.3, 129.2, 128.7, 128.6, 127.9, 127.8, 127.4, 127.3, 127.3, 127.2, 125.8, 125.6, 118.5, 84.6, 78.0. HRMS (ASAP) calculated for C₂₈H₁₇Br [M]+ 432.051, found 432.051.

Synthesis of N-((9,10-diphenylanthracen-2-yl)ethynyl)-N,4-dimethylbenzenesulfonamide 5b

A solution of TsNHCH₃ (66 mg, 0.355 mmol), CuSO₄·5H₂O (8 mg, 0.032 mmol), 1,10-phenanthroline (12 mg, 0.065 mmol), K₂CO₃ (180 mg, 1.302 mmol) and bromo alkyne 4b (140 mg, 0.323 mmol) in dry toluene (10 mL) was heated to 90 °C under a nitrogen atmosphere for 60 h. The reaction was then
cooled to room temperature, diluted with EtOAc and filtered through celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 9:1) to give ynamide 5b (155 mg, 0.288 mmol, 89%) as an orange solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.80 (m, 2H), 7.75 (dd, $J = 1.7$, 0.7 Hz, 1H), 7.73 – 7.56 (m, 9H), 7.54 – 7.46 (m, 4H), 7.41 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.25 (dd, $J = 9.0$, 1.7 Hz, 1H), 3.16 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.9, 138.8, 138.8, 137.3, 137.1, 133.1, 131.5, 131.4, 130.5, 130.5, 130.2, 129.9, 129.5, 128.9, 128.7, 128.6, 128.0, 127.8, 127.5, 127.2, 127.1, 125.5, 125.5, 119.2, 84.9, 70.2, 39.4, 21.8. HRMS (ESI MeOH/CH$_2$Cl$_2$ 90/10) calculated for C$_{36}$H$_{27}$NO$_2$NaS [M+Na]$^+$ 560.166, found 560.166;

Synthesis of N,4-dimethyl-N-(1,1,4,4-tetracyano-3-(9,10-diphenylanthracen-2-yl)buta-1,3-dien-2-yl)benzenesulfonamide DPA-TCBD

A solution of ynamide 5b (52 mg, 0.097 mmol) and TCNE (12.4 mg, 0.097 mmol) in CH$_2$Cl$_2$ (3 mL) was stirred at room temperature for 15 h. The reaction mixture was purified by column chromatography (cyclohexane:ethyl acetate 1:0 to 8:2) to give DPA-TCBD (40 mg, 0.060 mmol, 62%) as a dark purple solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 2.1$ Hz, 1H), 7.90 (d, $J = 9.3$ Hz, 1H), 7.87 – 7.80 (m, 1H), 7.80 (m, 1H), 7.74 – 7.59 (m, 9H), 7.57 – 7.43 (m, 6H), 7.42 – 7.35 (m, 2H), 3.26 (s, 3H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.2, 164.0, 147.4, 141.2, 138.2, 137.7, 137.4, 134.5, 132.7, 132.4, 131.6, 131.3, 130.9, 130.9, 130.3, 129.6, 128.8, 128.8, 128.7, 128.5, 128.3, 128.2, 127.8, 127.7, 127.5, 127.5, 126.6, 122.3, 112.4, 112.3, 110.8, 110.5, 87.5, 79.0, 41.1, 21.9. HRMS (ESI MeOH/CH$_2$Cl$_2$ 90/10) calculated for C$_{42}$H$_{27}$N$_5$O$_2$NaS [M+Na]$^+$ 688.178, found 688.178;
3. $^1$H NMR and $^{13}$C NMR spectra

**Figure S1.** $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 4a recorded at 25°C.

**Figure S2.** $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 4a recorded at 25°C.
Figure S3. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 5a recorded at 25°C.

Figure S4. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 5a recorded at 25°C.
Figure S5. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 6 recorded at 25°C.

Figure S6. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 6 recorded at 25°C.
Figure S7. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 7 recorded at 25°C.

Figure S8. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 7 recorded at 25°C.
Figure S9. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of A-TCBD recorded at 25°C.

Figure S10. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of A-TCBD recorded at 25°C.
Figure S11. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 2b recorded at 25°C.

Figure S12. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 2b recorded at 25°C.
Figure S13. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 3b recorded at 25°C.

Figure S14. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 3b recorded at 25°C.
Figure S15. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 4b recorded at 25°C.

Figure S16. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 4b recorded at 25°C.
Figure S17. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of 5b recorded at 25°C.

Figure S18. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of 5b recorded at 25°C.
Figure S19. $^1$H (400 MHz, CDCl$_3$) NMR spectrum of DPA-TCBD recorded at 25°C.

Figure S20. $^{13}$C (101 MHz, CDCl$_3$) NMR spectrum of DPA-TCBD recorded at 25°C.
4. Electrochemical data

Figure S21. Cyclic voltammograms of compounds A-TCBD (blue) and DPA-TCBD (red) in CH2Cl2 with nBu4NPF6 (0.1 M) as the supporting electrolyte and saturated calomel electrode as the reference electrode; the potentials are reported relative to Fc/Fc+.

Table S1. Electrochemical properties of A-TCBD and DPA-TCBD measured in CH2Cl2 with nBu4NPF6 (0.1 M) as the supporting electrolyte and saturated calomel electrode as the reference electrode; the potentials are reported relative to a Fc/Fc+ internal standard.

| Compound      | E\text{red1} (V) | E\text{red2} (V) | E\text{ox} (V) |
|---------------|------------------|------------------|----------------|
| A-TCBD        | -0.57            | -1.06            | 1.13\text{a}   |
| DPA-TCBD      | -0.60            | -1.09            | 1.02           |

\text{a} irreversible process

5. Photophysical data

Figure S22. Structure of the four TCBD-functionalized NIR dyes.
Table S2. UV-vis data for compound 5a, 5b, A-TCBD and DPA-TCBD in dichloromethane, as well as compounds Pyr-TCBD and Pery-TCBD for comparison.\textsuperscript{a}

| Compound      | $\varepsilon(\lambda_{\text{max}})$ [M$^{-1}$ cm$^{-1}$ (nm)] /10$^4$ |
|---------------|---------------------------------------------------------------------|
| 5a            | 6.5 (260); 6.5 (278); 0.47 (335); 0.72 (352); 0.93 (370); 0.70 (392) |
| 5b            | 6.7 (275); 6.3 (287); 0.50 (352); 0.85 (367); 1.3 (387); 1.2 (409)   |
| A-TCBD        | 3.3 (269); 2.1 (298); 1.5 (340); 1.2 (377); 0.35 (527)               |
| DPA-TCBD      | 3.6 (275); 2.1 (318); 2.1 (349); 1.4 (387); 0.43 (557)               |
| Pyr-TCBD\textsuperscript{a} | 2.3 (284); 1.8 (369); 0.34 (545)                                    |
| Pery-TCBD\textsuperscript{a} | 3.8 (260); 2.0 (451); 0.64 (639)                                    |

\textsuperscript{a} reported in A. T. Bui, C. Philippe, M. Beau, N. Richy, M. Cordier, T. Roisnel, L. Lemiègre, O. Mongin, F. Paul, Y. Trolez, Chem. Commun. 2020, 56, 3571.

Figure S23. Excitation spectra of A-TCBD and DPA-TCBD in PMMA matrix (detector: R928), in frozen organic glass (MeTHF at 77K, detector: R928) and powders (detector: InGaAs).

Table S3. Summary of relevant excitation and PL data for compounds A-TCBD and DPA-TCBD, and compounds Pyr-TCBD and Pery-TCBD\textsuperscript{a} in PMMA, MeTHF at 77 K, and powders.

| Compound     | Excitation $\lambda_{\text{max}}$ (nm) | Photoluminescence $\lambda_{\text{max}}$ (nm) |
|--------------|----------------------------------------|-----------------------------------------------|
|              | PMMA | MeTHF 77K | Powders | PMMA | MeTHF 77K | Powders |
| A-TCBD       | 498  | 505       | 515     | 630  | 640       | 865     |
| DPA-TCBD     | 515  | 531       | 515     | 640  | 695       | 875     |
| Pyr-TCBD\textsuperscript{a} | 498  | 533       | 635     | 680  | 706       | 810     |
| Pery-TCBD\textsuperscript{a} | n.d. | n.d.      | 735     | n.d. | n.d.      | 890     |

\textsuperscript{a} reported in A. T. Bui, C. Philippe, M. Beau, N. Richy, M. Cordier, T. Roisnel, L. Lemiègre, O. Mongin, F. Paul, Y. Trolez, Chem. Commun. 2020, 56, 3571.
6. Full computational details

All calculations reported in this paper were performed using the Amsterdam Density Functional (ADF) software.[1] Equilibrium structures and transition structure geometries were optimized using the BLYP functional[2,3] and the TZ2P basis set.[4] Solvent effects of dichloromethane (DCM) were accounted for using the conductor-like screen model (COSMO) of solvation.[5] Dispersion interactions were included using Grimme’s DFT-D3 correction with Becke-Johnson damping.[6] This level is referred to as COSMO(isopropanol)-BLYP-D3(BJ)/TZ2P. All stationary points have been verified, through vibrational analysis, to be minima (zero imaginary frequencies) or transition structures (one imaginary frequency). The character of the normal mode associated with the imaginary frequency has been analyzed to ensure it resembles the reaction under consideration and intrinsic reaction coordinate (IRC) calculations were used to unambiguously connect stationary points on the potential energy surface. Optimized structures were illustrated using CYLview.[7]

Quantitative analyses of the activation barriers associated with the transition structures were obtained by means of the activation strain model (ASM) of reactivity,[8] which involves decomposing the electronic energy of the transition structure $\Delta E^\ddagger$ into the strain $\Delta E^{\ddagger}_{\text{strain}}$ associated with the structural deformation of the reactants from their equilibrium geometry and the interaction $\Delta E^{\ddagger}_{\text{int}}$ between the deformed reactants [Eq. 1]. The $\Delta E^{\ddagger}_{\text{strain}}$ is determined by the rigidity of the reactants and by the extent to which they must deform to achieve the geometry of the transition structure. The $\Delta E^{\ddagger}_{\text{int}}$ is usually stabilizing and is related to the electronic structure of the reactants and how they are mutually oriented over the course of the reaction.

$$\Delta E^\ddagger = \Delta E^{\ddagger}_{\text{strain}} + \Delta E^{\ddagger}_{\text{int}} \quad \text{(1)}$$

References

[1] (a) G. te Velde, et al. J. Comput. Chem., 2001, 22, 931; (b) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, Theor. Chem. Acc., 1998, 99, 391; (c) ADF2019.102, SCM Theoretical Chemistry, Vrije Universiteit: Amsterdam (The Netherlands). http://www.scm.com.

[2] (a) J. C. Slater, Quantum Theory of Molecules and Solids, McGraw-Hill, New York, 1974; (b) A. D. Becke, J. Chem. Phys., 1986, 84, 4524; (c) A. D. Becke, Phys. Rev. A, 1988, 38, 3098.

[3] C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.

[4] E. van Lenthe and E. J. Baerends, J. Comput. Chem., 2003, 24, 1142.

[5] (a) A. Klamt and G. Schüürmann, J. Chem. Soc. Perkin Trans. 2, 1993, 799; (b) A. Klamt, J. Phys. Chem., 1995, 99, 2224; (c) A. Klamt and V. Jonas, J. Chem. Phys. 1996, 105, 9972; (d) C. C. Pye and T. Ziegler, Theor. Chem. Acc., 1999, 101, 396.

[6] (a) S. Grimme, J. Antony, S. Ehrlich and S. Krieg, J. Chem. Phys., 2010, 132, 154104; (b) A. D. Becke and E. R. Johnson, J. Chem. Phys., 2005, 123, 154101.

[7] Legault, C. Y. CYLview (Université de Sherbrooke: Sherbrooke, QC, Canada, 1.0b, 2009) http://www.cylview.org.

[8] (a) P. Vermeeren, S. C. C. van der Lubbe, C. Fonseca Guerra, F. M. Bickelhaupt and T. A. Hamlin, Nature Protoc. 2020, 15, 649; (b) F. M. Bickelhaupt and K. N. Houk, Angew. Chem. Int. Ed. 2017, 56, 10070; Angew. Chem. 2017, 129, 10204; (d) I. Fernández and F. M. Bickelhaupt, Chem. Soc. Rev. 2014, 43, 4953.
**Table S4.** Cartesian coordinates (in Å), energies (in kcal mol\(^{-1}\)), and number of imaginary frequencies of all stationary points, computed at COSMO(DCM)-BLYP-D3(BJ)/TZ2P.

**TCNE**

\[ E = -1834.0 \]

\[ N_{\text{imag}} = 0 \]

|    |    |    |    |
|----|----|----|----|
| C  | -0.688227 | 0.000000 | 0.000000 |
| C  | 0.688227  | 0.000000 | 0.000000 |
| C  | 1.429071  | -1.217648 | 0.000000 |
| C  | 1.429071  | 1.217648  | 0.000000 |
| C  | -1.429071 | -1.217648 | 0.000000 |
| C  | -1.429071 | 1.217648  | 0.000000 |
| N  | -2.037151 | 2.207230  | 0.000000 |
| N  | 2.037151  | 2.207230  | 0.000000 |
| N  | 2.037151  | -2.207230 | 0.000000 |
| N  | -2.037151 | -2.207230 | 0.000000 |

**5a′**

\[ E = -5319.0 \]

\[ N_{\text{imag}} = 0 \]

|    |    |    |    |
|----|----|----|----|
| C  | -2.687964 | -0.100118 | 0.106833 |
| C  | -1.481000 | -0.155980 | -0.031230 |
| C  | 6.438771  | -0.490572 | -0.177006 |
| C  | 5.479606  | -0.669782 | 2.471609 |
| H  | 0.450690  | -0.404420 | 1.829842 |
| H  | -0.284087 | -0.007266 | -2.407603 |
| H  | 2.141048  | -0.079801 | -2.862976 |
| C  | 7.316572  | -0.612885 | 0.875678 |
| C  | 6.830881  | -0.703558 | 2.215049 |
| H  | 8.388435  | -0.641097 | 0.692953 |
| H  | 7.539818  | -0.799022 | 3.034556 |
| H  | 4.474472  | -0.253972 | -2.031572 |
| H  | 6.807031  | -0.420749 | -1.199015 |
| H  | 5.108631  | -0.738235 | 3.492692 |
| H  | 2.777369  | -0.575204 | 2.659026 |
| C  | 3.147101  | -0.505964 | 1.637016 |
| C  | 4.105062  | -0.324725 | -1.009467 |
| C  | 5.026234  | -0.450977 | 0.044444 |
| C  | 4.531505  | -0.543733 | 1.406529 |
| C  | -0.077427 | -0.204646 | -0.242703 |
| C  | 0.426970  | -0.111202 | -1.592499 |
| C  | 1.773198  | -0.151396 | -1.841160 |
| C  | 2.723868  | -0.284794 | -0.778218 |
| C  | 2.226413  | -0.378914 | 0.582679 |
| C  | 0.819619  | -0.335549 | 0.809172 |
| N  | -4.023914 | -0.021473 | 0.256160 |
| C  | -4.638135 | -0.561451 | 1.504178 |
| H  | -5.252232 | -2.431229 | -0.976709 |
| H  | -4.546179 | -1.652618 | 1.549270 |
| H  | -5.686041 | -0.264859 | 1.529855 |
| H  | -4.110298 | -0.112250 | 2.347668 |
| S  | -4.954344 | -0.081827 | -1.202826 |
| O  | -4.269287 | 0.779622  | -2.160858 |
O  -6.334332  0.192677  -0.809086
C  -4.815738  -1.792734  -1.747368
H  -3.756536  -2.009786  -1.899740
H  -5.372677  -1.872177  -2.683454

5a'-INT1
E = -7169.1
N\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{Imag}}} = 0}}}}}}}}$
\begin{align*}
C & : -2.305514  -0.980478  0.020166 \\
C & : -1.099249  -0.959246  -0.182147 \\
H & :  7.178564  -0.309937  -0.997664 \\
H & :  5.216042   0.302758  -0.929406 \\
H & :  2.951910  -0.112230  2.637526 \\
C & :  1.228111  2.024295  -0.486585 \\
C & :  0.015591  2.164963   0.141684 \\
C & :  0.112228  2.287616  -1.553433 \\
C & :  1.212265  2.290417  -0.609073 \\
C & :  2.445571  2.066677  0.237655 \\
C & :  1.307930  1.896665  -1.226590 \\
N & :  2.190806  2.416668   1.226590 \\
N & :  0.187658  2.380713  -0.761939 \\
N & : -3.456931  2.105179   0.814057 \\
C & :  3.382046  -0.242361  1.646247 \\
C & :  4.485857  -0.583755  -0.929406 \\
C & :  5.339624  -0.301900  0.154405 \\
C & :  4.770615  -0.123463  1.477088 \\
C & :  0.289791  -0.894101  -0.368527 \\
C & :  0.862132  -1.041222  -1.680979 \\
C & :  2.216299  -0.944857  -1.858477 \\
C & :  3.103412  -0.691100  -0.761939 \\
C & :  2.534439  -0.523336   0.561578 \\
C & :  1.128780   0.625180  0.722512 \\
C & :  6.752140  -0.177437  -0.005384 \\
C & :  5.645734   0.168985  2.568932 \\
H & :  0.699639  -0.516247  1.713993 \\
H & :  0.200549  -1.222588  -2.522369 \\
H & :  2.641658  -1.056290  -2.853342 \\
C & :  7.561915   0.106450  1.072550 \\
C & :  7.003466  0.281238  2.372256 \\
H & :  8.636871  0.199900   0.936657 \\
H & :  7.659842   0.505073  3.209884 \\
H & :  4.913659  -0.707644  -1.922555 \\
N & : -3.604284  -0.967762  0.256128 \\
C & : -4.149506  -1.186891  1.625428 \\
H & : -5.106017  -3.259771  -0.807664 \\
H & : -4.215693  -2.257653  1.840079 \\
H & : -5.132554  -0.721694  1.683116 \\
H & : -3.472125  -0.701976   2.329752 \\
S & : -4.680505  -0.946748  -1.128261 \\
O & : -4.003922  -0.148559  -2.140437 \\
O & :  -5.984108  -0.560965  -0.602685 \\
C & : -4.711043  -2.668602  -1.636160 \\
H & : -5.368098  -2.722607  -2.507530
### 5a'-TS1

\( E = -7150.5 \)

\( N_{\text{imag}} = 1, -241.8 \text{ cm}^{-1} \)

| Atom | X      | Y      | Z        |
|------|--------|--------|----------|
| C    | -1.151691 | 9.456846 | 0.977220 |
| C    | 0.903032   | 9.528552 | -0.273427|
| N    | 1.466575   | 9.979454 | -1.180331|
| N    | 3.532243   | 9.013053 | 2.098273 |
| N    | -0.328489  | 8.455064 | 4.297115 |
| N    | -2.253654  | 9.801973 | 1.079253 |
| C    | -1.220352  | 6.776043 | 0.282494 |
| C    | -0.013045  | 7.185986 | 0.367350 |
| H    | 7.211999   | 2.933608 | 0.644011 |
| C    | 0.202052   | 8.929521 | 0.855201 |
| C    | 0.273301   | 8.671590 | 3.317480 |
| C    | 2.364278   | 8.957305 | 2.109983 |
| C    | 0.959683   | 8.917557 | 2.116913 |
| H    | 4.151221   | 2.592335 | 4.584165 |
| H    | 2.548042   | 4.122247 | 3.469214 |
| C    | 3.213170   | 4.190658 | 2.610165 |
| C    | 4.935191   | 4.372820 | 0.380313 |
| C    | 5.313984   | 3.581646 | 1.477485 |
| C    | 4.426647   | 3.485302 | 2.622688 |
| C    | 1.236492   | 6.422755 | 0.370130 |
| C    | 2.103574   | 6.507087 | -0.769163|
| C    | 3.306180   | 5.849970 | -0.761920|
| C    | 3.717826   | 5.065227 | 0.361608 |
| C    | 2.834121   | 4.974541 | 1.509370 |
| C    | 1.595143   | 5.678523 | 1.478220 |
| C    | 6.547183   | 2.858354 | 1.502338 |
| C    | 4.818824   | 2.665534 | 3.727887 |
| H    | 0.932866   | 5.625235 | 2.338193 |
| H    | 1.799437   | 7.096513 | -1.628074|
| H    | 3.968400   | 5.917513 | -1.622204|
| C    | 6.885999   | 2.080370 | 2.585059 |
| C    | 6.012031   | 1.981922 | 3.709227 |
| H    | 7.825663   | 1.532763 | 2.590457 |
| H    | 6.298130   | 1.359457 | 4.553859 |
| H    | 5.599745   | 4.443083 | -0.479093|
| N    | -2.450610  | 6.496372 | 0.168098 |
| C    | -3.421864  | 6.373028 | 1.291797 |
| H    | -3.687079  | 3.993745 | -0.703889|
| H    | -3.724039  | 5.329473 | 1.399887 |
| H    | -4.285641  | 6.997013 | 1.056581 |
| H    | -2.931882  | 6.725182 | 2.199404 |
| S    | -3.081398  | 6.118346 | -1.566550|
| O    | -2.051375  | 6.650174 | -2.437025|
| O    | -4.450815  | 6.600129 | -1.566695|
| C    | -3.015048  | 4.326000 | -1.496592|
| H    | -1.977894  | 4.041362 | -1.311871|
| H    | -3.357168  | 3.977884 | -2.474279|
**5α'-INT2**

\[ E = -7152.7 \]

\[ N_{\text{imag}} = 0 \]

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -0.911096 | 9.565893 | 0.760622 |
| C    | 1.437099 | 9.128203 | 1.011235 |
| N    | 2.500523 | 9.498152 | 0.743636 |
| N    | 1.814312 | 8.804353 | 4.503161 |
| N    | -2.478880 | 7.720384 | 3.506347 |
| N    | -1.760546 | 10.231057 | 0.336852 |
| C    | -1.289875 | 6.873252 | 0.247593 |
| C    | -0.099662 | 7.204596 | 0.669030 |
| H    | 6.460398 | 1.953350 | 0.340937 |
| C    | 0.087248 | 8.637407 | 1.337214 |
| C    | -1.388805 | 8.072042 | 3.252036 |
| C    | 0.927744 | 8.658503 | 3.749360 |
| C    | -0.116888 | 8.476496 | 2.843620 |
| H    | 5.274441 | 3.913500 | 4.786974 |
| H    | 3.386437 | 5.135201 | 3.743038 |
| C    | 3.644998 | 4.705319 | 2.777133 |
| C    | 4.310580 | 3.596538 | 0.265936 |
| C    | 5.083707 | 3.264657 | 1.391001 |
| C    | 4.739889 | 3.834047 | 2.682418 |
| C    | 1.026142 | 6.246276 | 0.618844 |
| C    | 1.353519 | 5.670695 | -0.656529 |
| C    | 2.415876 | 4.812962 | -0.773999 |
| C    | 3.216367 | 4.465568 | 0.359791 |
| C    | 2.875611 | 5.038528 | 1.649857 |
| C    | 1.762874 | 5.921757 | 1.742424 |
| C    | 6.202706 | 2.378414 | 1.309041 |
| C    | 5.534046 | 3.485182 | 3.820980 |
| H    | 1.493875 | 6.319973 | 2.714943 |
| H    | 0.778989 | 5.964493 | -1.529761 |
| H    | 2.673419 | 4.394758 | -1.744605 |
| C    | 6.939372 | 2.068502 | 2.428589 |
| C    | 6.601342 | 2.627344 | 3.698161 |
| H    | 7.788409 | 1.392985 | 2.352757 |
| H    | 7.197408 | 2.368473 | 4.570122 |
| H    | 4.568889 | 3.168987 | -0.701354 |
| N    | -2.391087 | 6.568472 | -0.248103 |
| C    | -3.637664 | 6.197115 | 0.479312 |
| H    | -3.123706 | 4.226582 | -1.920092 |
| H    | -3.780356 | 5.117162 | 0.401004 |
| H    | -4.466787 | 6.724322 | 0.005237 |
| H    | -3.518709 | 6.498536 | 1.520909 |
| S    | -2.477657 | 6.491264 | -2.202400 |
| O    | -1.280279 | 7.204591 | -2.608169 |
| O    | -3.822281 | 6.933380 | -2.525363 |
| C    | -2.282103 | 4.716897 | -2.411162 |
| H    | -1.321531 | 4.441238 | -1.972378 |
| H    | -2.296062 | 4.543774 | -3.490299 |
### 5a'-INT1*

$E = -7171.9$

$N_{\text{imag}} = 0$

| Element | x     | y     | z     |
|---------|-------|-------|-------|
| C       | -2.614248 | -0.463181 | 0.079000 |
| C       | -1.406159 | -0.517392 | -0.064054 |
| H       | 6.882650  | -0.697272 | -1.121517 |
| H       | 5.139677  | 0.038997  | 3.502797  |
| H       | 2.821950  | -0.809000 | 2.642112  |
| C       | 3.966497  | -0.752525 | 0.463181  |
| C       | 3.400453  | 0.524229  | 0.463181  |
| C       | 1.996934  | 0.699304  | 0.463181  |
| C       | 4.221127  | 1.654957  | 0.463181  |
| C       | 3.145415  | 0.517392  | 0.463181  |
| C       | 5.368632  | -0.942274 | 0.463181  |
| N       | 6.524852  | 2.567924  | 0.463181  |
| N       | 4.920419  | 2.567924  | 0.463181  |
| N       | 0.838414  | 2.567924  | 0.463181  |
| C       | 2.449377  | -2.825521 | 0.463181  |
| C       | 3.202061  | 1.637952  | 0.463181  |
| C       | 4.179477  | -0.965592 | 0.463181  |
| C       | 5.098421  | 1.433976  | 0.463181  |
| C       | 4.593353  | 0.266115  | 0.463181  |
| C       | 0.506913  | -1.591841 | 0.463181  |
| C       | 1.860283  | -1.821738 | 0.463181  |
| C       | 2.793729  | -0.753278 | 0.463181  |
| C       | 2.284772  | 0.586229  | 0.463181  |
| C       | 0.886515  | 0.799520  | 0.463181  |
| C       | 6.503772  | -0.114461 | 0.463181  |
| C       | 5.520266  | 2.498099  | 0.463181  |
| H       | 0.507650  | 1.805130  | 0.463181  |
| H       | -0.194717 | -2.414175 | 0.463181  |
| H       | 2.236950  | -2.830391 | 0.463181  |
| C       | 7.374555  | 0.943341  | 0.463181  |
| C       | 6.880308  | 2.255443  | 0.463181  |
| H       | 8.447560  | 0.770340  | 0.463181  |
| H       | 7.580130  | 3.073524  | 0.463181  |
| H       | 4.559376  | -1.976270 | 0.463181  |
| N       | -3.940654 | 0.232500  | 0.463181  |
| C       | -4.564015 | 1.511969  | 0.463181  |
| H       | -5.243436 | -0.993878 | 0.463181  |
| H       | -4.522567 | 1.606023  | 0.463181  |
| H       | -5.96608  | 1.531594  | 0.463181  |
| H       | -4.005635 | 2.327209  | 0.463181  |
| S       | -4.893732 | -1.219508 | 0.463181  |
| O       | -4.194965 | -2.178818 | 0.463181  |
| O       | -6.258367 | -0.802952 | 0.463181  |
| C       | -4.802434 | -1.768656 | 0.463181  |
| H       | -3.751229 | -1.938296 | 0.463181  |
| H       | -5.374461 | -2.697327 | 0.463181  |
**5a'-TS1**

$E = -7152.6$

$N_{imag} = 1, -135.2i$ cm$^{-1}$

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -2.376387 | -2.530362 | -0.359595 |
| C       | -1.221238 | -2.161415 | -0.474538 |
| H       | 6.866460  | -1.135960 | -1.253853 |
| H       | 4.976034  | -1.780395 |  3.323788 |
| H       | 2.752214  | -0.919667 |  2.450155 |
| C       | 5.097259  |  1.416263 |  2.473750 |
| C       | 1.904359  |  1.491065 |  1.541608 |
| N       | 0.808098  |  1.836860 |  1.687877 |
| C       | 6.721256  |  2.277967 | -0.012701 |
| N       | 3.164044  |  1.703745 |  3.372472 |
| C       | 4.178075  |  0.520315 | -1.015872 |
| C       | 5.098464  | -1.302986 | -0.013818 |
| C       | 4.566193  | -1.208953 |  1.285775 |
| C       | 0.117333  | -1.736995 | -0.625076 |
| C       | 0.655345  | -1.513610 | -1.921321 |
| C       | 1.971706  | -1.108286 | -2.082987 |
| C       | 2.800807  | -0.947904 |  0.956025 |
| C       | 2.259797  | -1.135094 |  0.342161 |
| C       | 0.936867  | -1.514975 |  0.510400 |
| C       | 6.455745  | -1.296794 | -0.260514 |
| C       | 5.380141  | -1.666611 |  2.321163 |
| H       | 0.520190  | -1.635073 |  1.506114 |
| H       | 0.018447  | -1.660849 | -2.788289 |
| H       | 2.372663  | -0.932779 | -3.077724 |
| C       | 7.256918  | -1.781683 |  0.774608 |
| C       | 6.721256  | -1.971470 |  2.056966 |
| H       | 8.303918  | -2.005476 |  0.587901 |
| H       | 7.355055  | -2.344813 |  2.857154 |
| H       | 4.583997  |  0.218672 | -1.979057 |
| N       | 3.648000  | -2.923224 | -0.239015 |
| C       | 4.100973  |  3.585740 |  1.018093 |
| H       | 3.995543  |  5.565368 | -1.533395 |
| H       | 3.737531  | -4.617994 |  1.068617 |
| H       | 5.189533  |  3.562348 |  1.049435 |
| H       | 3.696552  |  3.009811 |  1.852446 |
| S       | 4.507193  | -3.251340 | -1.714902 |
| O       | 4.142001  | -2.187216 | -2.642046 |
| O       | 5.897219  | -3.461100 | -1.322690 |
| C       | 3.801652  | -4.802211 | -2.289604 |
| H       | 2.732291  | -4.646506 | -2.445236 |
| H       | 4.304762  |  5.043503 | -3.228878 |
\textbf{5a'-INT2*}  
\textit{E} = -7168.0  
\(N_{\text{imag}} = 0\)

|        |        |        |        |        |
|--------|--------|--------|--------|--------|
| C      | -2.422990 | -2.565362 | -0.286750 |
| C      | -1.279373 | -2.168328 | -0.399719 |
| H      | 6.621095  | -1.467171 | -1.289524 |
| H      | 4.714405  | -2.041819 |  3.294978 |
| H      | 2.674808  | -0.667611 |  2.509641 |
| C      | 3.369220  |  1.053480 | -1.279373 |
| C      | 4.007153  |  1.245595 | -2.168328 |
| C      | 5.354701  |  1.816930 | -0.209179 |
| C      | 3.159657  |  2.097987 | -1.046045 |
| C      | 4.298075  |  1.510484 |  2.335499 |
| C      | 2.102037  |  1.775216 |  1.439655 |
| N      | 1.073508  |  2.292609 |  1.567245 |
| N      | 2.487347  |  2.723760 | -1.751967 |
| N      | 6.441646  |  2.217422 | -0.141258 |
| C      | 5.028447  |  1.815468 |  3.181340 |
| C      | 3.091756  | -0.534947 |  1.510514 |
| C      | 4.091791  | -0.231329 | -0.888418 |
| C      | 4.963859  | -1.057299 |  0.031279 |
| C      | 4.427375  | -1.219066 |  1.320004 |
| C      | 0.050822  | -1.697095 | -0.551177 |
| C      | 0.601771  | -1.521594 | -1.843842 |
| C      | 1.905875  | -1.052283 | -2.009577 |
| C      | 2.679695  | -0.768034 | -0.884702 |
| C      | 2.141654  | -0.936786 |  0.402900 |
| C      | 0.841092  | -1.387864 |  0.583587 |
| C      | 6.203678  | -1.603879 | -0.294935 |
| C      | 5.126352  | -1.928147 |  2.295241 |
| H      | 0.426304  | -1.501992 |  1.581053 |
| H      | -0.006477 | -1.753283 | -2.713176 |
| C      | 2.312113  | -0.911322 | -3.008093 |
| C      | 6.900960  | -2.331329 |  0.679787 |
| C      | 6.366824  | -2.491736 |  1.964528 |
| H      | 7.865598  | -2.769460 |  0.436446 |
| H      | 6.919037  | -3.053561 |  2.713596 |
| H      | 4.508240  | -0.111374 | -1.889302 |
| N      | -3.693645 | -2.987186 | -0.170798 |
| C      | -4.103094 | -3.709777 |  1.068304 |
| H      | -3.921077 | -5.650995 | -1.467594 |
| H      | -3.642719 | -4.703196 |  1.115543 |
| H      | -5.189322 | -3.791739 |  1.078441 |
| H      | -3.773505 | -3.109931 |  1.918824 |
| S      | -4.515308 | -3.355220 | -1.651411 |
| O      | -4.183979 | -2.280076 | -2.579905 |
| O      | -5.902913 | -3.619913 | -1.280768 |
| C      | -3.744007 | -4.878770 | -2.218828 |
| H      | -2.678447 | -4.683784 | -2.355762 |
| H      | -4.221523 | -5.137116 | -3.166695 |
\begin{align*}
\mathbf{E} &= -8357.6 \\
N_{\text{imag}} &= 0 \\
\end{align*}

| C     | -2.692336 | -0.086348 | 0.109465  |
|-------|-----------|-----------|-----------|
| C     | -1.484094 | -0.146675 | -0.015169 |
| C     | 6.438302  | -0.523561 | -0.174296 |
| C     | 5.492938  | -0.674593 | 2.470361  |
| H     | 0.445540  | -0.420462 | 1.833475  |
| H     | -0.288307 | 0.043766  | -2.388515 |
| C     | 2.124751  | -0.033958 | 2.211377  |
| H     | 8.391638  | -0.691825 | 0.680163  |
| H     | 7.551183  | -0.813011 | 3.031647  |
| H     | 4.955936  | 1.902930  | -2.329540 |
| H     | 6.807336  | -0.465581 | -1.193773 |
| C     | 5.134457  | -0.729729 | 3.493537  |
| C     | 2.780765  | -2.750255 | 3.161849  |
| C     | 3.144224  | -0.508057 | 1.667418  |
| C     | 4.109085  | -0.322730 | -1.021548 |
| C     | 5.024533  | -0.463878 | 0.047481  |
| C     | 4.533993  | -0.552795 | 1.411671  |
| C     | -0.080791 | -0.187232 | -0.227569 |
| C     | 0.420399  | -0.074468 | -1.573309 |
| C     | 1.765529  | -0.117879 | -1.821153 |
| C     | 2.723637  | -0.271872 | -0.764973 |
| C     | 2.229007  | -0.371700 | 0.596894  |
| C     | 0.819079  | -0.333764 | 0.818749  |
| N     | -4.030408 | -0.007697 | 0.235557  |
| C     | -4.663839 | -0.513384 | 1.487934  |
| H     | -5.200014 | -2.461936 | -0.969186 |
| H     | -4.543694 | -1.598451 | 1.579946  |
| H     | -5.719503 | -0.246441 | 1.473069  |
| H     | -4.173147 | -0.015365 | 2.325810  |
| S     | -4.931149 | -0.114479 | -1.238955 |
| O     | -4.242342 | 0.736591  | -2.202579 |
| O     | -6.322518 | 0.146051  | -0.877197 |
| C     | -4.755519 | -1.833926 | -1.743915 |
| H     | -3.690229 | -2.038540 | -1.868261 |
| H     | -5.289984 | -1.941259 | -2.690187 |
| C     | 4.608940  | -0.223076 | -2.427706 |
| C     | 4.678126  | -1.364282 | -3.243090 |
| C     | 5.134969  | -1.269294 | -4.562242 |
| C     | 5.527870  | -0.030272 | -5.082132 |
| C     | 5.463531  | 1.112190  | -4.275488 |
| C     | 5.007619  | 1.015247  | -2.956208 |
| H     | 4.370411  | -2.326410 | -2.839432 |
| H     | 5.183156  | -2.161533 | -5.182805 |
| H     | 5.881274  | 0.044501  | -6.108119 |
| H     | 5.766543  | 2.078508  | -4.672378 |
| C     | 2.641893  | -0.600053 | 3.072615  |
| C     | 2.294958  | 0.561137  | 3.782672  |
| C     | 1.832750  | 0.478030  | 5.100594  |
| C     | 1.708951  | -0.769183 | 5.724443  |
C  2.049439 -1.932179  5.023271
C  2.513508 -1.847056  3.706026
H  2.391266  1.530075  3.297802
H  1.570531  1.386025  5.639336
H  1.350018 -0.834315  6.749164
H  1.954885 -2.904888  5.501064

Sb'-INT1
$E = -10208.7$
$N_{\text{imag}} = 0$
C  -2.166004 -1.179174  0.114048
C  -0.961437 -1.176979 -0.098149
H   7.265875 -0.246312 -1.192244
H   5.582332 -0.602465  3.481426
H   2.696340 -2.921427  3.012243
C  -1.061021  1.835083 -0.240094
C   0.142481  1.910878  0.473552
C   0.128288  1.900362  1.893622
C  -2.317290  1.843404  0.414790
C  -1.061632  1.824411 -1.660681
N  -1.043283  1.810502 -2.823806
N   2.405775  2.273256 -0.714606
N   0.081891  1.888656  3.056501
N  -3.356543  1.858666  0.940521
C   3.612490 -0.765308  1.631528
C   4.591784 -0.663673 -1.063348
C   5.493247 -0.541859  0.025998
C   4.998566 -0.612029  1.388499
C   0.421262  1.111597 -0.326022
C   0.932344  1.119773 -1.668642
C   2.274654  0.985433 -1.892356
C   3.217899 -0.843538 -0.820257
C   2.715895 -0.878024  0.540805
C   1.313472 -0.982792  0.746213
C   6.892045 -0.329769 -0.177125
C   5.943052 -0.524116  2.461210
H   0.923891 -0.980698  1.757391
H   0.237373 -1.218614 -2.496541
H   2.644890 -0.982446 -2.911932
C   7.763271 -0.231523  0.884966
C   7.285229 -0.342559  2.218822
H   8.823497 -0.070618  0.704107
H   7.984315 -0.279028  3.049364
H   4.278650  1.422486 -2.748477
N  -3.464036 -1.152062  0.352248
N  -4.014633  1.425726  1.708817
H  -5.023788 -3.333833 -0.853429
H  -4.087371 -2.504357  1.877200
H  -4.995270 -0.958041  1.783242
H  -3.337258 -0.975343  2.435974
S  -4.534869  1.018896 -1.029457
O  -3.836303 -0.177952 -1.991483
O  -5.831471 -0.635661 -0.485109
|  | X         | Y         | Z       |
|---|-----------|-----------|---------|
| C | -4.604306 | -2.705401 | -1.641418 |
| H | -5.252657 | -2.689260 | -2.520812 |
| H | -3.589276 | -3.007903 | -1.906275 |
| C |  5.092665 | -0.553072 | -2.465850 |
| C |  5.815160 | -1.599450 | -3.062158 |
| C |  6.276826 | -1.482531 | -4.377661 |
| C |  6.025875 | -0.315709 | -5.109568 |
| C |  5.307813 |  0.732414 | -4.521232 |
| C |  4.841974 |  0.613965 | -3.207768 |
| H |  6.010738 | -2.505662 | -2.493439 |
| H |  6.831331 | -2.301743 | -4.830008 |
| H |  6.386073 | -0.224577 | -6.131838 |
| H |  5.108927 |  1.641467 | -5.084445 |
| C |  3.095996 | -0.800642 |  3.031591 |
| C |  3.042374 |  0.373900 |  3.799473 |
| C |  2.558032 |  0.343804 |  5.109770 |
| C |  2.126852 | -0.862835 |  5.672180 |
| C |  2.176959 | -2.039303 |  4.914671 |
| C |  2.656170 | -2.007882 |  3.601227 |
| H |  3.372046 |  1.312450 |  3.361125 |
| H |  2.510155 |  1.263741 |  5.687645 |
| H |  1.750566 | -0.886361 |  6.692324 |
| H |  1.843243 | -2.980794 |  5.345235 |

**5b'-TS1**

\[ E = -10190.4 \]

\[ N_{\text{imag}} = 1, -279.1i \text{ cm}^{-1} \]

|  | X         | Y         | Z       |
|---|-----------|-----------|---------|
| C | -1.054389 |  9.470359 |  0.773184 |
| C |  1.202714 |  9.487129 | -0.062075 |
| N |  1.955807 |  9.962828 | -0.803423 |
| N |  3.292804 |  8.641902 |  2.747927 |
| N | -0.967556 |  8.057412 |  4.020872 |
| N | -2.138824 |  9.875015 |  0.707929 |
| C | -1.167941 |  6.749652 |  0.193535 |
| C |  0.044795 |  7.149504 |  0.229917 |
| H |  7.250974 |  2.864789 |  0.637092 |
| C |  0.267325 |  8.865568 |  0.862919 |
| C | -0.152176 |  8.353958 |  3.236643 |
| C |  2.148659 |  8.655280 |  2.507250 |
| C |  0.771288 |  8.690274 |  2.232747 |
| H |  4.201354 |  2.689181 |  4.574979 |
| H |  1.673823 |  2.097411 |  3.347953 |
| C |  3.222430 |  4.185638 |  2.540515 |
| C |  5.012094 |  4.344357 |  0.303432 |
| C |  5.354907 |  3.564049 |  1.433812 |
| C |  4.454790 |  3.493014 |  2.571946 |
| C |  1.292351 |  6.386126 |  0.216285 |
| C |  2.194991 |  6.498989 | -0.887312 |
| C |  3.393895 |  5.836133 | -0.852517 |
| C |  3.781088 |  5.031924 |  0.269921 |
| C |  2.872061 |  4.939622 |  1.396676 |
| C |  1.622144 |  5.619755 |  1.316501 |
| C |  6.582491 |  2.829025 |  1.491453 |
| C |  4.858851 |  2.725589 |  3.712393 |
|   | x     | y     | z     |
|---|-------|-------|-------|
| H | 0.926541 | 5.546013 | 2.144085 |
| H | 1.925182 | 7.110665 | -1.742249 |
| H | 4.076579 | 5.923850 | -1.691283 |
| C | 6.920014 | 2.088068 | 2.599636 |
| C | 6.052185 | 2.043284 | 3.727219 |
| H | 7.856559 | 1.535520 | 2.619841 |
| H | 6.337855 | 1.465162 | 4.602961 |
| H | 7.214755 | 5.915583 | 0.116965 |
| N | -2.410982 | 6.503267 | 0.231996 |
| C | -3.229023 | 6.408163 | 1.478151 |
| H | -4.022650 | 4.131463 | -0.399163 |
| H | -3.419456 | 5.358512 | 1.710379 |
| H | -4.166988 | 6.936247 | 1.300103 |
| H | -2.669150 | 6.882413 | 2.285296 |
| S | -3.273564 | 6.147189 | -1.396614 |
| O | -2.299664 | 6.536693 | -2.398673 |
| O | -4.574636 | 6.779756 | -1.271414 |
| C | -3.399386 | 4.362242 | -1.264445 |
| H | -2.387366 | 3.965489 | -1.168999 |
| H | -3.874237 | 4.029024 | -2.190638 |
| C | 5.957919 | 4.452942 | -0.849212 |
| C | 5.758378 | 3.696712 | -2.015576 |
| C | 6.640085 | 3.811460 | -3.095905 |
| C | 7.730559 | 4.686309 | -3.023100 |
| C | 7.936548 | 5.443694 | -1.863856 |
| H | 7.056041 | 5.326394 | -0.783353 |
| C | 4.909120 | 3.019442 | -2.073264 |
| H | 6.474070 | 3.220008 | -3.993571 |
| H | 8.414541 | 4.777790 | -3.863866 |
| H | 8.780668 | 6.126911 | -1.800706 |
| C | 2.285273 | 4.136357 | 3.701575 |
| C | 2.106227 | 5.268080 | 4.515733 |
| C | 1.204766 | 5.239022 | 5.583937 |
| C | 0.470369 | 4.077982 | 5.851744 |
| C | 0.642381 | 2.946142 | 5.045986 |
| C | 1.544899 | 2.974711 | 3.977810 |
| H | 2.671787 | 6.171705 | 4.301440 |
| H | 1.071262 | 6.124359 | 6.200738 |
| H | -0.234007 | 4.056216 | 6.680182 |
| H | 0.071649 | 2.041852 | 5.245843 |

**5b'-INT2**

\[ \varepsilon = -10191.9 \]

\[ N_{\text{imag}} = 0 \]

|   | x     | y     | z     |
|---|-------|-------|-------|
| C | 3.555671 | 11.456734 | 1.172421 |
| C | 5.088396 | 9.679147 | 1.704350 |
| N | 6.201599 | 9.363773 | 1.728962 |
| N | 4.374583 | 9.431431 | 5.125958 |
| N | 0.447328 | 10.282368 | 3.017268 |
| N | 3.363488 | 12.540598 | 0.807419 |
| C | 1.990484 | 9.608919 | -0.120518 |
| C | 2.941689 | 9.101889 | 0.618276 |
| H | 5.095545 | 0.974213 | 0.432299 |
| C | 3.664594 | 10.057881 | 1.653291 |
| Atom | $x$ (Å) | $y$ (Å) | $z$ (Å) |
|------|---------|---------|---------|
| H    | 3.358765 | 1.023420 | -3.526548 |
| H    | 5.599674 | 1.436568 | -4.535220 |
| H    | 7.263957 | 2.836481 | -3.317540 |

**5b'-TS2**

$E = -10191.0$

$N_{imag} = 1, -17.7i \text{ cm}^{-1}$

| C       | -0.705267 | 2.147880 | -7.997167 |
|---------|-----------|---------|-----------|
| H       | -0.722189 | 5.387677 | -10.714642 |
| C       | 7.215903  | 1.925097 | -8.526520 |
| C       | 6.372811  | 1.567749 | -5.866057 |
| H       | 1.358823  | 1.710109 | -6.315023 |
| H       | 0.413532  | 2.443658 | -10.473700 |
| H       | 2.796353  | 2.484826 | -11.010932 |
| C       | 8.138359  | 1.749173 | -7.520193 |
| C       | 7.712890  | 1.576982 | -6.174011 |
| H       | 9.200816  | 1.747621 | -7.752237 |
| H       | 8.452969  | 1.454472 | -5.386839 |
| C       | 5.608868  | 4.479087 | -10.413914 |
| H       | 7.548063  | 2.064793 | -9.549998 |
| H       | 6.052488  | 1.440378 | -4.837250 |
| H       | 4.076290  | 0.601586 | -5.166054 |
| C       | 3.959565  | 1.713386 | -6.576069 |
| C       | 4.859052  | 2.131854 | -9.283417 |
| C       | 5.812505  | 1.930966 | -8.252312 |
| C       | 5.376285  | 1.727855 | -6.882420 |
| C       | 0.709138  | 2.083457 | -8.332839 |
| C       | 1.147521  | 2.308404 | -9.683110 |
| C       | 2.480049  | 2.325208 | -9.985194 |
| C       | 3.486521  | 2.126019 | -8.979355 |
| C       | 3.049852  | 1.907956 | -7.613664 |
| C       | 1.656423  | 1.879131 | -7.340718 |
| C       | -1.620374 | 2.567402 | -8.861333 |
| C       | -1.727413 | 5.811470 | -10.689936 |
| H       | -1.702778 | 6.895837 | -10.553290 |
| N       | -2.376422 | 3.172612 | -9.621945 |
| C       | -3.299597 | 2.639549 | -10.655476 |
| H       | -2.330409 | 5.532745 | -11.554870 |
| H       | -3.234892 | 1.552367 | -10.649760 |
| H       | -3.010338 | 3.051157 | -11.625024 |
| H       | -4.306901 | 2.969347 | -10.393852 |
| S       | -2.537855 | 5.156897 | -9.224928 |
| O       | -1.699031 | 5.279145 | -8.046283 |
| O       | -3.968977 | 5.412215 | -9.228615 |
| C       | 5.315134  | 2.359388 | -10.689386 |
| C       | 5.399233  | 1.292908 | -11.598062 |
| C       | 5.831911  | 1.513252 | -12.910382 |
| C       | 6.184261  | 2.801765 | -13.328201 |
| C       | 6.101386  | 3.870937 | -12.427727 |
| C       | 5.670606  | 3.649943 | -11.115282 |
| H       | 5.127030  | 0.291445 | -11.272565 |
| H       | 5.894964  | 0.678566 | -13.605138 |
| H       | 6.521382  | 2.971935 | -14.348176 |
| H       | 6.372927  | 4.875160 | -12.745211 |
C  3.521039  1.483980  -5.180200
C  2.927015  2.522608  -4.442945
C  2.446115  2.289558  -3.151057
C  2.551680  1.016742  -2.580251
C  3.143321  -0.023661  -3.307047
C  3.626386  0.208940  -4.597665
H  2.836887  3.510504  -4.887931
H  1.982309  3.101000  -2.595405
H  2.170777  0.834607  -1.578081
H  3.222146  -1.017659  -2.872944
C  -1.308076  1.794852  -6.601548
C  -2.848763  1.693769  -6.702722
C  -3.397280  0.731967  -7.563790
C  -3.663182  2.370014  -5.795264
C  -0.921391  2.878196  -5.673838
C  -0.760011  0.508059  -6.096194
N  -0.426098  -0.534439  -5.712889
N  -4.348180  2.959290  -5.045388
N  -3.794806  -0.059563  -8.326087
N  -0.610013  3.744022  -4.971062

5b'-INT3
E = -10216.2
N\text{imag} = 0
C  -0.853139  3.451183  -5.518639
C  -0.505250  1.432742  -4.244725
C   7.282909  2.217323  -8.356716
C   6.688755  2.948641  -5.706192
H   1.738088  1.969056  -5.416187
H   0.385395  0.874343  -9.366915
H   2.672418  1.037272  -10.208199
C   8.279528  2.654058  -7.515660
C   7.977225  3.034306  -6.177286
H   9.304897  2.715129  -7.873059
H   8.772247  3.392731  -5.527509
H   5.292150  3.417576  -10.853690
H   7.519182  1.935034  -9.377731
H   6.462652  3.238739  -4.685096
H   4.878242  0.961904  -3.803622
C   4.296878  2.371419  -6.058294
C   4.888291  1.702899  -8.785296
C   5.923781  2.125971  -7.915875
C   5.621374  2.480271  -6.539481
C   0.904460  1.367907  -7.299690
C   1.193151  1.117390  -8.685041
C   2.473098  1.225337  -9.158087
C   3.565251  1.607300  -8.308885
C   3.270259  1.928012  -6.925676
C   1.933535  1.772808  -6.463785
N  -0.109645  0.956431  -3.264896
N  -3.514765  -0.250695  -4.216433
N  -3.997601  3.338163  -6.782813
N  -0.743685  4.603274  -5.579443
C  -1.634401  0.692508  -7.086631
|      |       |       |       |       |       |
|------|-------|-------|-------|-------|-------|
| **C** | -0.442281 | 1.283314 | -6.783063 |
| **N** | -2.039847 | -0.327749 | -7.917017 |
| **C** | -0.973051 | 1.994521 | -5.511875 |
| **C** | -2.458496 | 1.38289 | -5.966503 |
| **C** | -3.55604 | 2.450911 | -4.604985 |
| **C** | -3.082028 | 0.495828 | -4.989348 |
| **C** | -1.053995 | -1.312850 | -8.434083 |
| **C** | 5.194905 | 1.361706 | -10.208012 |
| **C** | 5.302479 | 0.021191 | -10.613271 |
| **C** | 5.86109 | -0.298019 | -11.945469 |
| **C** | 5.761482 | 0.720505 | -12.887952 |
| **C** | 5.653817 | 2.059347 | -12.494484 |
| **C** | 5.374366 | 2.377510 | -11.161404 |
| **H** | 5.164457 | -0.770009 | -9.879693 |
| **H** | 5.669346 | -1.340416 | -12.245153 |
| **H** | 5.980577 | 0.472842 | -13.925887 |
| **H** | 5.787461 | 2.855941 | -13.223078 |
| **C** | 3.960610 | 2.723224 | -4.646277 |
| **C** | 3.237779 | 3.891493 | -4.359246 |
| **C** | 2.884852 | 4.207631 | -3.043056 |
| **C** | 3.248053 | 3.52229 | -1.996457 |
| **C** | 3.968912 | 2.184719 | -2.272750 |
| **C** | 4.324587 | 1.872992 | -3.588858 |
| **H** | 2.948467 | 4.554947 | -5.173229 |
| **H** | 2.323846 | 5.116218 | -2.836732 |
| **C** | 2.968644 | 3.592085 | -0.973197 |
| **H** | 4.250496 | 1.513287 | -1.464655 |
| **H** | -2.646064 | 0.713897 | -10.597362 |
| **H** | -0.683764 | -1.039226 | -9.426204 |
| **H** | -1.532463 | -2.290741 | -8.476751 |
| **H** | -0.222578 | -1.343642 | -7.728973 |
| **S** | -3.598356 | -0.278686 | -8.658926 |
| **O** | -4.526762 | 0.173342 | -7.627661 |
| **O** | -3.771318 | -1.573353 | -9.302524 |
| **C** | -3.438570 | 1.005398 | -9.905245 |
| **H** | -3.212005 | 1.945947 | -9.398638 |
| **H** | -4.402687 | 1.063423 | -10.416113 |

**Sb'-TS3**

$E = -10216.2$

$N_{imag} = 1, -375.9i \text{ cm}^{-1}$

|      |       |       |       |       |       |
|------|-------|-------|-------|-------|-------|
| **C** | -0.745732 | 3.641642 | -5.486286 |
| **C** | -0.700354 | 1.622387 | -4.141499 |
| **C** | 7.223208 | 2.167720 | -8.441345 |
| **C** | 6.734512 | 2.850333 | -5.756806 |
| **H** | 1.768424 | 1.929171 | -5.324981 |
| **H** | 0.265050 | 1.054623 | -9.274342 |
| **H** | 2.535980 | 1.167614 | -10.178336 |
| **C** | 8.257466 | 2.563695 | -7.624402 |
| **C** | 8.008700 | 2.919917 | -6.269869 |
| **H** | 9.271029 | 2.612297 | -8.015623 |
| **H** | 8.831987 | 3.248757 | -5.640095 |
| **H** | 5.134760 | 3.475534 | -10.856487 |
| **H** | 7.418131 | 1.906294 | -9.476493 |
| Atoms | x   | y   | z    |
|-------|-----|-----|------|
| H     | 6.54939 | 3.124614 | -4.723332 |
| H     | 5.01866 | 0.907209 | -3.825240 |
| C     | 4.319365 | 2.329789 | -6.040444 |
| C     | 4.805334 | 1.724258 | -8.803749 |
| C     | 5.879476 | 2.095887 | -7.956408 |
| C     | 5.630879 | 2.422027 | -6.562983 |
| C     | 0.863347 | 1.455013 | -7.211098 |
| C     | 1.102309 | 1.244292 | -8.610653 |
| C     | 2.370669 | 1.328328 | -9.117935 |
| C     | 3.496517 | 1.653906 | -8.289434 |
| C     | 3.254366 | 1.935854 | -6.886984 |
| C     | 1.931237 | 1.789672 | -6.387855 |
| N     | -0.548840 | 1.091476 | -3.118222 |
| N     | -3.843510 | -0.036822 | -4.320628 |
| N     | -3.835460 | 3.607147 | -6.946853 |
| N     | -0.699012 | 4.799193 | -5.590293 |
| C     | -1.646124 | 0.790609 | -6.981667 |
| C     | -0.472548 | 1.414226 | -6.659134 |
| N     | -1.921426 | -0.319307 | -7.759475 |
| C     | -0.879984 | 2.217126 | -5.433800 |
| C     | -2.667947 | 1.458505 | -6.079360 |
| C     | -3.347334 | 2.630461 | -6.549614 |
| C     | -3.373423 | 0.643714 | -5.137641 |
| C     | -0.865405 | -1.332103 | -8.021328 |
| C     | 5.058275 | 1.408730 | -10.242982 |
| C     | 5.146992 | 0.074943 | -10.673773 |
| C     | 5.375799 | -0.222040 | -12.021520 |
| C     | 5.515204 | 0.812181 | -12.954713 |
| C     | 5.427137 | 2.144370 | -12.533110 |
| C     | 5.202582 | 2.440748 | -11.184656 |
| H     | 5.036576 | -0.728143 | -9.948499 |
| H     | 5.444392 | -1.259324 | -12.341783 |
| H     | 5.690814 | 0.581689 | -14.003018 |
| H     | 5.533215 | 2.952875 | -13.253030 |
| C     | 4.038019 | 2.660754 | -4.612675 |
| C     | 3.314236 | 3.820875 | -4.284111 |
| C     | 3.022224 | 4.122923 | -2.950806 |
| C     | 3.446797 | 3.266708 | -1.928109 |
| C     | 4.167353 | 2.109427 | -2.245717 |
| C     | 4.463683 | 1.809364 | -3.579025 |
| H     | 2.981011 | 4.484183 | -5.078884 |
| H     | 2.462398 | 5.024156 | -2.711911 |
| H     | 3.215774 | 3.498539 | -0.891072 |
| H     | 4.496295 | 1.437653 | -1.456095 |
| H     | -1.903488 | 0.266696 | -10.643440 |
| H     | -0.287447 | -1.105385 | -8.922074 |
| H     | -1.341997 | -2.306391 | -8.122174 |
| H     | -0.195959 | -1.336593 | -7.157068 |
| S     | -3.299191 | -0.313846 | -8.807250 |
| O     | -4.363454 | 0.366840 | -8.076171 |
| O     | -3.464301 | 1.687696 | -9.261482 |
| C     | -2.780221 | 0.723832 | -10.180287 |
| H     | -2.563821 | 1.719767 | -9.787902 |
| H     | -3.617059 | 0.755526 | -10.881783 |
|    |        |        |        |        |        |        |        |        |
|----|--------|--------|--------|--------|--------|--------|--------|--------|
|    | $E = -10243.5$ |        |        |        |        |        |        |        |
|    | $N_{\text{imag}} = 0$ |        |        |        |        |        |        |        |
| C  | -2.458926 | 1.358922 | -8.935931 |        |        |        |        |        |
| C  | -3.425209 | 0.516494 | -9.557336 |        |        |        |        |        |
| C  | 7.316841  | 1.988323 | -8.274926 |        |        |        |        |        |
| C  | 6.630288  | 2.349877 | -5.571687 |        |        |        |        |        |
| H  | 1.572872  | 2.035164 | -5.721383 |        |        |        |        |        |
| H  | 0.410548  | 1.778986 | -9.873440 |        |        |        |        |        |
| H  | 2.759155  | 1.816991 | -10.547728 |        |        |        |        |        |
| C  | 8.297617  | 2.128578 | -7.319748 |        |        |        |        |        |
| C  | 7.950492  | 2.323736 | -5.954423 |        |        |        |        |        |
| H  | 9.345432  | 2.097136 | -7.608790 |        |        |        |        |        |
| H  | 8.734932  | 2.454552 | -5.212966 |        |        |        |        |        |
| H  | 5.767696  | 3.827101 | -10.651230 |        |        |        |        |        |
| H  | 7.589268  | 1.848334 | -9.315783 |        |        |        |        |        |
| H  | 6.371057  | 2.501774 | -4.529414 |        |        |        |        |        |
| H  | 4.599017  | 0.353579 | -4.171609 |        |        |        |        |        |
| C  | 4.215133  | 2.185328 | -6.138454 |        |        |        |        |        |
| C  | 3.563170  | 1.950985 | -8.531394 |        |        |        |        |        |
| C  | 3.205062  | 2.070146 | -7.128857 |        |        |        |        |        |
| C  | 1.830728  | 2.030395 | -6.773482 |        |        |        |        |        |
| C  | -2.661250 | 2.763568 | -9.075617 |        |        |        |        |        |
| C  | -2.501356 | 2.102002 | -5.866585 |        |        |        |        |        |
| C  | -0.538083 | 3.454982 | -5.522232 |        |        |        |        |        |
| N  | -0.075119 | 4.326599 | -4.905893 |        |        |        |        |        |
| N  | -2.830957 | 3.907327 | -9.202909 |        |        |        |        |        |
| N  | -4.262591 | -0.149686 | -10.012682 |        |        |        |        |        |
| N  | -3.576221 | 1.834157 | -5.510625 |        |        |        |        |        |
| C  | -1.396765 | 0.869921 | -8.196399 |        |        |        |        |        |
| C  | -0.572934 | 1.790604 | -7.351029 |        |        |        |        |        |
| C  | 0.995257  | 1.703782 | -9.628267 |        |        |        |        |        |
| C  | -1.173252 | 2.426583 | -6.279988 |        |        |        |        |        |
| H  | 1.519789  | -0.747670 | -9.587049 |        |        |        |        |        |
| C  | 5.283079  | 1.746610 | -10.350787 |        |        |        |        |        |
| C  | 5.204175  | 0.482638 | -10.958551 |        |        |        |        |        |
| C  | 5.543543  | 0.319897 | -12.305695 |        |        |        |        |        |
| C  | 5.961917  | 1.420882 | -13.062036 |        |        |        |        |        |
| C  | 6.041586  | 2.684222 | -12.464076 |        |        |        |        |        |
| C  | 5.705733  | 2.845728 | -11.115850 |        |        |        |        |        |
| H  | 4.880344  | -0.372786 | -10.369746 |        |        |        |        |        |
| H  | 5.481095  | -0.664884 | -12.763210 |        |        |        |        |        |
| H  | 6.224048  | 1.295317 | -14.110020 |        |        |        |        |        |
| H  | 6.363896  | 3.544311 | -13.046643 |        |        |        |        |        |
| C  | 3.835523  | 2.302502 | -4.701523 |        |        |        |        |        |
| C  | 3.189122  | 3.454898 | -4.222627 |        |        |        |        |        |
| C  | 2.823385  | 3.556538 | -2.876781 |        |        |        |        |        |
s-trans-DPA-TCBD'

$E = -10245.1$

$N_{\text{imag}} = 0$

C -1.526801 2.428681 -8.299402
C -2.454754 2.693557 -9.344274
C 7.377010 2.604864 -8.448683
C 6.764824 3.311269 -5.796184
H 1.926934 1.920193 -5.431385
H 0.623329 0.623630 -9.337347
H 2.858960 1.028472 -10.229406
C 8.347134 3.12981 -7.624419
C 8.035057 3.499324 -6.287144
H 9.358679 3.269874 -7.998339
H 8.806139 3.930826 -5.653579
H 5.323033 3.658912 -10.891602
H 7.622407 2.334532 -9.470406
H 6.529521 3.593919 -4.775576
H 5.252919 1.236452 -3.855947
C 4.428757 2.523942 -6.105172
C 5.027586 1.898114 -8.845005
C 6.039496 2.406979 -7.988021
C 5.730373 2.743845 -6.608989
C 1.123118 1.200692 -7.288511
C 1.405645 0.992755 -8.684149
C 2.658283 1.215544 -9.179784
C 3.729467 1.690035 -8.349172
C 3.431950 1.977746 -6.957948
C 2.135916 1.691301 -6.467726
C -0.708220 3.531429 -7.916377
C -1.866691 0.750881 -4.968786
C 0.431069 0.265533 -4.474944
N 1.164749 -0.112936 -3.653480
N -0.061054 4.452330 -7.620494
N -3.172369 2.922028 -10.231781
N -2.958968 0.814214 -4.570010
C -1.375667 1.186187 -7.693501
C  -0.212315   0.984381  -6.769519
C   -2.298579  -2.248111  -6.411310
C    -0.525978   0.671786  -5.448532
H    -1.613346  -1.907752  -5.636056
C     5.340895   1.591857  -10.273941
C     5.514684   0.264156  -10.697853
C     5.802392  -0.021283  -12.036614
C     5.915971  1.017776  -12.967841
C     5.742462  2.343776  -12.553336
C     5.458434   2.628999  -11.214021
H     5.423943  -0.543102  -9.974632
H     5.936548  -1.053719  -12.351645
H     6.137386   0.795836  -14.009261
H     5.826798   3.155933  -13.271940
C     4.0895  74   2.850918  -4.690255
C     3.232384   3.926153  -4.396414
C     2.891697   4.219914  -3.072733
C     3.397863   3.438456  -2.027668
C     4.250158   2.365143  -3.212339
C     4.597145   2.075037  -3.634709
H     2.834847   4.529252  -5.209351
H     2.229377   5.055748  -2.859299
H     3.127710   3.662671  -0.998416
H     4.641268   1.749950  -1.505267
H    -2.213064  -3.326134  -6.567053
N    -2.304843   0.179249  -7.812978
C    -3.747443   0.431680  -8.055707
H    -3.330592  -1.969412  -6.193799
H    -4.317831  -0.367230  -7.577633
H    -3.989053   0.459819  -9.118540
H    -4.004853   1.377570  -7.577583
S    -1.808304  -1.505034  -7.968630
O    -0.357719  -1.501230  -8.087141
O    -2.646223  -2.039155  -9.033435

5b'-INT1*
\[ E = -10212.2 \]
\[ N_{imag} = 0 \]
C    4.182132  -0.554733  -1.005166  
C    5.088276  -0.399756   0.086408  
C    4.576183  -0.150483  2.466983  
C    0.496043  -0.267464  2.466983  
C    0.472043  -0.267464  1.767676  
C    2.224501  -0.569092  2.873629  
C    7.367848  -0.253772  0.956535  
C    6.870616  -0.064771  2.240638  
C    8.440321  -0.308861   0.789211  
C    7.561724  -0.275158  3.052763  
C    5.789027   0.934981  -2.686645  
C    -3.956216  -0.373231   0.210386  
C    -4.552846  -0.851121  1.490762  
C    -5.208710  -2.768374  -0.998612  
C    -4.450428  -1.937832  1.585594  
C    -5.603310  -0.563993  1.508378  
C    -4.023793  -0.356271  2.307219  
S    -4.921278  -0.420849  -1.235516  
O    -4.249261   0.441407  -2.199735  
O    -6.289034  -0.145057  -0.807092  
C    -4.794234  -2.130061  -1.781473  
C    -3.739574  -2.345564  -1.964420  
C    -5.377400  -2.209224  -2.701774  
C    2.667072  -0.062706  3.054742  
C    1.852146   0.994779  3.494258  
C    1.403087   1.048207  4.816236  
C    1.748641   0.036029   5.718369  
C    2.546545  -1.031215  5.288782  
C    3.006194  -1.077835  3.970728  
C    1.565581   1.780871  2.804492  
C    0.784104   1.882172  5.138477  
C    1.398127   0.077137   6.746902  
C    2.814092  -1.826814   5.980255  
C    4.687695  -0.897351  -2.365447  
C    4.344496  -2.140685  -2.930573  
C    4.805688  -2.499050  -4.199606  
C    5.609199  -1.615776  -4.930205  
C    5.956377  -0.378002  -4.378007  
C    5.505705  -0.024930  -3.103468  
C    3.718925  -2.826881  -2.365418  
C    4.535878  -3.466150  -4.617490  
C    5.963049  -1.890639  -5.921050  
C    6.579217   0.315334  -4.938124
5b'-TS1*

\[ E = -10181.6 \]

\[ N_{\text{imag}} = 1, -311.0i \text{ cm}^{-1} \]

\begin{tabular}{cccc}
C & -2.401114 & -2.513115 & -0.423157 \\
C & -1.242015 & -2.155660 & -0.523189 \\
H & 6.878017 & -1.120940 & -1.254339 \\
H & 5.026398 & -1.863549 & 3.299983 \\
H & 2.781364 & -3.334329 & 2.181121 \\
C & 3.268906 & -1.120940 & 1.373308 \\
C & 3.880218 & 1.306645 & -0.044181 \\
C & 5.184801 & 1.898463 & 0.035857 \\
C & 2.960077 & 2.012976 & -0.888339 \\
C & 4.136752 & 1.363269 & 2.452397 \\
N & 0.846391 & 1.857396 & 1.627748 \\
N & 2.191777 & 2.509420 & -1.605005 \\
N & 6.274108 & 2.301266 & 0.089616 \\
C & 3.151605 & -0.807801 & 1.501140 \\
C & 4.189854 & -0.463079 & -1.023514 \\
C & 5.110731 & -1.050804 & -0.014857 \\
C & 4.585149 & -1.261876 & 1.276604 \\
C & 0.103715 & -1.740722 & -0.663850 \\
C & 0.649571 & -1.499472 & -1.948090 \\
C & 1.969641 & -1.095608 & -2.087638 \\
C & 2.794945 & -0.950384 & -0.958159 \\
C & 2.253970 & -1.171757 & 0.327069 \\
C & 0.923796 & -1.549311 & 0.472920 \\
C & 6.468084 & -1.304362 & -0.267441 \\
C & 5.418559 & -1.740722 & -0.663850 \\
H & 0.498414 & -1.693698 & 1.459309 \\
H & 0.022436 & -1.624677 & -2.825649 \\
H & 2.368222 & -0.985444 & -3.076556 \\
C & 1.969641 & -1.095608 & -2.087638 \\
C & 2.794945 & -0.950384 & -0.958159 \\
C & 2.253970 & -1.171757 & 0.327069 \\
C & 0.923796 & -1.549311 & 0.472920 \\
C & 6.468084 & -1.304362 & -0.267441 \\
C & 5.418559 & -1.740722 & -0.663850 \\
C & 0.103715 & -1.740722 & -0.663850 \\
C & 0.649571 & -1.499472 & -1.948090 \\
C & 1.969641 & -1.095608 & -2.087638 \\
C & 2.794945 & -0.950384 & -0.958159 \\
C & 2.253970 & -1.171757 & 0.327069 \\
C & 0.923796 & -1.549311 & 0.472920 \\
C & 6.468084 & -1.304362 & -0.267441 \\
C & 5.418559 & -1.740722 & -0.663850 \\
C & 0.103715 & -1.740722 & -0.663850 \\
C & 0.649571 & -1.499472 & -1.948090 \\
C & 1.969641 & -1.095608 & -2.087638 \\
C & 2.794945 & -0.950384 & -0.958159 \\
C & 2.253970 & -1.171757 & 0.327069 \\
C & 0.923796 & -1.549311 & 0.472920 \\
C & 6.468084 & -1.304362 & -0.267441 \\
C & 5.418559 & -1.740722 & -0.663850 \\
C & 0.103715 & -1.740722 & -0.663850 \\
C & 0.649571 & -1.499472 & -1.948090 \\end{tabular}
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | 5.609252 | 1.020820 | -4.289807|
| C    | 5.080787 | 0.967059 | -2.993984|
| H    | 4.733988 | -2.403748| -2.706711 |
| H    | 6.236832 | -0.106559| -6.021238 |
| H    | 5.850387 | 1.987388 | -4.724979 |
| C    | 2.587769 | -1.285167| 2.840943 |
| C    | 1.843330 | -0.466275| 3.900727 |
| C    | 1.683105 | -1.023981| 5.085062 |
| C    | 1.577635 | -2.407947| 5.226045 |
| C    | 1.976918 | -3.238192| 4.170640 |
| C    | 2.474582 | -2.681535| 2.993906 |
| H    | 2.244327 | 0.613114 | 3.843562 |
| H    | 1.375848 | -0.364606| 5.892799 |
| H    | 1.189346 | -2.837847| 6.146165 |
| H    | 1.901295 | -4.318828| 4.263677 |

5b'-INT2*

\( E = -10185.9 \)

\( N_{\text{imag}} = 0 \)
