

# Search for a Small Chromophore with Efficient Singlet Fission: Biradicaloid Heterocycles

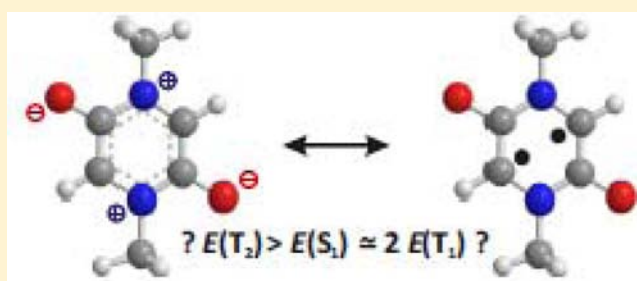
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**S** Supporting Information

**ABSTRACT:** Of the five small biradicaloid heterocycles whose  $S_1$ ,  $S_2$ ,  $T_1$ , and  $T_2$  adiabatic excitation energies were examined by the CASPT2/ANO-L-VTZP method, two have been found to meet the state energy criterion for efficient singlet fission and are recommended to the attention of synthetic chemists and photophysicists.



## ■ INTRODUCTION

Recent intense interest in singlet fission (SF) is motivated by its potential utility in solar cell applications.<sup>1</sup> SF is an often fast process in which a singlet excited chromophore and its ground-state neighbor share energy to produce a pair of triplet excited species. The process is spin-allowed, because the two triplets are initially coupled into an overall singlet. Its detailed mechanism is not understood well. For example, it is not known with certainty why triplet yields in covalent dimers are only a few percent,<sup>2,3</sup> whereas those in polycrystalline solids containing the same chromophores range up to 200%.<sup>4,5</sup>

Theoretical investigations are hampered by the fact that only a handful of molecules are currently known to undergo SF with a triplet yield near 200%, and all are too large for really accurate calculations on dimers or higher oligomers. The best calculations published so far<sup>6</sup> still necessarily involve many approximations. Typical SF chromophores contain ~20 atoms from the first full row of the periodic table in the monomer (tetracene,<sup>4,7–9</sup> diphenyltetracene,<sup>10</sup> rubrene,<sup>11</sup> pentacene,<sup>12–15</sup> diphenylisobenzofuran,<sup>5</sup> zeaxanthin<sup>16</sup>), and it is difficult to reproduce the experimental order of excited states correctly even in the monomer,<sup>17</sup> let alone the dimer. A reasonably accurate rendition of the potential energy surfaces would be important before molecular dynamics can be examined seriously. It would be useful to find a much smaller, yet highly efficient SF chromophore, say with up to 10 first full row atoms, and this is our present aim.

A search for structures that will produce efficient SF can be based on known principles.<sup>1</sup> Presently, we focus on chromophore (monomer) choice, although we recognize the crucial importance of a later optimization of the mode of coupling of the chromophores into a dimer, higher aggregate, or a solid, without which no SF could take place.

Since SF has to compete with other possible processes that depopulate the initial excited state, it will only be highly efficient if it proceeds at least one and preferably 2 orders of magnitude faster than the rest of them combined. The initial excited state of the monomer therefore needs to be relatively long-lived. Since in almost all cases internal conversion rapidly depopulates higher excited singlets of organic molecules, efficient SF is most likely to occur from the lowest excited singlet state  $S_1$ . Then, in the best case it will only need to compete with fluorescence, and chromophores that have a high quantum yield of fluorescence would appear to be good candidates. In order to ensure that this case obtains, it will be helpful to avoid the presence of heavy atoms and other structural features that enhance intersystem crossing, and of easy photochemical paths, such as double bond cis–trans isomerization.

We recall that an electronic process that requires a conversion of a large amount of electronic into vibrational energy is hindered (energy gap law) and conclude that it is desirable for the SF process to be resonant (isoergic),  $E(S_1) = 2E(T_1)$ . At any rate, significantly endoergic SF is likely to be too slow to be competitive. Since it is not only important for SF to produce triplets rapidly, but also for the triplets to be reasonably long-lived if they are to be used for purposes such as charge separation, the reverse of SF should be slow, and therefore preferably somewhat endoergic. Overall, these considerations suggest that optimal SF should be slightly exoergic. Excessive exoergicity would slow it down and besides would represent a waste of energy and loss of solar cell efficiency.

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Unfortunately, triplet recombination is also capable of producing a higher triplet state and even a quintet state. Molecular quintet formation is energetically unlikely, would still preserve double excitation, and might possibly not be detrimental; however, recombination into a higher triplet state needs to be suppressed, most easily by making sure that it is endoergic. We conclude that we need to look for small chromophores with lowest singlet  $S_1$  and the first two triplet  $T_1$  and  $T_2$  energies such that the conditions  $E(T_2) > E(S_1) \geq 2E(T_1)$  are satisfied.<sup>1</sup>

## RESULTS

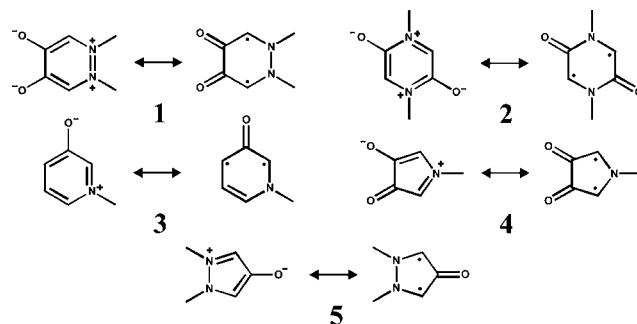
**Initial Search for SF Candidates.** Presently, we search for a suitable monomer for fundamental mechanistic studies and are not concerned with the many additional criteria that a practical SF chromophore will need to fulfill. A very important one among these will be to ensure that the triplets produced by SF act independently and both lead to separation of charges, but there also are the issues of appropriate redox potentials, high absorption coefficients, stability, etc. The requirement of large absorption coefficients makes  $\pi$ -electron systems into natural candidates for SF chromophores.

**Why Biradicaloids?** So far, two classes of parent structures have been identified<sup>18</sup> as likely to meet the condition  $E(T_2) > E(S_1) = 2E(T_1)$ : (i) alternant hydrocarbons and (ii) biradicaloids. These classes are not mutually exclusive.<sup>19</sup> Alternant hydrocarbons tend to have large and fairly size-independent  $S_1-T_1$  gaps for reasons related to the alternant pairing theorem,<sup>20</sup> and it is then sufficient to choose a size large enough to make the  $S_1-S_0$  gap equal to twice the  $S_1-T_1$  gap. Unfortunately for our purposes, this condition is not fulfilled until the  $\pi$ -system contains about 20 carbon atoms, nor does the argument say anything about the energy of the  $T_2$  state.

Therefore, we turn to biradicaloids.<sup>21,22</sup> In many pure biradicals of any size, the  $S_0-T_1$  gap is much smaller than the  $S_0-S_1$  gap; indeed, this can be viewed as a hallmark of biradicals. Since the  $T_2$  state originates from intershell as opposed to intrashell excitation as  $S_1$  and  $S_2$  do, it typically lies above  $S_1$ . A structural perturbation that stabilizes the biradical by removing the degeneracy of the two nonbonding orbitals and converting the biradical into a biradicaloid increases the  $S_0-T_1$  gap and affects the  $S_0-S_1$  gap less. When the strength of the perturbation reaches a critical value, the condition  $E(T_2) > E(S_1) = 2E(T_1)$  is fulfilled. Another advantage of making a search among small biradicaloids is that these structures are likely to be entirely distinct from those that have been examined for SF in the past and unlikely to represent mere minor variations on what is already known to work.

**Which Biradicaloids?** There are many ways to start with a known biradical structure and perturb it into a biradicaloid. Inspired by the structure of indigo, which can be viewed<sup>1</sup> as a biradicaloid derived by planarization of an orthogonally twisted ethylene biradical in which both radical centers are captodatively stabilized<sup>23</sup> and in which the condition  $E(S_1) = 2E(T_1)$  is fulfilled,<sup>24</sup> we have decided to look at planar structures in which two small captodatively stabilized radicals are joined into a single conjugated system. Some captodatively stabilized monoradicals show remarkable stability,<sup>25</sup> and one might hope that the corresponding biradicals will be somewhat stable as well. Guided by these thoughts, we have selected the structures 1–5 (Chart 1) for a closer examination. They were produced by starting with two radical centers, placing an amine donor and a carbonyl acceptor next to each, and closing an

Chart 1. Chemical Structures of Biradicaloids 1–5



aromatic ring. If each radical center has its own donor and acceptor, a six-membered ring results, and if they share donors and/or acceptors, the rings can be smaller. These are all heterocycles that do not have a ground-state Lewis structure without isolated dots or separated charges. We realize that placing a stabilizing amino nitrogen atom next to a carbonyl group in an effort to minimize the size of the molecule converts it into an amido nitrogen, reducing its stabilizing dative effect greatly,<sup>26</sup> but this need not be fatal.

**Are the Biradicaloids 1–5 Suitable? An Initial Look.** A cursory evaluation of vertical excitation energies for these five structures and a few others was done with TDDFT methods, using long-range corrected functionals considered suitable for structures with intramolecular charge transfer (Table 1).

Table 1. TDDFT Vertical Transition Energy (eV) for  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow T_1$ , and  $S_0 \rightarrow T_2$  Excitations (at Equilibrium Geometry of  $S_0$ )

|          | pbe/aug-cc-pvdz | pbe/cc-pvtz | pbe/tzvp | cam/aug-cc-pvdz | cam/cc-pvtz | cam/tzvp |
|----------|-----------------|-------------|----------|-----------------|-------------|----------|
| <b>1</b> |                 |             |          |                 |             |          |
| $S_1$    | 2.89            | 2.88        | 2.88     | 2.76            | 2.74        | 2.75     |
| $T_1$    | -1.26           | -1.33       | -1.35    | -0.61           | -0.73       | -0.76    |
| $T_2$    | 2.15            | 2.19        | 2.17     | 2.38            | 2.42        | 2.40     |
| <b>2</b> |                 |             |          |                 |             |          |
| $S_1$    | 2.43            | 2.42        | 2.48     | 2.43            | 2.44        | 2.48     |
| $T_1$    | -1.32           | -1.36       | -1.35    | -0.83           | -0.98       | -0.87    |
| $T_2$    | 3.03            | 3.07        | 3.11     | 3.28            | 3.33        | 3.35     |
| <b>3</b> |                 |             |          |                 |             |          |
| $S_1$    | 3.68            | 3.62        | 3.64     | 3.52            | 3.55        | 3.56     |
| $T_1$    | 1.03            | 0.93        | 0.91     | 1.56            | 1.50        | 1.49     |
| $T_2$    | 3.32            | 3.33        | 3.36     | 3.43            | 3.45        | 3.46     |
| <b>4</b> |                 |             |          |                 |             |          |
| $S_1$    | 1.80            | 1.80        | 1.84     | 1.74            | 1.74        | 1.78     |
| $T_1$    | -1.22           | -1.25       | -1.27    | -0.84           | -0.87       | -0.88    |
| $T_2$    | 1.24            | 1.21        | 1.27     | 1.22            | 1.21        | 1.26     |
| <b>5</b> |                 |             |          |                 |             |          |
| $S_1$    | 3.61            | 3.64        | 3.65     | 3.41            | 3.50        | 3.50     |
| $T_1$    | 1.11            | 0.98        | 0.94     | 1.43            | 1.35        | 1.33     |
| $T_2$    | 3.85            | 3.87        | 3.87     | 3.73            | 3.70        | 3.71     |

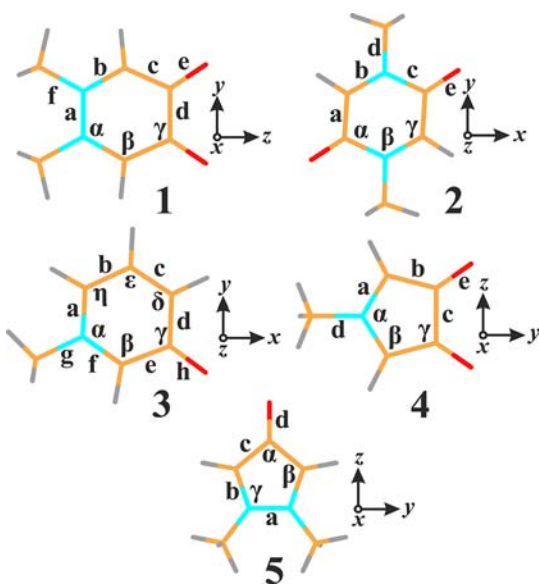
Compounds 1–5 all had quite low-lying  $T_1$  energies. A more detailed examination at ab initio level of theory (SACCI, Table 2) suggested that the extremely low triplet energies are artifacts of the DFT method, but that the condition  $E(T_2) > E(S_1) = 2E(T_1)$  for adiabatic state energies might nevertheless be satisfied.

**A Detailed Examination of 1–5.** All five molecules are small enough for a high-level CASPT2 calculation. In this

**Table 2.** SACCI Vertical Transition Energy (eV) for  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow T_1$ , and  $S_0 \rightarrow T_2$  Excitations (at Equilibrium Geometry of  $S_0$ )

|       | SACCI/aug-cc-pvdz | SACCI/tzvp |
|-------|-------------------|------------|
| 1     |                   |            |
| $S_1$ | 3.18              | 2.81       |
| $T_1$ | 1.20              | 0.80       |
| $T_2$ | 3.15              | 2.68       |
| 2     |                   |            |
| $S_1$ | 2.30              | 2.43       |
| $T_1$ | 0.49              | 0.41       |
| $T_2$ | 3.81              | 3.92       |
| 3     |                   |            |
| $S_1$ | 3.24              | 3.51       |
| $T_1$ | 1.70              | 1.80       |
| $T_2$ | 3.58              | 3.83       |
| 4     |                   |            |
| $S_1$ | 1.84              | 2.10       |
| $T_1$ | 0.72              | 0.75       |
| $T_2$ | 1.64              | 1.83       |
| 5     |                   |            |
| $S_1$ | 4.07              | 3.46       |
| $T_1$ | 1.80              | 1.86       |
| $T_2$ | 3.49              | 4.68       |

approximation, all have singlet ground states. Selected structural characteristics of  $S_0$ ,  $T_1$ ,  $S_1$ ,  $T_2$ , and  $S_2$  states (Figure 1) obtained by full geometry optimization with a double- $\zeta$

**Figure 1.** Definition of selected geometrical parameters and orientation of axes.

quality basis set are shown in Table 3 (cf. Supporting Information [SI], Table S2). The symmetry of each compound was found to be the same in each of its five optimized states. Excited state geometries differed from the ground state geometry only moderately, and the differences reflected the local bonding/antibonding character of the orbitals involved in the excitation as expected. The only exceptions are the  $S_1$  and  $T_2$  states of compound 4, in which the C–C bond is nearly broken at the optimized C–C distance of  $\sim 1.8$  Å.

Table 4 shows vertical and adiabatic excitation energies and vertical oscillator strengths obtained with a triple- $\zeta$  basis set and a large active space (cf. SI). In terms of the molecular orbitals involved, most of the excitations can be described quite adequately as one-electron transitions between two orbitals in the HOMO–LUMO region, either  $\pi \rightarrow \pi^*$  or  $n_O \rightarrow \pi^*$  (Figures 2–6). Only the  $S_2$  state of 2 is doubly excited and its  $S_0$ – $S_2$  transition involves the promotion of both HOMO electrons into the LUMO.

In Table S2 (SI) we show the vertical excitation energies of the  $S_0$ ,  $T_1$ ,  $S_1$ ,  $T_1$ , and  $S_2$  states of 1–5 at the equilibrium geometry in each initial state.

## DISCUSSION

A summary of the most important results, the gas-phase adiabatic excitation energies for 1–5, is provided in Figure 7. On the basis of our prior experience with this level of CASPT2 calculations, we believe that the computed relative state energies are reliable to within  $\sim 0.1$  eV. Within this uncertainty, the conditions  $E(T_2) > E(S_1) \geq 2E(T_1)$  are fulfilled for 2 and nearly fulfilled for 5, and we recommend these compounds for an experimental examination. The biradicaloids 1 and 3 do not meet our requirements, and in 4 the intervention of low-lying singlet and triplet  $n\pi^*$  states is likely to be unfavorable, and the  $T_2$  state seems to be much too low.

We note, however, that the ground and excited states of these compounds frequently differ dramatically in polarity (Table 3), which might make it possible to tune their energies by the choice of an appropriate polar environment. One could then satisfy the conditions  $E(T_2) > E(S_1) \geq 2E(T_1)$  in solution or in a solid even if they are not met in the gas phase. The high polarity might also be used to facilitate electron transfer from an excited state, e.g., to a semiconductor.

How realistic are these improbable looking structures? Compounds of this general type have been known for a long time and have often been called mesoionic (“mesomeric and ionic”) or betainic (after the zwitterion, betain) heterocycles.<sup>27,28</sup> Recently, the term mesoionic has mostly been associated with five-membered rings with one exocyclic atom, usually oxygen, and six-membered rings have more often been called betainic.<sup>29,30</sup> Many but not all mesoionic and betainic heterocycles are perfectly stable although they have no Lewis structures without separated charges or isolated dots. They have received only limited attention from organic chemists, and hardly any from photophysicists.

Of the compounds 1–5, only 3 and 5 have been prepared, and low-level calculations for both 3<sup>31,32</sup> and 5<sup>29</sup> have been reported. Compounds related to 3 have a venerable history<sup>33</sup> and have seen use as unisolated intermediate reagents in organic synthesis.<sup>34,35</sup> The heterocycle 3 itself has been observed spectroscopically but not isolated pure.<sup>36</sup> In 0.1 M NaOH solution in water, its first absorption band occurs at 3.9 and the second one at 5.1 eV.<sup>37</sup> The peak position is known to be strongly shifted to the red with decreasing solvent polarity,<sup>38</sup> and the vertical  $S_0$ – $S_1$  excitation energy of 3.3 eV obtained from our gas-phase CASPT2 calculation seems about right. The fluorescence of 3 in water peaks at 3.14 eV.<sup>39</sup> From the CASPT2 calculation, we would expect a vertical emission energy of 2.4 eV in the gas phase.

The heterocycle 5 has been prepared and its UV spectrum in water recorded.<sup>40</sup> The reported absorption peak occurs at 4.36 eV. According to our calculations, which yield very low oscillator strengths for the lower energy transition to  $S_1$  and  $S_2$ ,

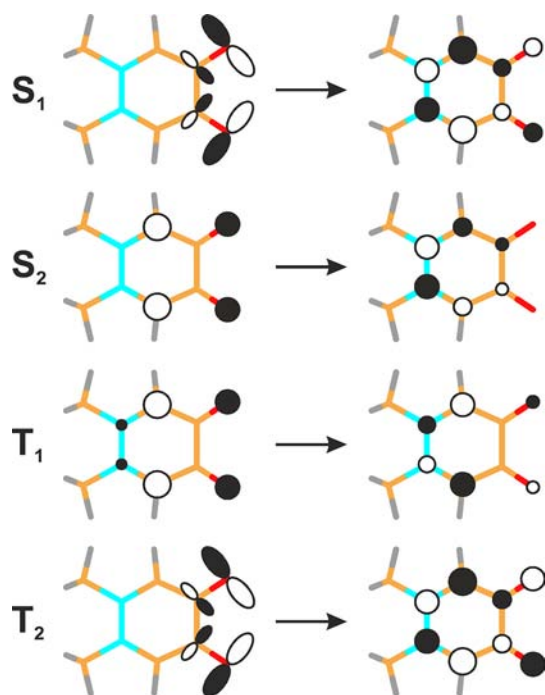
Table 3. Dipole Moment Components (Debye) and Selected Bond Distances (Å) and Bond Angles (deg) in CASPT2 Optimized Structures

| cmpd           | state          | dipole moment $\mu_x; \mu_y; \mu_z$ | geometric parameters (Figure 1) |       |       |       |       |       |       |       |          |         |          |          |            |        |
|----------------|----------------|-------------------------------------|---------------------------------|-------|-------|-------|-------|-------|-------|-------|----------|---------|----------|----------|------------|--------|
|                |                |                                     | a                               | b     | c     | d     | e     | f     | g     | h     | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ | $\epsilon$ | $\eta$ |
| 1              | S <sub>0</sub> | 0; 0; -11.8                         | 1.340                           | 1.373 | 1.448 | 1.504 | 1.243 | 1.468 |       | 119.9 | 125.6    | 114.6   |          |          |            |        |
|                | T <sub>1</sub> | 0; 0; 8.9                           | 1.417                           | 1.376 | 1.431 | 1.531 | 1.248 | 1.457 |       | 119.6 | 124.6    | 115.8   |          |          |            |        |
|                | S <sub>1</sub> | 0; 0; 8.0                           | 1.391                           | 1.395 | 1.400 | 1.623 | 1.250 | 1.452 |       | 119.6 | 126.4    | 114.1   |          |          |            |        |
|                | T <sub>2</sub> | 0; 0; 8.1                           | 1.392                           | 1.393 | 1.399 | 1.531 | 1.250 | 1.452 |       | 119.4 | 126.6    | 114.0   |          |          |            |        |
|                | S <sub>2</sub> | 0; 0; 12.1                          | 1.398                           | 1.396 | 1.442 | 1.502 | 1.258 | 1.458 |       | 119.5 | 124.4    | 116.1   |          |          |            |        |
|                | S <sub>0</sub> | 0; 0; 0                             | 1.429                           | 1.345 | 1.421 | 1.474 | 1.251 |       |       | 112.2 | 124.8    | 123.0   |          |          |            |        |
| 2              | T <sub>1</sub> | 0; 0; 0                             | 1.444                           | 1.379 | 1.411 | 1.466 | 1.240 |       |       | 116.7 | 120.6    | 122.7   |          |          |            |        |
|                | S <sub>1</sub> | 0; 0; 0                             | 1.436                           | 1.377 | 1.420 | 1.467 | 1.248 |       |       | 116.3 | 120.3    | 123.4   |          |          |            |        |
|                | T <sub>2</sub> | 0; 0; 0                             | 1.414                           | 1.388 | 1.381 | 1.466 | 1.291 |       |       | 116.9 | 122.7    | 120.4   |          |          |            |        |
|                | S <sub>2</sub> | 0; 0; 0                             | 1.462                           | 1.397 | 1.435 | 1.456 | 1.233 |       |       | 119.3 | 116.5    | 124.1   |          |          |            |        |
|                | S <sub>0</sub> | -6.5; 1.8; 0                        | 1.366                           | 1.410 | 1.394 | 1.461 | 1.456 | 1.358 | 1.476 | 1.245 | 122.8    | 122.9   | 113.3    | 121.6    | 121.2      | 118.2  |
|                | T <sub>1</sub> | -3.9; 1.3; 0                        | 1.405                           | 1.388 | 1.422 | 1.470 | 1.446 | 1.396 | 1.456 | 1.259 | 119.0    | 121.2   | 118.6    | 117.7    | 121.2      | 122.2  |
| 3              | S <sub>1</sub> | -2.4; -0.1; 0                       | 1.388                           | 1.381 | 1.434 | 1.419 | 1.396 | 1.407 | 1.455 | 1.351 | 120.0    | 118.8   | 123      | 115.6    | 121.7      | 120.9  |
|                | T <sub>2</sub> | -2.2; 0.0; 0                        | 1.388                           | 1.380 | 1.435 | 1.420 | 1.397 | 1.407 | 1.455 | 1.345 | 120.0    | 118.9   | 122.8    | 115.7    | 120.6      | 120.0  |
|                | S <sub>2</sub> | -3.7; 0.7; 0                        | 1.386                           | 1.386 | 1.435 | 1.413 | 1.407 | 1.409 | 1.459 | 1.332 | 119.2    | 119.4   | 122.1    | 116.6    | 120.8      | 121.8  |
|                | S <sub>0</sub> | -0.1; -7.0; 0                       | 1.367                           | 1.456 | 1.586 | 1.469 | 1.228 |       |       |       | 116.8    | 106.8   | 104.8    |          |            |        |
|                | T <sub>1</sub> | -0.0; -7.4; 0                       | 1.383                           | 1.451 | 1.515 | 1.460 | 1.247 |       |       |       | 109.0    | 110.8   | 104.7    |          |            |        |
|                | S <sub>1</sub> | 0.1; -5.9; 0                        | 1.379                           | 1.406 | 1.852 | 1.457 | 1.213 |       |       |       | 115.1    | 112.7   | 99.7     |          |            |        |
| 4              | T <sub>2</sub> | -0.0; -6.1; 0                       | 1.373                           | 1.409 | 1.831 | 1.458 | 1.228 |       |       | 115.0 | 112.6    | 99.9    |          |          |            |        |
|                | S <sub>2</sub> | -0.0; -11.3; 0                      | 1.374                           | 1.492 | 1.493 | 1.463 | 1.246 |       |       | 109.7 | 110.5    | 104.7   |          |          |            |        |
|                | S <sub>0</sub> | 0; 0; -8.6                          | 1.368                           | 1.456 | 1.258 |       |       |       |       | 101.1 | 110.6    | 108.5   |          |          |            |        |
|                | T <sub>1</sub> | 0; 0; -3.6                          | 1.466                           | 1.458 | 1.249 |       |       |       |       | 104.9 | 109.6    | 107.4   |          |          |            |        |
|                | S <sub>1</sub> | 0; 0; -1.3                          | 1.448                           | 1.403 | 1.346 |       |       |       |       | 108.7 | 108.5    | 106.9   |          |          |            |        |
|                | T <sub>2</sub> | 0; 0; -0.4                          | 1.451                           | 1.405 | 1.331 |       |       |       |       | 108.3 | 108.6    | 106.6   |          |          |            |        |
| S <sub>2</sub> | 0; 0; -2.5     | 1.446                               | 1.398                           | 1.370 |       |       |       |       | 108.9 | 108.2 | 106.9    |         |          |          |            |        |

**Table 4. Vertical Excitation Energy (eV), Transition Dipole Moments (au), Oscillator Strength for  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_2$ , and  $T_1 \rightarrow T_2$  Excitations, and Adiabatic Excitation Energy (eV;  $S_0 \rightarrow T_1$  gap in parentheses)<sup>a</sup>**

| cmpd          | transition                      | vertical excitation energy | transition dipole moment |          |          | oscillator strength | adiabatic excitation energy ( $S_0-T_1$ gap) |
|---------------|---------------------------------|----------------------------|--------------------------|----------|----------|---------------------|--|
|               |                                 |                            | <i>x</i>                 | <i>y</i> | <i>z</i> |                     |  |
| 1( $C_{2v}$ ) | $S_0(A_1) \rightarrow S_1(A_2)$ | 2.741                      | 0                        | 0        | 0        | 0                   | 2.485  |
|               | $S_0(A_1) \rightarrow S_2(B_2)$ | 2.973                      | 0                        | -1.7296  | 0        | 0.2592              | 2.892  |
|               | $T_1(B_2) \rightarrow T_2(A_2)$ | 0.978                      | -0.0254                  | 0        | 0        | 0.0000              | 0.773 (1.659)                                |
| 2( $C_{2h}$ ) | $S_0(A_g) \rightarrow S_1(B_u)$ | 2.207                      | -1.3236                  | 0.8978   | 0        | 0.1750              | 2.114  |
|               | $S_0(A_g) \rightarrow S_2(A_g)$ | 3.625                      | 0                        | 0        | 0        | 0                   | 3.216  |
|               | $T_1(B_u) \rightarrow T_2(A_u)$ | 2.665                      | 0                        | 0        | 0        | 0                   | 2.377 (1.145)                                |
| 3( $C_s$ )    | $S_0(A') \rightarrow S_1(A')$   | 3.251                      | 0.2139                   | 0.9596   | 0        | 0.0784              | 2.998  |
|               | $S_0(A') \rightarrow S_2(A'')$  | 3.438                      | 0                        | 0        | 0.0667   | 0.0004              | 3.090  |
|               | $T_1(A') \rightarrow T_2(A'')$  | 1.124                      | 0                        | 0        | -0.0055  | 0.0000              | 0.895 (2.075)                                |
| 4( $C_s$ )    | $S_0(A') \rightarrow S_1(A')$   | 1.329                      | -0.0043                  | 0.0021   | 0        | 0.0000              | 1.306  |
|               | $S_0(A') \rightarrow S_2(A'')$  | 1.764                      | 0                        | 0        | -0.0181  | 0.0000              | 1.549  |
|               | $T_1(A'') \rightarrow T_2(A')$  | 0.522                      | 0                        | 0        | -0.0081  | 0.0000              | 0.338 (0.757)                                |
| 5( $C_2$ )    | $S_0(A) \rightarrow S_1(B)$     | 3.181                      | 0.1461                   | 0.5627   | 0        | 0.0309              | 3.000  |
|               | $S_0(A) \rightarrow S_2(B)$     | 3.422                      | 0.0799                   | 0.5444   | 0        | 0.0269              | 3.043  |
|               | $T_1(B) \rightarrow T_2(B)$     | 1.487                      | 0                        | 0        | 0.0002   | 0.0000              | 1.181 (1.653)                                |

<sup>a</sup>Singlet transitions are calculated at  $S_0$  equilibrium geometry and triplet transitions at  $T_1$  equilibrium geometry).

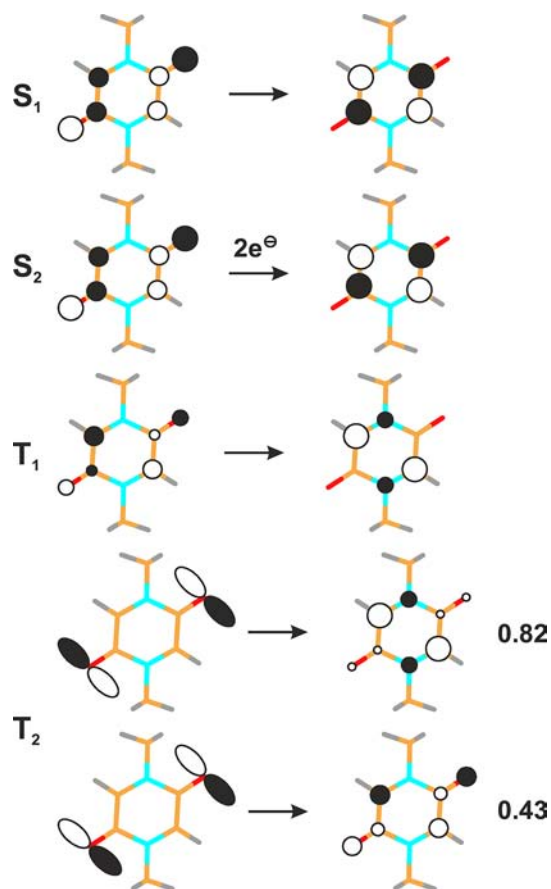


**Figure 2.** MO description of excitations in 1.

the observed peak probably corresponds to a transition to a singlet state higher than  $S_2$ .

The preparation of 1, 2, and 4 has apparently never been attempted. An adduct of a hydrogen atom to 2 was generated by hydrogen atom abstraction from sarcosine anhydride using a pulse radiolytic method and the radical was investigated as a short-lived transient.<sup>41</sup>

It is thus not known whether compounds 1–4 will be isolable and stable, but it seems quite possible. If experimental studies are attempted, it may be necessary to replace the hydrogens on carbon atoms and/or the methyl groups on nitrogen atoms with bulkier substituents such as methyl or *tert*-butyl, respectively, to suppress dimerization and polymerization. Such substitution would have minimal effect on relative state energies.



**Figure 3.** MO description of excitations in 2.

It has been long known that single reference methods are not suitable for the description of the  $S_0$  state of biradicaloids,<sup>42</sup> and the abject failure of the TDDFT method (Table 1) and the poor performance of the SACCI(R2) method (Table 2) are not surprising. In an effort to find a method suitable for a rapid survey of large numbers of biradicaloid structures, we examined the open-shell DFT description of the  $S_0$  state using the spin-flip technique, followed by open-shell TDDFT for the  $S_1$  state.

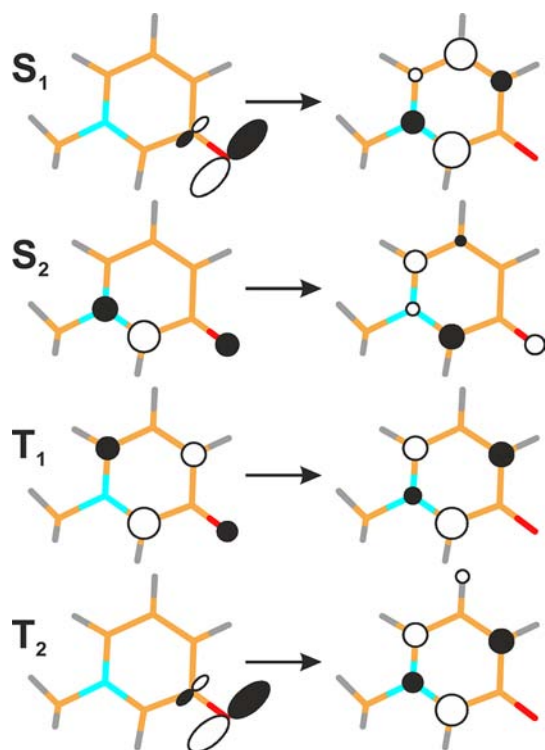


Figure 4. MO description of excitations in 3.

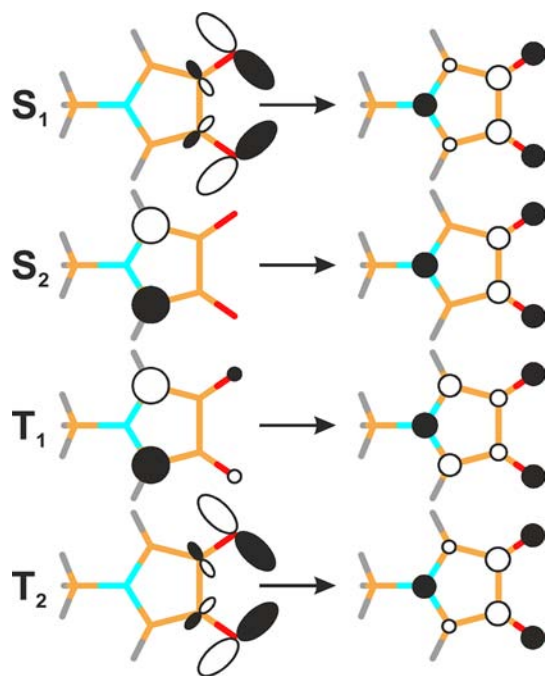


Figure 5. MO description of excitations in 4.

As shown in Table S1 (SI), this improves the description of the  $S_0$ - $T_1$  gap somewhat, but the calculated energies of the  $S_1$  states are much too low. It seems that the use of a multireference starting point is inevitable.

## CONCLUSIONS

We have computed reasonably reliable values of the vertical and adiabatic gas-phase excitation energies of the lowest few singlet and triplet states of the biradicaloid heterocycles 1–5 and

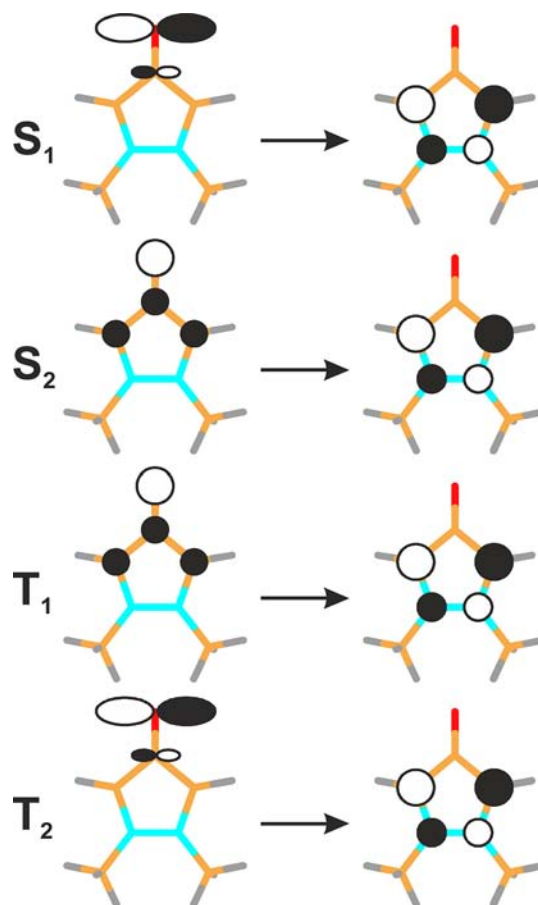


Figure 6. MO description of excitations in 5.

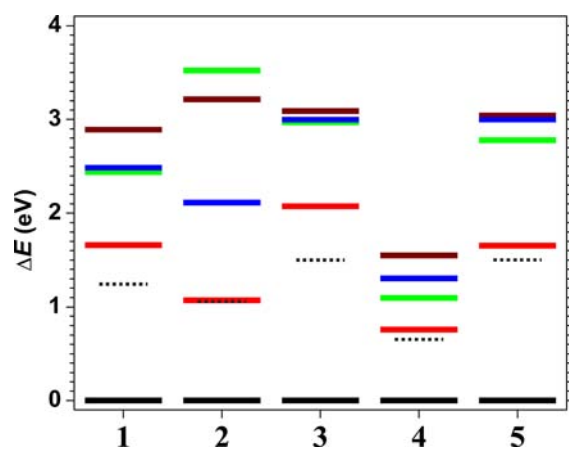


Figure 7. CASPT2 relative energies of adiabatic states. Color codes: black,  $S_0$ ; red,  $T_1$ ; blue,  $S_1$ ; green,  $T_2$ ; and brown,  $S_2$ . The dotted line is located at half of the excitation energy of the  $S_1$  state.

identified 2 and possibly 5 as worthy targets for a photophysical examination for the purposes of singlet fission. Conceivably, 4 is worth examining as well in spite of the low energy of its  $T_2$  state. We recognize that all of these compounds may have other deactivation channels that we have not examined, in particular intersystem crossing, internal conversion, and photochemical transformations, but the fact that 3 is known to fluoresce is encouraging.

## METHODS

The compounds 1-5 were first subjected to geometry optimization at the B3LYP/SVP level. Frequency calculations were used to ensure that the optimized geometries were true minima. When symmetry was imposed on 1 and 2, imaginary frequencies appeared, but they disappeared when the symmetry was lowered to  $C_1$ .

The optimized geometries were used to calculate the vertical excitation energies with the LC-PBE and CAM-B3LYP methods using aug-cc-pVDZ, cc-pVTZ, and TZVP basis sets. Next, vertical excitation energies at these geometries were obtained with the SAC-CI method using the aug-cc-pVDZ and TZVP basis sets. All TDDFT and SACCI calculations were performed with Gaussian09 Rev.A2.<sup>43</sup>

CASSCF/CASPT2 calculations were performed at geometries optimized for the for  $S_0$ ,  $S_1$ ,  $T_1$ , and  $T_2$  states at the CASPT2 level with a double- $\zeta$  quality basis set ANO-S-VDZP (C,N,O: 10s6p3d/3s2p1d; H: 7s3p/2s1p)<sup>44</sup> using the MOLCAS 7.6 program package.<sup>45</sup> Since the CASPT2 analytical gradient is not available, the optimization was run numerically. It was started at a perturbed geometry without symmetry, and the symmetry of the optimized structure is a result of the optimization process. Final optimization steps were run from the calculated symmetry. For 3 the calculated symmetry is  $C_1$ , due to a small torsion of the methyl group, but because of the proximity of  $S_1$  and  $S_2$  states it was advantageous to increase the symmetry to  $C_s$  and to separate these two states into different irreducible representations. The increase of the ground state energy due to this symmerization was very small (0.1 kcal/mol). The active space was selected to span the  $\pi$  orbitals plus oxygen lone pairs orbitals (for details, see the SI).

Excited state energies were calculated using the ANO-L-VTZP basis set (C,N,O: 14s9p4d3f/4s3p2d1f; H: 8s4p3d/3s2p1d).<sup>46</sup> The active space included all the  $\pi$  orbitals, lone pairs and selected  $\sigma$  orbitals up to program limits (SI). Energies of all states were calculated from state specific CAS wave functions except for the  $S_2$  state of 5, for which the calculation was done in the state average mode, because of the closeness of the energies of the  $S_1$  and  $S_2$  states, both of which are of B symmetry ( $n_O \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions).

## ASSOCIATED CONTENT

### Supporting Information

Figures S1–S5, full reference 43, Tables S1 (results of TDDFT calculations) and S2 (results of CASPT2 calculations, including optimized geometries). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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